

# Sorption of Monoaromatic Hydrocarbons to Wood

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The sorption of benzene, toluene and *o*-xylene to wood, a common subsurface fill material, was characterized. Sorptive equilibrium was attained within 24 h for water-saturated Douglas fir and Ponderosa pine chips of centimeter-sized dimensions, consistent with predictions of retarded diffusive transfer into the wood. Sorption to the chips exhibited linear sorption isotherms. When wood–water partition coefficients were normalized to the wood's lignin content, the resulting lignin–water partition coefficients,  $K_{\text{lignin}}$ , agreed to within a factor of 2 with literature values reported for chemically isolated lignins. Wood sorption was substantially overpredicted by an organic carbon-based model (i.e.,  $K_{\text{oc}}$ ). Wood–water partition coefficients for nonionic sorbates ( $10 < K_{\text{ow}} < 10^4$ ) can be predicted as the product of the wood's fractional lignin content,  $f_{\text{lignin}}$ , and a  $K_{\text{lignin}}$  estimated from the linear free energy relationship:  $\log K_{\text{lignin}} = (0.74 \pm 0.09) \log K_{\text{ow}} - (0.04 \pm 0.25)$ .

## Introduction

Wood is an absorbent material that is present as fill at many industrial sites. During recent investigations at a former manufactured gas plant, wood was found in the subsurface in the form of building rubble and chip waste from the gas manufacture process (1). The practice of burying such fill was common at other manufactured gas plants (2), and it likely has been conducted at a wide variety of other industrial sites as renovations were made or wastes were produced. Wood is also a significant component of solid waste, accounting for up to 25 wt % of materials at landfills that accept demolition wastes (3). To predict accurately organic contaminant transport through subsurface solids at these sites, an understanding of chemical sorption to wood is required.

The basis for understanding equilibrium sorption of organic compounds to wood can be developed using the results of sorption studies with isolated wood polymers (4). Wood is composed of three polymeric components: lignin (25–31% of softwood mass), cellulose (40–44% of softwood mass), and hemicellulose (remaining mass) (5). The sorption of organic compounds to these isolated polymers is consistent with those polymers' solubility parameters. [The solubility parameter ( $\delta$ ) is a measure of the molecular cohesive energy of a solid or liquid (6). The activity coefficient of a solute in a polymer is minimized as the difference between the  $\delta$  values of the pure-phase solute and the polymer is reduced (7, 8).]

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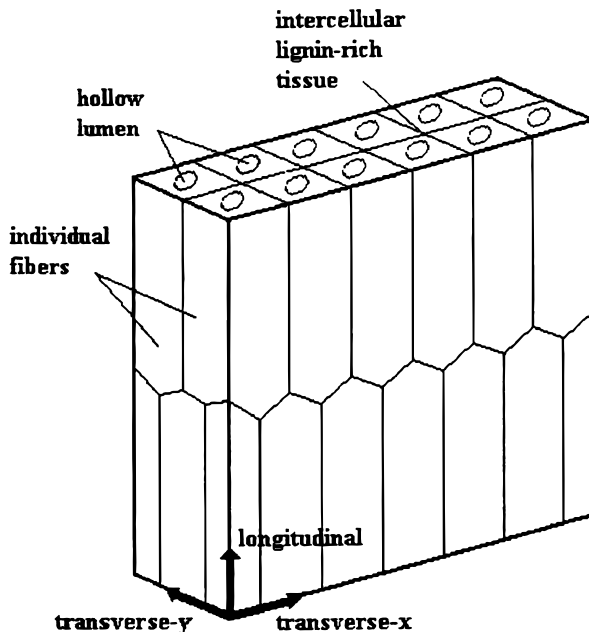


FIGURE 1. Schematic of wood particle structure denoting the orientation of the primary diffusion directions for the particle shapes studied.

