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Transport of Methyl *tert*-Butyl Ether through Alfalfa Plants

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Concentrations measured in alfalfa plant stem segments indicated that plants grown in methyl *tert*-butyl ether (MTBE)-contaminated soil took up the chemical through their roots. Assuming a cylindrical shape for the plant stem, a mathematical model was developed to describe the transport of MTBE through the stems. Simulation results from uniform and nonuniform initial concentration distributions across the stem radius were compared with steady-state experimental data. With known values of plant stem radius, water usage, water content, and the distance over which the concentration decreased by 50%, the diffusion coefficient of MTBE radial transport across the plant stem was estimated with 95% confidence to be in the range of $8.43-16.2 \times 10^{-8}$ cm^2/s with a mean of 1.23×10^{-7} cm^2/s. When the diffusion coefficient was calculated based on transient experimental data, the values with 95% confidence interval ranged from 4.14×10^{-7} to 8.00×10^{-7} cm^2/s with a mean value of 6.07×10^{-7} cm^2/s. The difference between these two results can be reduced by more accurate estimation of the water flow velocity through plant stems. The model is applicable to other species including sunflowers and poplars upon substitution of appropriate parameters.

Introduction

Vegetation uptake of organic pollutants is governed by the chemical and physical properties of the pollutant, the environmental conditions, and the plant species. There are several pathways through which organic pollutants enter vegetation. They may enter the plant by partitioning from contaminated soil to the roots and be translocated in the plant through the xylem while xylem transport of water from the roots to the leaves is driven by transpiration. They may also enter vegetation from the atmosphere by gas- and particle-phase deposition onto the waxy cuticle of the leaves or by uptake through the stomata and then be translocated by the phloem while phloem actively transports photosynthates to the roots and to other plant tissues. These pathways are a function of the chemical and physical properties of the pollutant, such as its lipophilicity, water solubility, vapor pressure, Henry's law constant, and organic carbon/water partition coefficient (*1*).

One of the ways in which plants accomplish contaminant removal is the mass transport through root and shoot system accompanied by adsorption to the tissue and volatilization to the atmosphere (*2*, *3*). Vroblesky et al. (*4*) investigated the potential for contaminant transport through flood-adapted trees at a flood plain site near the TNX area of the Savannah River Site, SC. They measured the temporal and spatial distribution of chlorinated ethenes within and among the trunks of mature trees growing on the contaminated soil. A recent study (*3*) used baldcypress seedlings grown in glass carboy mesocosms seasonally to test TCE gas flux and loss via transpiration and/or by diffusion. They found that evapotranspiration (ET) in the summer might serve as a good predictor for the potential of trichloroethylene (TCE) removal by baldcypress trees, while diffusive flux might better approximate contaminant loss in the winter from contaminated sites. In another study (*5*), hydroponically grown poplar and willow trees were dissected and measured for TCE distribution within the plant after being exposed to TCE solution of up to 10 μM.

In this study, we measured the methyl *tert*-butyl ether (MTBE) concentration distribution along alfalfa plants growing in contaminated soil channels and then simulated the transport of MTBE through the plants. With the model and the experimental data, we can estimate the diffusion coefficient of MTBE across the alfalfa plant stem.

Experimental Section

To investigate the distribution of MTBE concentration within alfalfa plants, MTBE concentration was measured in alfalfa plants growing in four soil channels. The channels had been contaminated with MTBE for more than 7 months by the time the plants were sampled. Details of the channel system can be found in refs *6*−*8* and the Supporting Information. The sampled plants were numbered as 7-31-1, 7-31-2, and 7-31-3. One month later, three more plants (plants 8-31-1, 8-31-2, and 8-31-3) were examined. This time, the leaves were taken off the stems before cutting the plant into segments so that only MTBE contained inside the stems was measured.

Alfalfa plant stems were cut from the usual harvesting point (about 6 cm above the soil surface) into segments with lengths of approximately 8 cm, transferred into 65-mL bottles, and sealed with mininert valves. For the first three plant samples, segments were cut from plant top down. For the second three samples, the whole plants were cut at the harvesting point and then dissected into segments. After allowing more than 2 h to approach equilibrium between the plant water and the bottle headspace, gas samples were withdrawn to analyze the headspace concentration of MTBE. Duplicate gas chromatography (GC) analyses were made for each bottle. Bottles with plants were weighed before and after oven drying at 80 °C for 24 h to obtain the amount of plant water and the dry plant biomass. With an assumed fresh plant density of 1.0 g/cm^3, the air volume within each bottle was estimated by subtracting the volume occupied by the fresh plant from the known bottle volume. From the plant water amount and air volume data, the measured headspace concentration was converted into plant water concentration in units of millimolar, assuming that Henry's law was satisfied and the room temperature was 25 °C (*8*). The concentration data were then normalized based on the feed concentration of MTBE to the channels (i.e., 0.84 mM) in order to get dimensionless concentrations in terms of the fraction of the channel influent concentration.

