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Lignin and Lipid Impact on Sorption and Diffusion of Trichloroethylene in Tree Branches for Determining Contaminant Fate during Plant Sampling and Phytoremediation

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Plants draw all they need from their surrounding environment and in doing so also draw anthropogenic contaminants from their surroundings. Several natural processes (e.g., active transport, diffusion, sorption, and degradation) occur within trees and affect chemical concentrations in tree samples. This study elucidates tree contaminant chemical interactions on equilibrium sorption and diffusion into branch tissue (i.e., wood core and bark), specifically the impacts of lipid and lignin content. Five tree species were selected to span a range of lignin and lipid contents. Linear isotherms were obtained for all sampled species over a limited concentration range (2 μg/mL $< C_{gas} <$ 12 μg/mL), and equilibrium distribution coefficients (K_d) were linearly correlated to lipid ($R^2 > 0.83$) but not lignin ($R^2 < 0.4$) content. Lipid content was generally higher in bark than in wood cores, so mass concentrated in this tissue. Diffusion into trees was modeled, showing mass transfer resistance in bark was different from wood cores. Diffusion coefficients for bark were 2−10 times less than those for wood cores for all species, and diffusion was linearly related to lipid content ($R^2 >$ 0.96) and sorption coefficients ($R^2 > 0.83$). Data from this study and previous research were used to develop the following correlation between the diffusion coefficient and relevant plant and chemical parameters for branch samples: $D = (-7 \times 10^{-11}) \times [f_{lipid} \times 10^{(1.48 \times \log Kow + 0.54)}] + 4 \times 10^{-8}$.

Introduction

Studies on plant contaminant interactions have led to phytoremediation applications to remove soil and groundwater contaminants via plant uptake, offering an inexpensive alternative to traditional pump-and-treat systems (*1*). In addition, several studies have demonstrated that trees can also serve as a low-cost, rapid, and relatively simple to use monitoring system (*2*−*4*). However, tree-based monitoring systems have generally allowed only qualitative mapping of plumes at contaminated soil and groundwater sites. Quantitative mapping of plumes through plant sampling remains a challenge and requires a better understanding of the relationship between contaminant concentrations in soil and groundwater and contaminant uptake, transport, and transformation mechanisms in trees.

Contaminants enter plants through three major pathways: (1) uptake of contaminated water by plant roots (*5, 6*), (2) diffusion of contaminants from soil gas into plant roots (*3*), and (3) diffusion of contaminants from the atmosphere into plant tissue (*7*−*9*). Once in the plant, contaminants are potentially subject to the following processes: (1) advective transport from roots to leaves via the xylem, (2) advective transport from leaves to roots via the phloem, (3) sorption to plant tissue (*10*−*13*), (4) diffusion from plant tissue to the atmosphere (*2, 14*), (5) transformation into byproducts (*15*−*19*), and (6) transpiration through leaves (*6, 19*−*22*). While these processes affect contaminant concentrations in trees and are not fully understood, this study focuses on sorption and diffusion in plant tissue.

A number of studies have focused on the mechanisms governing the sorption of organic chemicals in plant tissue. The effects of multiple plant parts and species, different organic sorbates, and plant chemistry have been investigated in field and laboratory studies (*3, 5, 9*−*13, 23*−*26*). Aqueous phase sorption of organic chemicals has been investigated using root tissue from barley plants (*5*), wood chips from pine, fir, basket willow and oak trees (*10, 11*), stem tissue from wheat and ryegrass (*12, 13*), and xylem tissue from poplar and willow trees (*3, 23, 24*). Atmospheric sorption of organic chemicals has been investigated primarily at field sites with leaf, needle, seed, and bark samples collected from white pine and sugar maple trees (*9*). At a field site, Meredith and Hites measured polychlorinated biphenyl (PCB) concentrations in the bark and wood of black walnut, tulip poplar, and white oak trees (*25*). Almost all of the PCBs were contained in the outer 1 cm of the bark. Water−wood and gas−wood sorption coefficients were different for the different plant parts and species investigated and were hypothesized to be a function of the chemical composition of plant tissue.