Lignin is hydrophobic [ $\delta = 10\text{--}12$  (cal/cm<sup>3</sup>)<sup>1/2</sup>; 9], and sorption isotherms for toluene [ $\delta = 9.2$  (cal/cm<sup>3</sup>)<sup>1/2</sup>; 6], trichloroethylene [ $\delta = 9.2$  (cal/cm<sup>3</sup>)<sup>1/2</sup>; 6], and chlorinated phenols (4, 10) associating with lignin are linear. In contrast, cellulose is more polar [ $\delta = 14.5\text{--}16.5$  (cal/cm<sup>3</sup>)<sup>1/2</sup>; 6] and exhibits little measurable uptake of monoaromatic hydrocarbons (10–12). Hemicelluloses are similar in molecular composition to cellulose and presumably also exhibit little nonpolar organic compound sorption. Thus, wood–water partition coefficients,  $K_{\text{wood}}$  [(mol/g<sub>wood</sub>)(mol/mL<sub>water</sub>)<sup>-1</sup>], have been hypothesized to be controlled by the wood lignin content; and indeed, chlorophenol sorption to wood fibers followed the relationship (4)

$$K_{\text{wood}} = f_{\text{lignin}} K_{\text{lignin}} \quad (1)$$

where  $f_{\text{lignin}}$  (g<sub>lignin</sub>/g<sub>wood</sub>) is the mass fraction lignin and  $K_{\text{lignin}}$  [(mol/g<sub>lignin</sub>)(mol/mL<sub>water</sub>)<sup>-1</sup>] is the lignin–water partition coefficient.

Since wood in the environment commonly exists as pieces greater in size than isolated fibers, one may expect attainment of equilibrium wood–water partitioning to be slowed by sorbate diffusion into the wood. First, we know from observations on the physical structure of wood that lignin-rich tissue is located intercellularly, between adjoining fibers within the wood particle (1, 13) (Figure 1). Within the fiber cell walls, cellulose strands are arranged as bundles imbedded in a lignin–hemicellulose matrix, decreasing in density with distance from the cell lumen (13, 14). Intermolecular hydrogen bonding gives rise to highly oriented regions making up about 65% of the cellulose, and X-ray observations indicate that this crystallinity is not disrupted by water adsorption (15). Thus, if wood particles include multifiber aggregates, sorbate diffusion into the wood is through cellulose-rich tissue and sorptive equilibrium may be limited in part by tortuous diffusion through this crystalline polymer.

Additionally, Burr and Stamm have shown that diffusivities of nonsorbing compounds in wood are markedly lower than

aqueous diffusivities. These investigators (16) estimated diffusivity reduction factors by comparing the electrical conductances measured across wood blocks saturated with 0.1 M salt solutions with conductance measures of the salt solution alone. Longitudinal wood conductances were 0.43–0.54 times smaller than the solution conductances, while transverse conductances were 0.020–0.032 times smaller than in solution (16, 17). Measures of wood diffusion coefficients have been made for salts (17, 18) and nonsorbing solutes (urea, glucose, glycerol; 19). Longitudinal and transverse wood diffusion coefficients were 0.43–0.64 and 0.01–0.06 times the solute free aqueous diffusivities, respectively (17, 18). Hence, depending on the orientation of the cut of a given piece of wood (Figure 1), the physical structure may slow diffusive transfer of relatively small solutes to the interior lignin sites by as much as a factor of 100. For sorbing chemicals, this penetration rate should also be reduced by a factor reflecting microscale partitioning to lignin polymers distributed throughout the wood sorbent.

The purpose of this research was to investigate the uptake of nonpolar organic compounds by wood particles, representative in size of fill materials. Equilibrium wood–water sorption coefficients were hypothesized to be controlled by partitioning to lignin (i.e., described by eq 1). Equilibrium  $K_{\text{wood}}$  values for intact wood chips were measured for two woods (Ponderosa pine and Douglas fir) and three sorbates (benzene, toluene, and *o*-xylene). These results were compared to predictions based on eq 1, using  $K_{\text{lignin}}$  values obtained for chemically isolated lignins. The effects of particle size and direction of cut on sorption kinetics were investigated with wood particles cut into different shapes. The effect of sorbate hydrophobicity on uptake times was also investigated to determine an applicable model for predicting wood sorption kinetics.