Recently, another batch of experiments was conducted with alfalfa sections harvested in identical ways from the six-channel system. Plant sections (6−10 with leaves re-

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moved) were harvested from the top down and then sealed into sample bottles. Then the gas-phase concentration in each bottle was monitored versus the time elapsed from the moment when the segments were sealed into the bottles. The half-time corresponding to 50% removal of the MTBE from the plant stems was determined from the collected data. Seventeen samples taken from four individual plants were examined. In most cases, the gas-phase concentration in the sample bottle reached a stable value after approximately 1 h, and this stable value was taken for the equilibrium state.

For the first series of experiments, after the GC analysis, lengths and diameters of the fresh stem segments were measured using a vernier caliper. Because most bottles contained more than 10 stem segments, only the shortest, the longest, and the middle ones were measured, and the averages were chosen as the representative values of the length and diameter for the stems in each bottle. In the most recent experiments, only the total length of stem per sample bottle was determined. Then using the plant weight per bottle, the radius was calculated assuming a density of 1.0 g/cm^3.

Model Development

To study MTBE contaminant transport through the plant stems and shoots, a simple mathematical model was developed based on the following assumptions:

(i) Alfalfa plant stems/shoots are of cylindrical shape.

(ii) No MTBE is transformed within the plants.

(iii) MTBE can diffuse out through the plant stem/shoot surface at flux J.

(iv) Adsorption of MTBE to plant biomass is small and can be neglected.

(v) Volumetric water content does not change along the plant stem.

(vi) No plant water is lost in the radial direction through the stem/shoot surface, i.e., mass flow rate of water in the z direction is constant and does not change with vertical position.

Although the experimental data for the plant gravimetric water content with plant height included some variation, the assumption of constant volumetric water content was used to simplify the model. The assumption that no MTBE is transformed within the plants simplifies the model. There is no experimental evidence that MTBE is not transformed; low rates of degradation may be present. From the mass balance of contaminant in plant water for an infinitesimal volume element of stem, we can have

$$\frac{\partial c}{\partial t} = -\frac{u}{\theta_w}\frac{\partial c}{\partial z} + \frac{D}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) \quad (1)$$

where c = dimensionless concentration of the contaminant in water phase, r = radial distance from the axis of the cylindrical stem (cm), t = time (s), u = superficial velocity of water through the stem (cm/s), z = axial distance (cm), D = radial diffusion coefficient of MTBE through the plant stem (cm^2/s), and θ_w = volumetric water content of the fresh plant stem (dimensionless).

At the time we harvested the plants and measured MTBE concentration in the plant water, the channel system was under steady-state operation, i.e., MTBE concentration in the groundwater was stable and equal to the inlet concentration (0.84 mM). Under steady-state conditions, the MTBE concentration within the plants varies with position, but it does not vary with time.

Contaminant transport through the plant stems is modeled as a steady-state process. Thus, eq 1 becomes

$$\frac{\partial c}{\partial z} = \frac{D\theta_w}{u}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) \quad (2)$$

The boundary conditions for eq 2 are

$$\begin{aligned} &\frac{\partial c}{\partial r} = 0 \quad \text{at } r = 0 \\ &c = 0 \quad \text{at } r = r_0 \\ &c = c_0 \quad \text{at } z = 0 \end{aligned} \quad (3)$$

where r_0 = radius of the stem (cm), and c_0 = dimensionless concentration within plant stems at the soil surface (i.e., at z = 0).