Sorption coefficients have been compared to various indicators of plant chemistry, including lipid content, carbohydrate content, and lignin content. However, conflicting results have been found. Mackay and Gschwend (*10*) and Trapp et al. (*11*) investigated the correlation between lignin content and water−wood sorption coefficients for wood chips and determined that higher lignin content corresponded to greater sorption capacity. Li et al. (*12*) and Barbour et al. (*13*) evaluated the role of lipid and carbohydrate content on water−plant sorption coefficients for grasses. The results indicate that plant lipids were the predominant storage component for hydrophobic organic compounds compared to carbohydrates. Similar results were obtained by Simonich and Hites for atmospheric sorption coefficients obtained in the field; they observed higher concentrations of polynuclear aromatic hydrocarbons (PAHs) with greater lipid content (*9*).

Sorption coefficients from different plant parts and species have been normalized by the lignin content (*11*) and lipid content (*9, 12*) in order to evaluate the effect of sorbate properties on sorption. The sorbates studied include volatile organics such as benzene, toluene, ethylbenzene, and xylene (BTEX) compounds and chlorinated solvents (*3, 10, 11, 23*), and PAHs and PCBs (*9, 12, 25*). Results from experiments conducted by Trapp et al. indicate that a linear relationship

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exists between the water−wood sorption coefficients normalized by the lignin content and the octanol−water partitioning coefficient (log K_{ow}) (*11*). A linear relationship was also found between the atmospheric−wood sorption coefficients normalized by the lipid content and the octanol−air partitioning coefficient (log K_{oa}) (*9*).

Compared to sorption, less work has focused on understanding the mechanisms that control diffusion in plants. Diffusion coefficients have typically been estimated from mathematical models applied to laboratory results using sorption and molecular properties of the chemical or from whole plant models of contaminant fate and transport in the field. On the basis of laboratory results, Mackay and Gschwend calculated diffusion coefficients of monoaromatic compounds in water-saturated wood as a function of the water−wood equilibrium sorption coefficients (K_{wood}) and the aqueous diffusivity of the chemical in question (D_{water}) (*10*). Diffusion in unsaturated wood tissue was modeled using a similar approach that included diffusion through pores filled with gas and pores filled with water (*11*). Diffusion coefficients in each phase were estimated on the basis of the fractions of contaminants in each phase and the tortuosity of the diffusion path. Baduru et al. measured diffusion coefficients in xylem plant tissue for the first time (*24*). Six organic chemicals and xylem tissue from poplars were used. The diffusion coefficient was linearly related to the molecular weight of the chemicals and decreased as molecular weight increased. There was no clear relationship between the water−wood equilibrium sorption coefficients and the diffusion coefficients in wood for the different chemicals.

In contrast to modeling efforts applied to controlled laboratory studies, whole plant models applied to field data are more complex and combine multiple concurrent processes, including advective transport, diffusion, sorption, transformation, and/or transpiration. Diffusion coefficients estimated by calibrating field data with whole plant models are typically 2−100 times greater than values determined from laboratory data (*4, 7, 26*). The reason for this discrepancy is not clear, but differences in plant tissues and chemistry likely play a role in this dynamic system as do environmental condition variability. The impacts of different plant parts and chemistry on diffusion coefficients has not heretofore been evaluated.

The goals of this study are to quantify the roles of lipid and lignin on equilibrium sorption and diffusion in tree branches and bark. Using five different plant species we determined the following: (1) equilibrium sorption coefficients for TCE between air and branches with and without bark, (2) kinetic profiles for TCE uptake from air into branches with and without bark, and (3) lipid and lignin contents of these plant tissues. Data from sorption experiments and from the literature were used to explore relationships between sorption capacity, plant composition (i.e., lipid and lignin content), and K_{ow}. Diffusion coefficients for whole branches (i.e., wood plus bark) and wood cores (i.e., branches without bark) were calculated from corresponding kinetic profiles using an existing model developed for diffusion into a homogeneous cylinder (*27*), and diffusion coefficients for bark were calculated from whole branch kinetic profiles using an existing model developed for diffusion into a composite core and shell cylinder (*28*). Diffusion coefficients from this work and the literature are used to explore relationships between diffusion coefficients and plant composition and sorption capacity.