## Methods

**Chemicals.** Neat benzene, toluene, and *o*-xylene were used as received from Alltech (Deerfield, IL). All experiments used purified water (18 M $\Omega$ ·cm) obtained from an Aries water purification system (Vaponics, Rockand, MA). Acetonitrile was Baker Analyzed HPLC solvent (J. T. Baker, Phillipsburg, NJ), and sodium azide was from Fluka (Switzerland). Kiln-dried Douglas fir and Ponderosa pine woods were obtained from Cambridge Lumber and Supply (Cambridge, MA). The wood was sanded before use to remove surficial materials.

**Sorption Isotherms.** Wood–water partition coefficients were calculated from five-point sorption isotherms. Douglas fir sticks (2 cm  $\times$  0.2 cm  $\times$  0.2 cm, longitudinal  $\times$  transverse  $\times$  transverse  $y$ , Figure 1) and Ponderosa pine chips (1 cm  $\times$  0.7 cm  $\times$  0.16 cm) were soaked for at least 18 d in water containing 1 mM sodium azide until they reached a constant wet mass. Saturated wood particles were then blotted with paper towel and transferred to 50- or 100-mL ground glass-stoppered glass equilibration flasks. Aqueous sorbate solutions of benzene, toluene, or *o*-xylene were made by diluting saturated stock solutions with water in a glass syringe containing mixing beads and sodium azide solution (final concentration 1 mM NaN<sub>3</sub>). The initial concentrations for each isotherm point were measured before transfer of the solution from the syringe to the equilibration flasks. The stoppers were clamped, and the flasks were wrapped with foil to minimize photodegradation. Wood-free controls were assembled in the same manner to quantify loss mechanisms other than sorption to wood. Sample and control flasks were inverted by hand several times daily to mix. (Sorbate peak areas were within 1% of values obtained at each time point for duplicates from a test with continuously tumbled flasks, indicating that hand agitation maintained sufficient mixing.) At the completion of equilibration, the solution-phase dissolved organic carbon was less than 30 mg of C/L, as

measured by high-temperature oxidation (Shimadzu TOC5000). The water content of the wood particles was quantified at the completion of the experiment. The wet weight was taken after blotting particles with paper towel, and the dry weight was defined as the mass after drying for 24 h at 103–105 °C.

Some of the wood-containing flasks and wood-free controls were used for kinetic monitoring. These flasks were subsampled at time intervals of  $1 \times 10^2$ ,  $3 \times 10^2$ , and  $8 \times 10^2$  min. The first value of  $n$  was 1, and sampling continued until aqueous concentrations in the wood-containing flasks remained at constant levels for several successive sampling points, at which time (5–21 d) the isotherm data were acquired.

Aqueous sorbate concentrations were quantified by high-pressure liquid chromatography (HPLC). Aliquots of 30  $\mu$ L were withdrawn from the equilibration flasks with a syringe and injected into a Hewlett-Packard 1050 HPLC equipped with a diode array detector. Compounds were eluted isocratically (85% acetonitrile:15% water) through a 250 mm Adsorbosphere C<sub>18</sub> column (5  $\mu$ m packing, Alltech) at a flow rate of 1 mL/min. Peak areas were quantified at a detection wavelength of 260 nm with a background reference wavelength of 550 nm. External standards were made up daily from the saturated stock solutions to calibrate the instrument response. Errors in aqueous concentrations were determined from the variability in peak areas of replicate injections and the fitting error of the HPLC response factor.