If we further choose the following dimensionless expressions for r, z, and c:

$$R = \frac{r}{r_0} \quad Z = \frac{z}{z_d} \quad C = \frac{c}{c_0} \quad (4)$$

where z_d is a distance along the plant stem, eq 2 can be rewritten as

$$\frac{\partial C}{\partial Z} = \frac{Dz_d\theta_w}{r_0^2 u}\left(\frac{\partial^2 C}{\partial R^2} + \frac{1}{R}\frac{\partial C}{\partial R}\right) \quad (5)$$

Letting $z_d = r_0^2 u/D\theta_w$, we can simplify the dimensionless eq 5 to

$$\frac{\partial C}{\partial Z} = \frac{\partial^2 C}{\partial R^2} + \frac{1}{R}\frac{\partial C}{\partial R} \quad (6)$$

The corresponding boundary conditions become

$$\begin{aligned} &\frac{\partial C}{\partial R} = 0 \quad \text{at } R = 0 \\ &C = 0 \quad \text{at } R = 1 \text{ for all } Z \\ &C = 1 \quad \text{at } Z = 0 \end{aligned} \quad (7)$$

The solution for eq 6 and 7 is obtained by introducing the Bessel function of the first kind of zero-order $J_0(x)$:

$$C = \sum_{n=1}^{\infty} \lambda \exp(-\beta_n^2 Z) J_0(\beta_n R) \quad (8)$$

in which

$$\lambda = \frac{2}{\beta_n J_1(\beta_n)} \quad (9)$$

and β_n values (n = 1, 2, 3, ...) are the roots of $J_0(\beta_n) = 0$.

To get the overall average concentration as a function of Z for each cross section, we integrate the concentration in eq 8 over the cross-sectional area as follows:

$$\bar{C} = \frac{1}{\pi R_0^2}\sum_{1}^{\infty} \lambda \exp(-\beta_n^2 Z)\int_0^{R_0} 2\pi R J_0(\beta_n R)\, dR \quad (10)$$

where R_0 = 1, and we obtain

$$\bar{C} = \sum_{1}^{\infty} \frac{4}{\beta_n^2}\exp(-\beta_n^2 Z) \quad (11)$$

The details of solving eqs 6 and 7 to get the results in eqs 8, 9, and 11 were presented in Appendix A of Zhang (*8*).

Results and Discussion

Experimental Results. The gravimetric water contents of fresh plant segments were measured versus the distance from

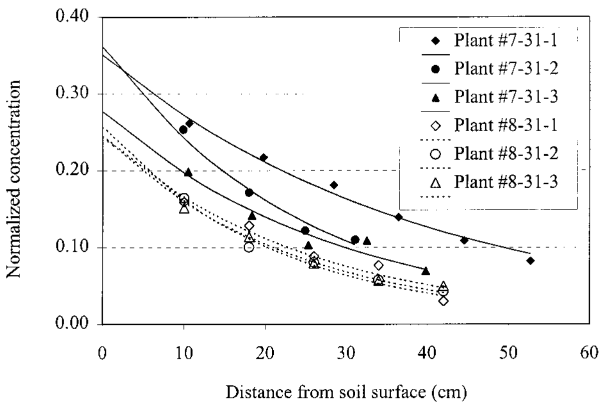

FIGURE 1. MTBE concentration in plant water as a function of stem position from the soil surface. The points are experimental data, and the solid lines are the exponential fittings of form $c = c_0 \exp(-\alpha z)$. For plant 7-31-1, $c_0 = 0.351$, $\alpha = 2.56 \times 10^{-2}$. For plant 7-31-2, $c_0 = 0.362$, $\alpha = 4.03 \times 10^{-2}$. For plant 7-31-3, $c_0 = 0.277$, $\alpha = 3.43 \times 10^{-2}$. For plant 8-31-1, $c_0 = 0.245$, $\alpha = 3.93 \times 10^{-2}$. For plant 8-31-2, $c_0 = 0.257$, $\alpha = 4.66 \times 10^{-2}$. For plant 8-31-3, $c_0 = 0.244$, $\alpha = 4.26 \times 10^{-2}$. The concentration is normalized to the inlet concentration (0.84 mM).

the soil surface. By assuming that the bulk density for fresh plants is 1 g/cm^3, we converted the gravimetric water content into the volumetric water content (θ_w) and found that the volumetric water content did not change significantly along the plant height and fell into the range of 0.736−0.763 for plants 7-31-1, 7-31-2, and 7-31-3; and the range was 0.688−0.742 for plants 8-31-1, 8-31-2, and 8-31-3. Accordingly, a value of 0.75 was taken for the first group of plants and 0.72 for the second group. The data of measured stem geometric sizes indicated that the average diameter of alfalfa plant stems only slightly deviated from 0.12 cm along the plant height. Therefore, a value of 0.06 cm was used as the stem radius for the simulations.