Materials and Methods

Trichloroethylene (TCE, 99.5% purity) and methanol (99.9% purity) were purchased from Supelco Inc., Bellefonte, Pennsylvania, and were used as received. Plant branch samples were collected from five different species of landscape trees on the University of Illinois campus at Urbana−Champaign and were used within 30 min after collection. The branch samples were collected by cutting branches ≤1 cm in diameter from trees using stainless steel shears. Samples, approximately 0.5 cm in diameter and 3 cm in length, were then cut from the branches and used for sorption experiments. Branch samples did not contain any detectable amounts of TCE. Selected physicochemical properties of TCE are listed in Table S1 of the Supporting Information; tree species and properties are listed in Tables S1 and S8 of the Supporting Information. The tree species were selected to span a range of lipid and lignin contents. Sorption coefficients were determined for branch samples with and without bark. Bark was removed from selected branch samples using a stainless steel knife, and these are referred to as "wood core samples". Samples were collected in October from all trees; samples were also collected in January from the red maple to confirm that the tree samples collected during different seasons gave reproducible sorption results. The results are given in the Supporting Information.

Experimental Setup and Analysis. Sorption isotherms for TCE between air and branch samples were determined using a batch equilibration method. An aqueous solution of TCE at the solubility limit was prepared by equilibrating 5 mL of pure phase TCE with 25 mL of distilled, deionized water. Approximately 0.2−0.8 mL of this solution was injected into a 2 mL glass vial placed inside a 30 mL glass bottle. Initial masses of TCE in the bottles ranged from 200 to 800 μg for all species. Preweighed branch and wood core samples were immediately inserted into the bottles, which were then crimp-sealed with Teflon-lined aluminum caps and allowed to incubate at 21 ± 1 °C.

The incubation time for all branch samples at the highest TCE mass loading was initially varied between 2 and 96 h to determine the time for apparent equilibrium. Different incubation times were used to capture different points during uptake, which were then used to generate kinetic profiles. Incubation times greater than or equal to the apparent equilibration time resulted in identical isotherms, so all isotherms were equilibrated for 24 to 72 h (depending on the plant species). Sorption isotherms for bark were calculated from the corresponding branch and wood core samples based on mass balance.

After incubation, headspace concentrations in the jars were measured by direct injection of between 50 and 60 μL of headspace into a 5890 Hewlett-Packard gas chromatograph (GC) equipped with an electron capture detector (ECD). The amount of TCE present in branch and wood core samples was calculated using the difference between the initial mass of TCE injected and the final mass of TCE in the headspace and water, with the assumption that no degradation is expected for TCE in an aerobic environment. The mass of TCE in the headspace was determined by multiplying the TCE headspace concentration by the volume of headspace; the latter was obtained by subtracting the volume of the plant sample from the volume of the jar, assuming that the branch/wood sample is approximately cylindrical. To calculate the mass of TCE in the water, we assumed that TCE in headspace and water was spatially uniform, and partitioning between these two phases was described by Henry's law. The data was used to generate air−branch sorption isotherms.

Three different control experiments were performed to verify sorption isotherm methods. Two control experiments were performed to confirm that TCE uptake into branches was controlled by radial diffusion and not diffusion along the (cylinder) axis. Details and results of control experiments are in the Supporting Information.

The lignin, lipid, and moisture contents of all plant samples were analyzed by Servitech Laboratory, Dodge City, Kansas. The lipid content was analyzed using petroleum ether extraction (*29*). Lignin content was analyzed using the Klason analytical method (*30*). Moisture content was analyzed using the method in Li et al. (*12*). Each plant sample is assumed to consist of water, air, and solid fractions (*11*). The volume fraction of water in each sample was calculated using the difference between the initial weight of the plant sample and the weight after the sample was placed in a drying oven at 105 °C for 12 h, multiplied by the density of water at the ambient temperature (21 °C). The volume fraction of air present in each sample was calculated using the difference between the initial weight of the plant sample and the weight after the sample was placed in water for 7 days, multiplied by the density of water at the same temperature (21 °C) (*24*). The volume fraction of solid was calculated from the difference between the volume of a cylinder with the same dimensions as the plant branch and the volume of the air plus water.