Sorption isotherms were developed from mass balances on the equilibration flasks with the sorbed compound concentration calculated by difference from the initial concentration as follows:

$$C_s = \frac{C_i V - C_w (V + V_{pw})}{M} \quad (2)$$

where  $C_s$  (mg/g) is the sorbed concentration;  $V$  (mL) is the bulk water volume;  $M$  (g) is the dry mass of wood;  $C_i$  (mg/mL) is the initial aqueous concentration based on concentrations found in the negative control flasks after the incubations were completed;  $C_w$  (mg/mL) is the final aqueous concentration; and  $V_{pw}$  is the volume of water-filled wood porosity, measured as the mass of water lost upon drying the saturated wood particles. Initial aqueous concentrations were determined from high concentration wood-free controls that were sealed until isotherm sampling. At the time of isotherm sampling, the mass of solute remaining in these controls was  $90 \pm 3\%$  ( $n = 6$ ) of the mass at time zero. This represents the maximum sorbate loss since system losses are proportional to aqueous-phase concentrations (20). Uncertainties in solid-phase concentrations were determined by propagating aqueous concentration measurement uncertainties through eq 2 and were typically 10% of  $C_s$ .

Wood partition coefficients were calculated from regressions of sorbed concentration versus aqueous concentration:

$$K_{\text{wood}} = \frac{C_s}{C_w} \quad (3)$$

The linearity of the fits was examined by fitting the log-transformed data to the log-transformed Freundlich equation:

$$\log C_s = (1/n) \log C_w + \log K_f \quad (4)$$

where  $1/n$  is the Freundlich exponent and  $K_f$  is the Freundlich coefficient.

**Dependency of Sorption Kinetics on Wood Shapes.** Sorption kinetics were monitored for wood particles of various shapes with toluene as the sorbate. Douglas fir and Ponderosa

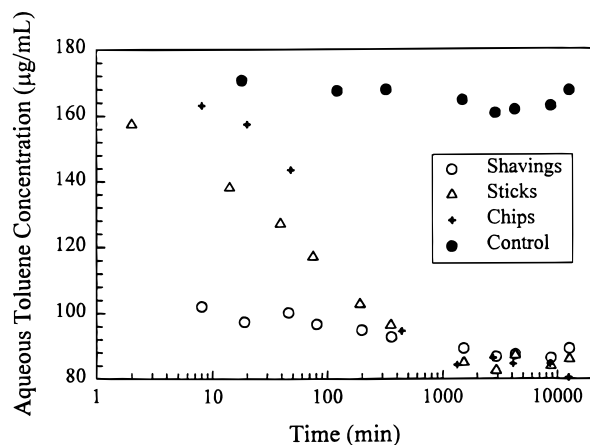


FIGURE 2. Decrease in aqueous toluene concentrations for varied Ponderosa pine wood particle shapes. Time is expanded on a logarithmic scale to detail early data.

pine shavings, retained between 1000 and 1400 mm screens, were broken fiber fragments with solution-exposed lignin. "Sticks" (pine:  $1 \times 0.16 \times 0.16$  cm; fir:  $2 \times 0.2 \times 0.2$  cm) and "chips" (pine:  $1 \times 2 \times 0.16$  cm; fir:  $2 \times 2 \times 0.2$  cm), tens to hundreds of fiber diameters thick, were also cut from wood and rinsed of fines after being saturated with water. Water-saturated wood particles were transferred to individual flasks as described for the sorption isotherms, but only one toluene concentration was used for all of the particle shapes and the control flask. The ratio of sorbent mass-to-solution volume was the same for all particle shapes.

## Results and Discussion

**Equilibrium Sorption to Wood.** Benzene, toluene, and *o*-xylene were sorbed by Douglas fir and Ponderosa pine wood. The decrease in aqueous sorbate concentrations in wood-containing flasks, about 50% of sorbate mass relative to controls (Figure 2), was greater than could be accounted for by dilution into the water-filled wood porosity. Wood porosity accounted for about 12% of the total wood porosity plus bulk solution volume. A total of 93% of the sorbed masses at times greater than 10 000 min were recovered by successive desorption steps, indicating that compound sorption was reversible. This mass recovery was consistent with losses observed in wood-free controls.