The measured concentrations of MTBE in plant water are plotted in Figure 1 versus stem position from the soil surface. The figure illustrates the concentration distribution profiles of several plants from different locations in the channels. The curves for plants 7-31-1, 7-31-2, and 7-31-3 are the results measured from stems with the leaves on, while those for plants 8-31-1, 8-31-2, and 8-31-3 are results from stems where the leaves had been removed after harvesting. With the leaves present, the concentration obtained was higher than that without leaves on the stems.

In order for the plants to remain healthy and regrow, we left 6 cm long stems. However, the concentrations of contaminants in the plant at the soil surface were essential for us to estimate fluxes of contaminant in the plants and to determine the diffusion coefficients of contaminants through plants with the model developed. By fitting the data in Figure 1 with exponential equations, we could extrapolate and estimate the MTBE concentrations in the plant water at the soil surface. These values differ from plant to plant and are listed in the caption of Figure 1.

Model Validation. The roots for the equation $J_0(\beta_n) = 0$ were obtained by using software MAPLE V (release 3.0). With these roots and eqs 8 and 9, it is possible for us to compute the concentration distribution within the stem at different plant heights. The results are shown in Figure 2, which shows that the distribution profile only depends on the values of the characteristic distance

$$Z = \frac{z}{z_d} = \frac{D}{r_0^2}\frac{z\theta_w}{u}$$

This conclusion will be the same as what was reported by

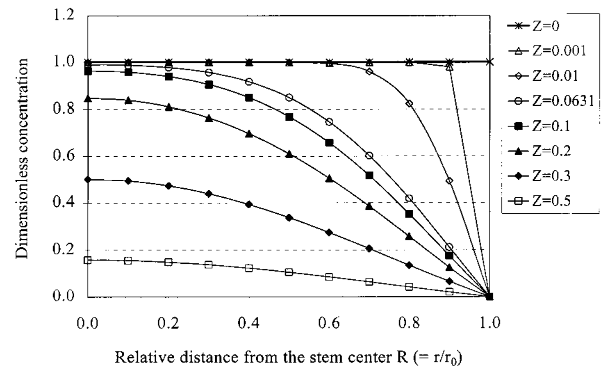

FIGURE 2. Concentration distribution within the plant stem as a function of R and the characteristic distance Z ($=\theta_w Dz/ur_0^2$) with uniform concentration at $Z = 0$. Concentration reduced to the overall concentration at $Z = 0$.

Rose (*9*) when we convert $(z\theta_w)/u$ to the time (t) taken for the plant water to move a distance of z from the soil surface and consider a porous medium rather than a homogeneous one. Rose (*9*) found that when the overall average concentration reached 50% of that at time zero (z = 0 in our case), the value of

$$\frac{Dt_{1/2}}{r_0^2}$$

equaled 0.0631. In the computation using our model eq 11, the overall average concentration became 49.98% of that at the soil surface when

$$\frac{(\theta_w D z_{1/2})}{u r_0^2} = 0.0631 \qquad (12)$$

Therefore, with eq 12, we will be able to estimate the diffusion coefficient of contaminants diffusing out through plant stems if we have the data for the stem radius, the superficial water velocity through plants, the volumetric water content of the plant, and the height at which the overall average concentration becomes 50% of that in the stems at the soil surface.

The superficial water velocity through the stem was obtained by uniformly distributing the transpiration rate of each experimental channel among all the plant stems in that channel. The transpiration rate of every channel was obtained by subtracting the evaporation rate of the unplanted channel from the evapotranspiration rate of the planted channel, and the stems were counted for each channel. To calculate the half distances ($z_{1/2}$), we used the exponential fittings in Figure 1 to solve for z at $c/c_0 = 0.50$ for each individual plant case. The diffusion coefficients were estimated and are listed as D in Table 1. The values fall into the range of 0.483−1.11 × 10^{-7} cm^2/s with the mean value of 0.844 × 10^{-7} cm^2/s and a standard deviation of 0.258 × 10^{-7} cm^2/s. These values are significantly smaller than the diffusion coefficient of MTBE in water, which is 8.20 × 10^{-6} cm^2/s estimated by the correlation equation recommended in ref *10*.