Models for Diffusion Coefficient Estimation. Diffusion coefficients for whole branch and wood core samples were calculated assuming radial diffusion into an infinitely long cylinder with radius a (*27*). In this study, control experiments (Supporting Information) indicated that radial diffusion was the primary mass transfer process. The governing equation for mass flux into the branch or wood core is given by Fick's second law as

$$\frac{\partial(C_{\text{brch}})}{\partial t} = \frac{D_{\text{brch}}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{\text{brch}}}{\partial r}\right);\ 0 < r < a \tag{1}$$

where C_{brch} is the concentration of TCE in the branch (mg/g), D_{brch} is the effective diffusion coefficient in the branch (cm^2/s), and r is the radial distance from the center (cm).

The initial concentration in the cylinder was assumed to be zero. The measured concentration in the headspace decreased exponentially with time. The concentration at the surface of the branch or wood core surface ($r = a$) is given by

$$C_{\text{brch},r=a}(t) = C_{\text{hspace}} \times K_{\text{brch}} \tag{2}$$

The data was approximated by an exponential decay function

$$C_{\text{brach},r=a}(t) = C_{\text{brch},r=a,0}\exp(-\beta t) \tag{3}$$

where $C_{\text{brch},r=a,0}$ is the initial concentration at the surface of the cylinder ($C_{0,\text{hspace}} \times K_{\text{brch}}$), $C_{0,\text{hspace}}$ is the initial concentration in the headspace (mg/L), K_{brch} is the equilibrium partitioning coefficient (mL/g), β is the exponential decay term, and t is time (s).

A no mass flux boundary is assumed at the center of the cylinder ($r = 0$) and is given by

$$\frac{\partial C_{\text{brch}}}{\partial r} = 0 \quad \text{for } r = 0 \tag{4}$$

It follows that the solution for the concentration in the cylinder is given by (*27*)

$$C_{\text{brch}} = \frac{2D_{\text{brch}}}{a}\sum_{n=1}^{\infty}\exp(-D_{\text{brch}}\alpha_n{}^2 t)\frac{\alpha n J_0(r\alpha_n)}{J_1(a\alpha_n)} \times \int_0^1 \exp(D_{\text{brch}}\alpha_n{}^2\lambda)C_{\text{brch},r=a}d\lambda \tag{5}$$

where J_0 is the Bessel function, order 0; J_1 is the Bessel function, order 1; α_n is the root of the equation $J_0(a\alpha_n) = 0$; and n is the number of roots.

Using Equation 5, the mass in the cylinder at a given time t is given by

$$M = \frac{2\pi h}{M_{\text{brch}}}\int_{r=0}^{a} C_{\text{brch}} r\,dr$$
$$M = \frac{4\pi D h C_{0,\text{hspace}} K_{\text{brch}}}{M_{\text{brch}}} \times \sum_{n=1}^{\infty}\exp(-D\alpha_n{}^2 t)\frac{(\exp(D\alpha_n{}^2-\beta)t - 1)}{D\alpha_n{}^2-\beta} \tag{6}$$

where M is the normalized mass of TCE in the cylinder at time t (mg/g), h is the height of the cylinder (cm), and M_{brch} is the mass of the branch (g).

The model was run until there was no change in the calculated value of mass as the number of roots n was increased. The diffusion coefficient was calculated to minimize the error between the calculated normalized mass from eq 6 and the experimental value of the normalized mass in the branch. Parameters for the model ($C_{\text{brch},r=a,0}$, β and n) are given in Table S2 of the Supporting Information.

The diffusion coefficient for the bark was determined by modeling the branch as a composite cylinder consisting of a wood core with radius b and an outer skin of bark between radius b and a (Figure S1 of the Supporting Information) and by using the diffusion coefficient for the wood core obtained from application of eq 6. The governing equations are

$$\frac{\partial(C_{\text{w}})}{\partial t} = \frac{D_{\text{w}}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{\text{w}}}{\partial r}\right);\ 0 < r < b \tag{7}$$

$$\frac{\partial(C_{\text{b}})}{\partial t} = \frac{D_{\text{b}}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{\text{b}}}{\partial r}\right);\ b < r < a \tag{8}$$

where C_{w} is the concentration in the wood core (mg/g), C_{b} is the concentration in the bark (mg/g), D_{w} is the diffusion coefficient of the wood core (cm^2/s), D_{b} is the diffusion coefficient of the bark (cm^2/s), a is the radius of the branch (bark and wood core) (cm), and b is the radius of the wood core (cm).