Wood particle shape was varied to assess this factor's effect on uptake kinetics and to allow us to ascertain when equilibrium applied. Not surprisingly, the times required to reach sorptive equilibrium were longer with increasing particle size (Figure 2). Shavings composed of broken fiber cell wall fragments exhibited the fastest uptake times, reaching equilibrium in 10 (Ponderosa pine) to 30 (Douglas fir) min. Aqueous toluene concentrations decreased at earlier times for the stick-containing flasks than for the chip-containing flasks. Ultimately, sorption equilibrium was verified by measuring the Douglas fir toluene and *o*-xylene isotherms twice (toluene after 13 000 and 31 000 min and xylene after 7200 and 21 000 min). After approximately 80  $\mu$ g/mL overall solution concentration drops, aqueous concentrations varied by less than 1  $\mu$ g/mL between these two isotherm sampling times, below our limit to detect further changes.

Despite the differences in time to equilibrium sorption for the various particle shapes, wood distribution coefficients, calculated using eq 2 and data on residual sorbate concentrations in solution after 2000 min, were the same for all particle shapes. For example, toluene sorption to pine shavings exhibited a  $K_{\text{wood}}$  of  $12 \pm 1$  mL/g, sticks had a  $K_{\text{wood}}$  of  $14 \pm 1$  mL/g, and chips had a  $K_{\text{wood}}$  of  $11 \pm 1$  mL/g. Likewise,

TABLE 1. Experimental Partition Coefficients and Physical Constants for Sorbate-Sorbent Pairs

parameter	benzene	toluene	<i>o</i> -xylene
<b>Ponderosa Pine</b>			
$K_{\text{wood}}$ (mL/g)	$6.6 \pm 0.3$	$13 \pm 1$	$26 \pm 1$
$K_{\text{lignin}}$ (mL/g) <sup>a</sup>	20	40	90
<b>Douglas Fir</b>			
$K_{\text{wood}}$ (mL/g)	$12 \pm 0.6$	$17 \pm 1$	$28 \pm 6$
$K_{\text{lignin}}$ (mL/g) <sup>a</sup>	40	60	90
<b>Partition Coefficients</b>			
$K_{\text{lignin}}$ (mL/g) <sup>b</sup>	30	90	180
$K_{\text{ow}}$ (mL/g) <sup>c</sup>	135	450	1350
$K_{\text{oc}}$ (mL/g) <sup>d</sup>	100	250	550
$K_{\text{d}}$ (mL/g) <sup>e</sup>	50	120	280

<sup>a</sup>  $K_{\text{lignin}} = K_{\text{wood}}/f_{\text{lignin}}$ , assuming  $f_{\text{lignin}} = 0.3$  (22). <sup>b</sup> Ref 12. <sup>c</sup> Ref 27. <sup>d</sup> Ref 24. <sup>e</sup>  $K_{\text{d}} = f_{\text{oc}}K_{\text{oc}}$ ,  $f_{\text{oc}} = 0.5$  (22).

the  $K_{\text{wood}}$  value obtained from the isotherm study was  $13 \pm 1$  mL/g for Ponderosa pine. The agreement of partition coefficients for each of the particle sizes indicated that all lignin in water-saturated wood particles was ultimately accessible for sorptive partitioning. Hence, the same equilibrium sorption model is applicable to all wood particles, regardless of size.

Wood sorption isotherms were linear over the range of sorbate concentrations used (Figure 3). Isotherm linearity was tested by fitting data to the Freundlich isotherm (eq 4). For all sorbate-sorbent pairs ( $N = 6$ ), the average value of the Freundlich exponent was  $0.96 \pm 0.12$ . Although a Freundlich fit with data that spans only 1 order of magnitude in concentration does not conclusively verify isotherm linearity, our data are consistent with isotherm linearity. Evidence in support of linear wood isotherms in our data included the following: (i) the average Freundlich exponent was not significantly different than 1, (ii) the linear regression intercepts were not significantly different than zero (Figure 3), and (iii) we saw no trends in the mass fraction dissolved at equilibrium with differing initial aqueous concentrations.