For the experiments monitoring the transient concentration changes inside the sample bottles, the process of MTBE diffusing out from rod-shaped stems into the surrounding gas phase was the same as that described by Rose (*9*) and Philip (*11*). Assuming uniform concentration distribution across the plant stem radius at time zero (i.e., when the segments were sealed into the bottle), the relationship of Rose (*9*) and Philip (*11*), i.e.

$$\frac{Dt_{1/2}}{r_0^2} = 0.0631 \qquad (13)$$

TABLE 1. Estimation of MTBE Diffusion Coefficients through Alfalfa Stems Based on Equations 12 and 12′

plant no.	7-31-1	7-31-2	7-31-3	8-31-1	8-31-2	8-31-3
no. of stems in each channel	107	80	127	102	111	79
transpiration rate (L day^{-1} channel^{-1})	0.55	0.47	0.40	0.62	0.43	0.39
water content (θ_w), cm^3/cm^3	0.75	0.75	0.75	0.72	0.72	0.72
stem radius (r_0), cm	0.06	0.06	0.06	0.06	0.06	0.06
superficial velocity (u), cm/s	0.0053	0.0060	0.0032	0.0062	0.0040	0.0051
Initial concentration (c_0), dimensionless	0.351	0.362	0.277	0.245	0.257	0.244
half-distance ($z_{1/2}$), cm	27.1	17.2	20.2	17.6	14.9	16.3
$D \times 10^7$, cm^2/s[a]	0.588	1.06	0.483	1.11	0.841	0.980
$D' \times 10^7$, cm^2/s[b]	0.857	1.54	0.704	1.62	1.22	1.43

[a] Uniform concentration condition at $Z = 0$ was assumed, i.e., $Z'_{1/2} = 0.0631$. [b] Nonuniform concentration condition at $Z = 0$ was assumed, i.e., $Z'_{1/2} = 0.0919$.

TABLE 2. Diffusion Coefficient Values Estimated by Monitoring Transient Concentration Changes inside Sample Bottles Holding Alfalfa Stem Sections

Diffusion Coefficient ($D \times 10^7$ cm^2/s)

June 28, 2000					
11.8	5.04	13.3	7.84	8.97	16.0
June 29, 2000					
2.12	3.19	1.92	3.18	4.24	4.53
3.28	3.6	4.61	1.88	7.71	

Statistical Analysis

mean value ($\times 10^7$ cm^2/s)	SD ($\times 10^7$ cm^2/s)	sample SE ($\times 10^7$ cm^2/s)	$t_{0.05}$ for sample 17	95% CI ($\times 10^7$ cm^2/s)
6.07	4.24	0.925	2.120	4.14−8.00

Half-Distance $z_{1/2}$ (cm) for Four Individual Plants

plant 1	plant 2	plant 3	plant 4
13.3	20.4	15.4	14.7

was used together with the measured half-time and stem radius for each sample to estimate the values for diffusion coefficient D. The resulting values of D that are presented in Table 2 range from 1.88×10^{-7} to 1.60×10^{-6} cm^2/s. The mean value of D is 6.07×10^{-7} cm^2/s, and the sample standard error is 0.93×10^{-7} cm^2/s. The 95% confidence interval for this group of diffusion coefficient values is $4.14{-}8.00 \times 10^{-7}$ cm^2/s. The GC readings of the gas phase inside these sample bottles at equilibrium were plotted as a function of plant height. Each curve was fitted by an exponential trend-line automatically by Microsoft Excel. From the fitting equations of the form $y = e^{-az}$ (y represents the peak height per unit mass of water, z represents the distance, m and a are the fitting constants), the half-distance for a concentration to drop to a 50% level of the selected point (e.g., y_1) can be calculated from the following equation:

$$\left.\frac{y_1}{y_2}\right|_{y_2=0.5y_1} = \exp(az_{1/2}) = 2 \qquad (14)$$

The resulting values for $z_{1/2}$ are given in Table 2. The curves, which are included in the Supporting Information, not only present a similar trend as those in Figure 1 but also give values of $z_{1/2}$ in the range close to that in Table 1.