Equations 2, 3, and 4 are used for the boundary conditions at the surface and center of the branch, respectively, with the sorption coefficient for the bark replacing the sorption coefficient for the branch used in eq 2. Equilibrium is assumed at the interface between the bark and wood ($r = b$) such that $C_{\text{w}} = C_{\text{b}} \times K_{\text{wood}}/K_{\text{bark}}$, where K_{wood} and K_{bark} are the equilibrium sorption coefficients for the wood core and bark, respectively. The initial concentration in the cylinder is assumed to be zero, and the initial concentration of the solute in the headspace is given by $C_{0,\text{hspace}}$. The concentration in the headspace at time t is given by the mass balance between the initial mass and the mass in the branch

$$VC_{0,\text{hspace}} = VC + L\int_0^b 2\pi r(C_{\text{w}})\text{d}r + L\int_b^a 2\pi r(C_{\text{b}})\text{d}r \tag{9}$$

where V is the volume of the headspace gas (ml), h is the height of the cylinder (cm), and C is the concentration in the headspace at time t (mg/L).

No analytical solution for this system of equations is available. However, a very similar system of equations was solved numerically by Crank and Godson (*28*), and this approach is used herein. The range $0 \le r \le b$ is divided into L equal intervals δr_{b}, and the range $0 \le r \le a$ is divided into p equal intervals δr_{a} such that $L\delta r_{\text{b}} = m\delta r_{\text{a}} = b$. The value of p is calculated as $p = m \times a/b$. The time period t for which the system is being solved is divided into T equal intervals δt. The model was solved by increasing the values of L, m, and T for the concentration in the headspace until the solution

TABLE 1. Diffusion Coefficients, Sorption Coefficients, Lipid, Lignin, and Moisture Content for All Samples

tree species	calculated diffusion coefficient ($\times 10^{-8}$ cm^2/s)	K_d (mL/g)	R^2 for K_d results	lignin (%)	moisture (%)	lipid (%)	theoretical diffusion coefficient ($\times 10^{-8}$ cm^2/s)
red maple branch	2.79 ± 0.39	120.0	0.99	13.3	46.0	1.0	6.92
linden branch	2.02 ± 0.56	240.3	0.98	8.9	54.1	6.3	2.28
silver maple branch	2.49 ± 0.31	201.1	0.99	18.2	47.2	3.9	5.38
white pine branch	1.53 ± 0.33	292.2	0.99	30.4	55.0	6.7	2.58
tulip tree branch	2.6 ± 0.17	166.1	0.95	10.4	48.4	2.9	2.60
red maple wood core	12.8 ± 1.10	55.9	0.95	10.1	44.2	0.6	22.48
linden wood core	4.32 ± 0.32	204.4	0.95	7.7	53.3	6.6	4.29
silver maple wood core	11.1 ± 0.74	128.0	0.98	10.7	44.4	2.3	9.69
white pine wood core	4.64 ± 0.22	157.2	0.94	23.7	53.3	2.5	5.11
tulip tree wood core	11.4 ± 0.38	93.9	0.91	6.3	53.5	2.1	6.56
red maple bark	2.57 ± 0.78	231.6	0.99	30.1	48.3	2.7	4.03
linden bark	2.24 ± 0.56	265.1	0.99	10.5	56.8	5.9	2.32
silver maple bark	2.35 ± 0.39	260.4	0.99	25.2	49.5	5.6	2.41
white pine bark	1.64 ± 0.32	439.5	0.99	37.7	57.7	11.3	0.38
tulip tree bark	2.53 ± 0.25	234.5	0.96	18.4	50.8	4.1	1.47

converged to within 7% of the previous solution. The diffusion coefficient was calculated to minimize the error between the calculated headspace concentration from eq 9 and the experimental values of the headspace concentration. Final values of L, m, and T are given in Table S2 of the Supporting Information.

Experimental diffusion coefficients obtained in this work for the branch and wood core samples are compared to those obtained from the relationship developed by Trapp et al. (*11*) and later by Baduru et al. (*24*), using tree core samples in the laboratory. This relationship is shown in eq S1 of the Supporting Information.