A previously reported nonlinear isotherm and the failure of eq 1 to predict benzene partitioning to pine sawdust (1, 21) may have been due to incomplete water saturation of the sawdust before undertaking sorption studies. Water uptake by dry wood is a complex process involving capillary condensation as water forms hydrogen bonds with cellulose within the cell walls (14, 15). Water penetrated the wood particles in our experiments at a much slower rate (time scale of 10 days) than the sorbates penetrated water-saturated wood (time scale of about 1 day). Therefore, sorbate uptake may be slowed by the penetration of the water front into wood that is not fully saturated. This complexity was minimized in our experiments by fully saturating all wood particles before use.

The lignin-water partition coefficients for benzene, toluene, and *o*-xylene interacting with intact wood were calculated from Ponderosa pine and Douglas fir partition coefficients ( $K_{\text{wood}}$ ). The range of softwood lignin contents (25–31%; 5) is too narrow to examine variations of  $K_{\text{wood}}$  as a function of  $f_{\text{lignin}}$  for several test woods. Thus, to examine the effectiveness of eq 1 for predicting equilibrium partitioning to intact wood particles, our observations of pine and fir  $K_{\text{wood}}$  values were normalized by the lignin content (assuming 0.3 for both woods; 22), and the resultant  $K_{\text{lignin}}$  values were compared to literature values of  $K_{\text{lignin}}$  obtained for chemically isolated lignins. Calculated  $K_{\text{lignin}}$  values (Table 1, Figure 4) for benzene, toluene and *o*-xylene were similar for both species of wood and showed good agreement (within a factor of 2) with literature partition coefficients for isolated lignins. The good consistency observed between partition coefficients