The values of D in Table 1 are lower than those in Table 2, although within the same order of magnitude. The cause of this is likely due to underestimation of the actual velocity of the water in the xylem. The half-time is equal to $z_{1/2}\theta_w/u$ if the water flows through all of the void space as it moves up the stem. If only 20% of the plant void space is xylem and the half-time is taken as $0.2z_{1/2}\theta_w/u$, the estimated values of D in Table 1 are 5 times larger. In the analysis, we assumed that the daily transpiration rate was uniformly partitioned among all the stems in each channel, while the transpiration rates might vary significantly from plant to plant. Moreover, the plants we sampled were taller ones in each channel such that we could establish the concentration profile over the plant height of up to 52 cm. But quite a few stems and plants were shorter (some even shorter than 10 cm) and needed less water to support their growth (*6*). Thus, a greater portion of the water transpired should have gone through the more vigorously growing plants. The values of diffusion coefficient in Table 2 are about 7 times larger than those in Table 1. This is attributed to the actual velocity in the xylem being greater than u/θ_w, the vigorousness of plant growth, and measurement errors.

Model Modification. Note that the above results were obtained based on the boundary conditions in eq 3 or eq 7, in which we assumed a uniform composition over the stem cross section, i.e., $c = c_0$ at $z = 0$ or $C = 1$ at $Z = 0$. This assumption is the same condition as what was used by Rose (*9*) and Philip (*11*) when they were dealing with the dynamics of diffusion between an individual cell and a large body of solution in which it was placed.

However, from the soil water MTBE concentration data obtained earlier (*8*), it was found that the MTBE concentration in the soil water immediately below the soil surface was much lower than that in the plant water within stems at the soil surface. This implies that the concentration inside the stems at this position may not be uniform; rather it is a function of r (or R). In the experiment, we could not measure the distribution of concentration across the radial distance. The known conditions about the distribution within stems at $Z = 0$ were

$$\begin{aligned} \frac{\partial C}{\partial R} &= 0 \quad \text{at } R = 0 \\ \bar{C} &= 1 \quad \text{at } Z = 0 \\ C &= C_{sw} \quad \text{at } R = 1 \end{aligned} \qquad (15)$$

where C_{sw} is the concentration in the soil water at $Z = 0$ that has been normalized to the initial overall concentration for each plant case.

To find a distribution that satisfies the above three conditions, a function of the form

$$C = aR^2 + b \qquad (16)$$

was chosen. This function automatically satisfies the first condition in eq 15, and the two constants are yet to be determined according to the other two conditions. The second condition gives

$$\bar{C}|_{z=0} = \frac{1}{\pi \cdot 1^2}\int_0^1 (aR^2 + b)2\pi R \, dR = 1$$

TABLE 3. Statistical Analysis for Values of Characteristic Distance $Z'_{1/2}$ in Modeling When Nonuniform Concentration Distributions ($C = aR^2 + b$) at $Z = 0$ Are Considered[a]

plant no.	7-31-1	7-31-2	7-31-3	8-31-1	8-31-2	8-31-3
half-distance ($z_{1/2}$), cm	27.1	17.2	20.2	17.6	14.9	16.3
characteristic distance ($Z'_{1/2}$), dimensionless	0.0961	0.0967	0.0916	0.0887	0.0899	0.0886
deviation from mean ($\Delta Z'_{1/2}$), dimensionless	0.00420	0.00472	−0.000340	−0.00322	−0.00205	−0.00331
deviation squared $(\Delta Z'_{1/2})^2$, $\times 10^6$	17.6	22.3	0.116	10.4	4.20	11.0

[a] $\overline{Z'_{1/2}} = \sum_1^6 Z'_{1/2}/n = 0.0919$,

$$s_Z^2 = \frac{\sum_1^6 (\Delta Z_{1/2})^2}{n-1} = \frac{6.55 \times 10^{-5}}{5} = 1.31 \times 10^{-5},\ s_z = 0.00362,$$

$s_{\overline{z_{1/2}}}\ s_z/\sqrt{n} = 0.00148$

That is

$$2\left(\frac{a}{4}R^4 + \frac{b}{2}R^2\right)\Big|_0^1 = \frac{a}{2} + b = 1 \qquad (17)$$

The third condition gives

$$C_{sw} = a + b \qquad (18)$$

By solving eqs 17 and 18, we can find the values of a and b that are functions of C_{sw}. To obtain the value for C_{sw}, the available soil water concentrations in Zhang (*8*) were used. There are four measured values from different channels in the soil 2 cm below the surface. We used the arithmetic average value of these four dimensionless values as our soil water concentration at $Z = 0$, namely

$$c_s = \frac{1}{4}(0.111 + 0.174 + 0.113 + 0.0865) = 0.121$$

This value was then normalized to the corresponding overall concentrations at $Z = 0$ for the actual plants to get values for C_{sw}. The resulting data for C_{sw}, a, and b for the six experimental cases were then used in the simulation.