Results and Discussion

The time to equilibrium for all samples is shown in Table S8 of the Supporting Information and ranged from 12 to 72 h. Similar equilibration times (24−96 h) were obtained for TCE and tetrachloroethene (PCE) exposure to tree cores via headspace and via the aqueous phase (*3, 23*) and for lindane, hexachlorane, benzene, 1,2-dichlorobenzene, and phenanthrene exposure to wheat and ryegrass seedlings via the aqueous phase (*12, 13*). Less time was required to reach equilibrium in this study for all wood core samples compared to branch samples, suggesting that the bark acts as a barrier to mass transport into tree branches.

Equilibrium sorption coefficients (K_d) and corresponding R^2 values for all samples are listed in Table 1, together with lignin and lipid contents. Corresponding isotherms for all samples are presented in Figure S2 of the Supporting Information. The isotherms were linear over the concentration range measured (0.29 mg/g < C_{branch}< 2.38 mg/g), indicative of a partitioning dominated process (*12*). Linear aqueous phase isotherms were also obtained by Ma and Burken (*23*) for TCE, TCA, and CCl_4 sorption to poplar core and cutting samples between 0.1 to 120 mg/kg, by Li et al. (*12*) for lindane and hexachlorobenzene sorption to ryegrass and wheat samples between 1 and 600 mg/kg, and by Barbour et al. (*13*) for benzene, 1,2-dichlorobenzene, and phenanthrene sorption to ryegrass, fescue, and spinach between 2000 and 12000 mg/kg.

The sorption contribution of bark for each species is presented in Figure S3 of the Supporting Information. Approximately 42−60% of TCE was stored in the bark, and the ratio of TCE concentration in bark to TCE concentration in wood varies from 1.5 to 3.2 for all tree species. This indicates that the TCE preferentially accumulates in the bark rather than the wood core.

The dependence of sorption coefficients on lignin or lipid content was evaluated using linear regression. Corresponding coefficients and R^2 values are listed in Table 2; corresponding graphs are in Figure S4 of the Supporting Information. The results for branch, wood core, and bark samples are similar; R^2 values for the regression between K_d and lignin content are all less than 0.40, whereas R^2 values for the regression between K_d and lipid content are all greater than 0.83. Values of R^2 for the regression between K_d and lipid are also greater than 0.86 when the data from branch, wood, and bark samples are combined. This suggests that partitioning to lipids dominates sorption in all samples, and that lipid characteristics are similar between samples. In contrast, Mackay and Gschwend found that sorption coefficients are a function of lignin content; lignin contents were above 30% in their samples (*10*). In this study, nine of twelve samples had lignin contents less than 30%, and this may explain the discrepancy. An additional reason for this could be structural differences between dry lignin in the wood chip samples used by Mackay and Gschwend and hydrated lignin in the samples used in this study (*31*). The sorption of 1-methylcyclopropene was found to be different for hydrated and dry samples taken from avocado, asparagus, and plantain plants (*32*).

Lipid normalized sorption coefficients (K_{lipid}) were calculated for branch, wood, and bark samples.

$$K_{lipid} = K_d / f_{lipid} \tag{10}$$

Logarithms of these values and K_{lipid} values determined by Simonich and Hites (*9*) are plotted versus logarithms of K_{ow} values in Figure 1. The corresponding relationship with an R^2 of 0.98 is obtained

$$\log(K_{lipid}) = 1.48 \log(K_{ow}) + 0.54 \tag{11}$$

These results indicate that sorption coefficients for the plants in this study can be predicted from the lipid content and K_{ow} values using eqs 10 and 11. However, further work is required to determine if this relationship applies to other species or to plant tissues at different stages of maturity other than those investigated here as lignin and lipid composition change over the lifespan of a tree.

Model and experimental kinetic profiles for all branch, wood core, and bark samples are presented in Figure S5 of the Supporting Information. Corresponding diffusion coefficients are presented in Table 1. Concentrations and mass uptake results determined from modeling were within 5% of experimental results at all times. Diffusion coefficients for branch, wood core, and bark ranged from 1.6×10^{-8} to 1.2×10^{-7} cm^2/s. These results compare favorably with the range of values (10^{-7} to 3×10^{-8} cm^2/s) obtained from earlier