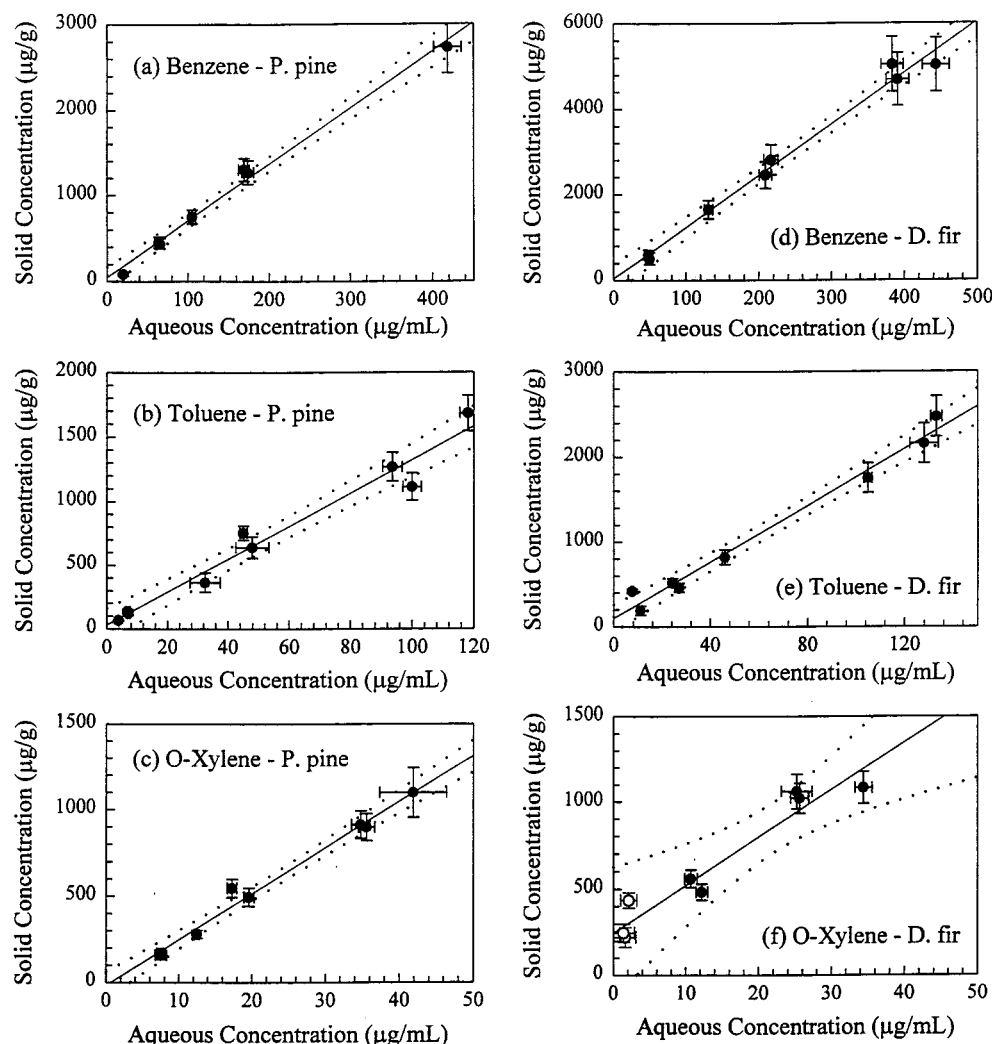


FIGURE 3. Wood sorption isotherms for Ponderosa pine (panels a–c) and Douglas fir (panels d–f). Error bars for each data point represent analytical uncertainty. Partition coefficients (Table 1) were determined with best fit linear regressions (solid lines, with dotted 95% confidence intervals). Open data points represent aqueous concentrations below the HPLC detection limit that were omitted from the regression.

for intact wood particles (open symbols, Figure 4) and lignin isolated by various chemical methods (solid symbols, Figure 4) suggests that the sorption properties of lignin are not substantially altered from its native form in intact wood particles by these extraction procedures. Therefore, it appears that a measured fraction lignin content ( $f_{\text{lignin}}$ ) for the wood of interest together with a  $K_{\text{lignin}}$  measured for the sorbate of interest interacting with isolated lignin can be used to predict partition coefficients for wood particles, such as found in fill materials.

Traditionally, partition coefficients for subsurface solids are estimated on an organic carbon basis (i.e.,  $K_{\text{oc}}$  model); however, this is a poor model for wood. We calculated partition coefficients ( $K_d$ , Table 1) by multiplying the wood fraction organic carbon (0.5; 23) by each sorbate's organic carbon-normalized partition coefficient,  $K_{\text{oc}}$ , estimated from the  $K_{\text{ow}}-K_{\text{oc}}$  free energy relationship reported by Schwarzenbach and Westall for similar sorbates and organic matter of a terrestrial source (24) (Table 2). The resultant calculated  $K_d$  values overestimated measured  $K_{\text{wood}}$  values by 4–6 times for benzene, 7–9 times for toluene, and about 10 times for *o*-xylene (Table 1). This discrepancy could result from not knowing  $K_{\text{oc}}$  very well, but it could also result from including all of the wood carbon, as would be measured by combustion of a bulk sample. Studies with isolated wood polymers indicate that only the lignin polymeric component is

TABLE 2. Effective Wood Diffusivities for Sorptive Mass Transfer

parameter	benzene	toluene	<i>o</i> -xylene
Douglas Fir			
$R = 1 + r_{\text{sw}}K_{\text{wood}}$	10	14	23
$\alpha$	1.5	1	0.67
$r_{\text{sw}}$ (g/mL)	0.78	0.78	$0.78 \pm 0.04$
$D_w$ ( $10^{-8}$ cm <sup>2</sup> /s) <sup>a</sup>	1060	940	850
$\xi$	0.01–0.025	0.01–0.025	0.01–0.025
Calculated Effective Diffusivities			
eq 5, $D_{\text{eff}}$ ( $10^{-8}$ cm <sup>2</sup> /s)	1–3	0.7–2	0.4–0.9
Experimental Effective Diffusivities			
$D_{\text{expt}}$ ( $10^{-8}$ cm <sup>2</sup> /s)	6	5	0.6

<sup>a</sup> Calculated by the Hayduk-Laudie equation (29).

important for organic compound sorption (10). If the wood carbon content were scaled to reflect only the lignin-associated carbon [lignin formula weight 74% carbon (13), wood fraction lignin 30%],  $K_d$  values would be 40% of the values reported in Table 1, within a factor of 2 of measured  $K_{\text{wood}}$  values for all compounds except *o*-xylene.