With the initial nonuniform composition distribution of $C = aR^2 + b$ at $Z = 0$, we can find the integration constant in eq 9 as the following:

$$\lambda' = \frac{2(a+b)\beta_n J_1(\beta_n) - 4aJ_2(\beta_n)}{\beta_n^2 J_1^2(\beta_n)} \qquad (9')$$

As a consequence, the overall concentration resulting from eqs 9′ and 10 becomes

$$\bar{C} = 2\sum_1^\infty \left[\exp(-\beta_n^2 Z)\frac{2(a+b)\beta_n J_1(\beta_n) - 4aJ_2(\beta_n)}{\beta_n^2 J_1(\beta_n)}\right] \qquad (11')$$

Notice that $\bar{C}$ is now a function not only of Z but also of a and b, the parameters of the starting concentration distribution. Again, the details of developing eqs 9′ and 11′ can be found in Appendix A of Zhang (*8*).

Simulation with Modified Model. With eqs 8, 9′, and 11′, we computed the concentration profiles within the stems and the overall average concentration as a function of the characteristic distance Z. Figure 3 shows the concentration profiles for several values of Z for plant 7-31-1. Computation of the overall concentration from eq 11′ as a function of Z manifested that when $\bar{C} = 0.50$, the corresponding value of Z ($Z'_{1/2}$) slightly varied from plant to plant, unlike for the uniform starting concentration case. This observation results from the effects of parameters a and b in eq 11′, which indicates that $Z'_{1/2}$ is a function of a and b. The values of $Z'_{1/2}$ for each of the six plants are listed in the second row of Table 3. For brevity, in the simulation process, the mean of the six values, $Z'_{1/2} = 0.0919$, was used. That is, with nonuniform conditions in eq 17, the relationship between the diffusion coefficient D' and the half-distance $z_{1/2}$ becomes

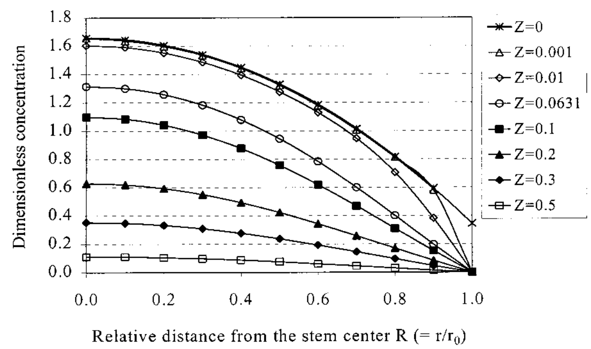

FIGURE 3. Concentration distribution within the plant stem as a function of R and the characteristic distance Z ($=\theta_w Dz/ur_0^2$) for plant 7-31-1, with nonuniform concentration at $Z = 0$. Concentration reduced to the overall concentration at $Z = 0$.

$$Z'_{1/2} = \frac{\theta_w D' z_{1/2}}{ur_0^2} \qquad (12')$$

The diffusion coefficient values estimated using eq 12′ for the six experimental cases are presented as D' in Table 1. Note that $D'/D = Z'_{1/2}/Z = 0.919/0.631 = 1.46$. When there is nonuniform concentration distribution at $Z = 0$, the concentration gradient along the radial direction is reduced, so it needs a greater value for the diffusion coefficient to maintain the same diffusion flux across the stem surface.

With the diffusion coefficients (D and D') in Table 1 and the corresponding superficial water velocities, we simulated the overall concentration as a function of the distance from the soil surface (z) and then compared the simulation results with the experimental data. The average absolute relative deviations of the simulation results using the uniform and nonuniform concentrations at $Z = 0$ from the six sets of experimental data are compared in a table in the Supporting Information. All the average absolute relative deviations from simulation are smaller for the nonuniform case than that for the uniform case. This suggests a better fit for the more realistic starting steady-state assumption with nonuniform radial distribution.