TABLE 2. Relationships between Parameters for All Samples

relationship	branch	R^2 for branch results	wood core	R^2 for wood core results	bark	R^2 for bark results
K_d (mL/g) as a function of lipid content (%)	$K_d = 27.15 \times f_{lipid} + 91.0$	0.95	$K_d = 23.12 \times f_{lipid} + 62.3$	0.83	$K_d = 25.88 \times f_{lipid} + 133.2$	0.94
K_d (mL/g) as a function of lignin content (%)	$K_d = 4.81 \times f_{lignin} + 125.8$	0.39	$K_d = 1.78 \times f_{lignin} + 107.0$	0.05	$K_d = 5.25 \times f_{lignin} + 158.3$	0.40
diffusion coefficient (cm^2/s) as a function of lipid content (%)	$D = -1 \times 10^{-9} \times f_{lipid} + 3 \times 10^{-8}$	0.96	$D = -1 \times 10^{-8} \times f_{lipid} + 1 \times 10^{-8}$	0.99	$D = -9 \times 10^{-10} \times f_{lipid} + 3 \times 10^{-8}$	0.99
diffusion coefficient (cm^2/s) as a function of lignin content (%)	$D = -3 \times 10^{-9} \times f_{lignin} + 1 \times 10^{-7}$	0.24	$D = -4 \times 10^{-10} \times f_{lignin} + 3 \times 10^{-8}$	0.44	$D = 3 \times 10^{-11} \times f_{lignin} + 5 \times 10^{-9}$	0.01
diffusion coefficient (cm^2/s) as a function of the sorption coefficient (mL/g)	$D = -7 \times 10^{-11} \times K_d + 4 \times 10^{-8}$	0.94	$D = -6 \times 10^{-10} \times K_d + 2 \times 10^{-7}$	0.83	$D = -4 \times 10^{-11} \times K_d + 3 \times 10^{-8}$	0.96
diffusion coefficient (cm^2/s) as a function of log K_{ow}	$D = -7 \times 10^{-11} \times [f_{lipid} \times 10^{(1.48 \times \log Kow + 0.54)}] + 4 \times 10^{-8}$	0.94	$D = -6 \times 10^{-10} \times [f_{lipid} \times 10^{(1.48 \times \log Kow + 0.54)}] + 2 \times 10^{-7}$	0.83	$D = -4 \times 10^{-11} \times [f_{lipid} \times 10^{(1.48 \times \log Kow + 0.54)}] + 3 \times 10^{-8}$	0.96

FIGURE 1. K_{lipid} as a function of K_{ow}. Experimental data for TCE is compared to literature values from Simonich and Hites (*9*).

laboratory studies of TCE diffusion in plant tissue (*11, 14, 21, 24*). Diffusion coefficients for bark are between 2−10 times smaller than diffusion coefficients for wood cores for the same species. This indicates that bark acts as a barrier to transport of TCE in the plant samples examined here and can control TCE uptake rates. Meredith and Hites found that at a field site the majority of PCBs in white oak, black walnut, and tulip poplar trees were in the outermost 1 cm of bark, suggesting that bark preferentially sorbs PCBs and/or acts as a diffusion barrier to PCB transport into trees from the atmosphere (*25*).

As noted in the introduction and supported by our results diffusion coefficients measured in the laboratory are 2−100 times smaller than values determined from whole plant models applied to data from field sites (*4, 14*). A primary reason for this discrepancy may be that whole plant models assume the diffusion length scale is equal to the distance of the conducting tissue (xylem) from the outer surface (0.7−1.0 *R*, where *R* is the tree radius) (*14*). However, this assumption has not been verified in the field, and our results indicate that bark thickness may be a more appropriate length scale when mass transfer resistance in bark dominates. A smaller length scale would result in a smaller diffusion coefficient and closer agreement with laboratory data. A second reason for this discrepancy could be due to the presence of larger average values of gas porosity in full grown trees in the field versus small tree samples used in the laboratory as suggested by Trapp et al. (*11*) and Baduru et al. (*24*). A third reason could be that mechanical dispersion enhances the radial transport of pollutants in the xylem of actively transpiring whole plants. This occurs because tracheids and vessel elements in the xylem can have lateral connections and mix flow transverse to the primary direction of transport. All three likely impact the movement of contaminants and likely play a role in the difference of up to 2 orders of magnitude between laboratory tissue-based studies and whole plant modeling efforts.

The dependence of diffusion coefficients on lignin and lipid content was evaluated using linear regression. Corresponding coefficients and R^2 values are listed in Table 2; corresponding graphs are in Figure S6 of the Supporting Information. The results for branch, wood core, and bark samples are similar. When all samples are considered, R^2 values for the regression between diffusion coefficients and lignin content are less than 0.40, and R^2 values for the regression between diffusion coefficients and lipid content are greater than 0.60. When all samples except the white pine are considered, R^2 values for lignin content are all less than 0.40, whereas R^2 values for lipid content are all greater than 0.89. This suggests that sorption to lipids controls retardation during diffusion in the tree samples, and that lipid characteristics in wood cores or bark are similar for different plant samples. The anomalous result for white pine

samples may be due to the presence of a resin layer in the pine (*33*) acting as an additional barrier to mass transport of TCE.

Given the dependence of sorption and diffusion on lipid content, the relationship between the diffusion coefficient and K_d was evaluated using linear regression. The corresponding coefficients and R^2 values are listed in Table 2; corresponding graphs are in Figure S7 of the Supporting Information. The R^2 value is greater than 0.83 for all samples, indicating diffusion and sorption are strongly correlated as expected, which is similar to previous results for aqueous phase diffusion (*24*). The corresponding relationships between the diffusion coefficient and the octanol−water partition coefficient were developed by replacing K_d with eq 11 and are presented in Table 2. The relationship for the wood core was used to predict diffusion coefficients for the six chemicals evaluated by Baduru et al. (*24*) with the measured lipid content of 0.5% for the poplar tree core samples; the results are given in Table S9 of the Supporting Information. The predicted diffusion coefficients were close to or within the range of experimental values measured by Baduru et al. (*24*) for all chemicals except tetrachloroethene (PCE). One reason for this discrepancy could be the relatively higher value of log K_{ow} for PCE (3.4) as opposed to the other chemicals (log K_{ow} between 1.06 and 2.69). This result suggests that the relationships developed in this study can be used to predict diffusion coefficients on the basis of the lipid content and log K_{ow} for a range of chemicals; however, the limits of these relationships will need to be evaluated further to accept this hypothesis beyond the ranges of chemicals and species tested in this study.

The mass transport mechanism was further probed by calculating theoretical diffusion coefficients using the relationship provided by Trapp et al. (*11*) and comparing these to diffusion coefficients measured in this work. The results are shown in Table 1. Agreement for all 10 branch and wood core samples is within a factor of 2.5, and agreement for four of these are within a factor of 1.2. Similar agreement was found by Baduru et al., when using diffusion coefficients for multiple contaminants obtained in the laboratory with poplar xylem tissue (*24*). The agreement of current and previous independently determined findings is encouraging and supports the model assumptions (i.e., diffusion in plant tissue occurs in gas and water filled pores and is subject to tortuous travel paths and retardation due to sorption).

In summary, diffusion and sorption processes occurring in plant branches were found to be influenced by plant chemistry. Specifically, results suggest that the primary constituent governing both processes is the lipid content for the range of lipid and lignin contents evaluated. The impact of bark versus wood on the transport of TCE in plants is significant. The bark dominates sorption and acts as a barrier to mass transport into or out of tree branches, with diffusion coefficients for TCE in bark being 2−10 times less than diffusion coefficients in wood. Greater mass transfer resistance in the bark is directly related to greater lipid content.

These results contribute to understanding the factors governing the transport of chemicals in plant tissue and, hence, better estimation of model parameters for diffusion and sorption. These findings have value in considering contaminant fate in phytoremediation, in understanding potential contamination of food crops, and in the use of plants in phytomonitoring of subsurface contaminants. However, these processes were studied in the laboratory; the next obvious step is to determine why diffusion coefficients measured in the laboratory are 2 to 100 times less than diffusion coefficients estimated from field data using whole plant uptake models.

Supporting Information Available

Physicochemical properties of TCE, tree species and properties, sorption results, details and results of control experiments, parameters for the model ($C_{brch,r=a,0}$, β and n), final values of L, m, and T, experimental diffusion coefficients for the branch and wood core samples compared to tree core samples, time to equilibrium for all samples, sorption contribution of bark for each species, model and experimental kinetic profiles for all branch, wood core, and bark samples, and various graphs. This material is available free of charge via the Internet at http://pubs.acs.org.

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