TABLE 4. Statistical Analysis for Values of Diffusion Coefficient Estimated Using Model Where Nonuniform Concentration Distributions ($C = aR^2 + b$) at $Z = 0$ Are Considered[a]

plant no.	7-31-1	7-31-2	7-31-3	8-31-1	8-31-2	8-31-3
$Z'_{1/2}$, dimensionless	0.0961	0.0967	0.0916	0.0887	0.0899	0.0886
diffusion coeff (D'),[b] $\times 10^8$ cm^2/s	9.02	16.2	6.97	15.6	12.1	13.9
deviation from mean ($\Delta D'$), $\times 10^8$ cm^2/s	−3.28	3.90	−5.33	3.30	−0.198	1.60
deviation squared ($(\Delta D')^2$)	10.7	15.2	28.4	10.9	0.0393	2.57

[a] $\overline{D'} = \sum_1^6 D'/n = 12.3 \times 10^{-8}$ cm^2/s

$$s_D^2 = \frac{\sum_1^6 (\Delta D')^2}{n-1} = \frac{67.9 \times 10^{-16}}{5} = 13.6 \times 10^{-16},\ s_D = 3.68 \times 10^{-8}\ \text{cm}^2/\text{s}$$

$$s_{\overline{D'}} = s_D/\sqrt{n} = 1.50 \times 10^{-8}\ \text{cm}^2/\text{s}$$

[b] When D' was calculated by using eq 12′, the corresponding values for $Z'_{1/2}$ and the superficial velocity u were used for each plant case.

Analysis for the Parameters. From the six values of $Z'_{1/2}$ in Table 3, we can examine the confidence interval estimate for $Z'_{1/2}$. By assuming that the six plants represent a normally distributed population, with 5 df (= number of samples − 1), we found the entry in the t-distribution table for 95% confidence, i.e., $t_{0.05} = 2.571$ (*12*). The calculations and values of statistical parameters for interval estimate of $Z'_{1/2}$ are given in Table 3, in which n is the sample number $\overline{Z'_{1/2}}$ is the mean, s_Z is the standard deviation, and $s_{Z_{1/2}}$ is called the sample standard error (*12*). Using the quantities in Table 3, we first calculate the quantity

$$t_{0.05} \times s_{\overline{Z_{1/2}}} = 2.571 \times 0.00148 = 0.00380$$

This value is used to find the confidence interval (*12*) as

$$0.0881 \le Z'_{1/2} \le 0.0957$$

That is, we can say with confidence of 95%, that interval 0.0881−0.0957 includes the half-distance $Z'_{1/2}$.

Similarly, with a confidence of 95%, we can find the interval for the diffusion coefficient D'. The calculations of statistical parameters, i.e., mean $\overline{D'}$, standard deviation s_D, and the sample standard error $s_{\overline{D'}}$, for interval estimate of D' are given in Table 4. We can calculate the quantity

$$t_{0.05} \times s_{\overline{D'}} = 2.571 \times 1.50 \times 10^{-8} = 3.87 \times 10^{-8}$$

and then obtain the confidence interval as follows:

$$8.43 \times 10^{-8} \le D' \le 16.2 \times 10^{-8}$$

The values of D' reported in Table 4 are for the respective values of $D'_{1/2}$ that are given in Table 4. Note that these values differ from the values reported in the last row of Table 1 where the average value 0.919 of $Z'_{1/2}$ was used to obtain D'.

Therefore, with a confidence of 95%, the diffusion coefficient of MTBE through stems of live alfalfa plants is within the range of 8.43−16.2 $\times 10^{-8}$ cm^2/s for the experimental conditions for this work. This is about 2 orders of magnitude below the rate in pure water and may be limited by diffusion through "solid" phases including cuticle. Similar values were estimated for movement of TCE through sunflower or poplar stems (*5*) using a simpler approximation of the radial diffusive loss during vertical transfer through the stem. The present model allows a reliable estimate of diffusion rate and is applicable to other species upon substitution of appropriate parameters.

These estimated values of diffusion coefficient are based on the actual water velocity in the stem being equal to u/θ_w and the half-time being equal to $z_{1/2}\theta_w u/u$. If the actual water velocity in the xylem is greater than u/θ_w, then the estimated value of diffusion coefficient would also be larger.

The transient method of analysis which was used to obtain the data in Table 2 does not require knowledge of the transpiration rate. The estimates in Table 2 are based on the assumption of a uniform concentration at $t = 0$. Thus, the actual values of D may be as much as 46% larger than those in Table 2.

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Supporting Information Available

Detailed description of the experimental setup, conditions, and methods used and additional experimental data of diffusion loss of water and of MTBE across alfalfa plants (20 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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