The  $K_{\text{lignin}}-K_{\text{ow}}$  free energy relationship of Severtson and Banerjee (4) was expanded to enable predictions of lignin–water partition coefficients. Lignin exhibits noncompetitive



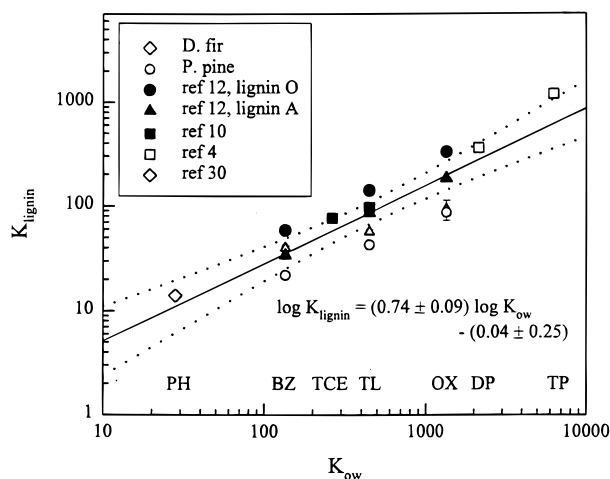


FIGURE 4. Lignin–octanol linear free energy relationship for wood particles (open symbols) and chemically isolated lignins (solid symbols). Confidence intervals (95%, dotted lines) are shown around the best fit linear regression (solid line). Compound abbreviations follow: phenol (PH), benzene (BZ), trichloroethylene (TCE), toluene (TL), *o*-xylene (OX), dichlorophenol (DP), and trichlorophenol (TP).  $K_{ow}$  values are from refs 27 and 28.

compound uptake with low heats of sorption (1.6–2.8 kcal/mol; 4). This suggests that organic compounds sorb to lignin by a partitioning mechanism, such as that by which hydrophobic nonionic compounds distribute between octanol and water. Thus, our measured  $K_{lignin}$  values for intact wood particles were combined with literature  $K_{lignin}$  values and examined relative to corresponding octanol–water partition coefficients (Figure 4). The regression of  $\log K_{lignin}$  with  $\log K_{ow}$  gives the following:  $\log K_{lignin} = (0.74 \pm 0.09) \log K_{ow} - (0.04 \pm 0.25)$ . The observation that  $K_{lignin}$  is less than  $K_{ow}$  indicates that lignin is a less favorable partition medium than octanol for the sorbates studied. This may result from octanol [ $\delta = 10.3$  (cal/cm<sup>3</sup>)<sup>1/2</sup>; 9] being a more favorable partition medium for nonpolar organic compounds [ $\delta \sim 9.2$  (cal/cm<sup>3</sup>)<sup>1/2</sup>; 6] than lignin [ $\delta = 10$ –12 (cal/cm<sup>3</sup>)<sup>1/2</sup>; 9].

**Sorption Kinetics Model for Uptake of Hydrophobic Compounds by Wood.** In light of the physical structure of wood, the available literature on uptake of solutes by wood, and the recognition that lignin is the key absorbent of nonpolar compounds, we hypothesized that our time course data reflected diffusive mass transfer of our nonpolar sorbates to the lignin distributed throughout the wood. Thus, such water–wood transfer would be influenced by a combination of the following: (i) the sorbate’s aqueous diffusivity, since we presume transport through water-filled spaces; (ii) some degree of physical hindrance depending upon whether most of the diffusive flux occurred from a longitudinal or a transverse direction; and (iii) the extent of microscale partitioning to lignin distributed along the diffusion path. Given this conceptualization, an appropriate formulation of the effective wood diffusion coefficients would be

$$D_{eff} = \xi \frac{D_w}{1 + r_{sw} K_{wood}} = \xi \frac{D_w}{R} \quad (5)$$

where  $\xi$  (dimensionless) is a factor reflecting physical hindrances;  $D_w$  (cm<sup>2</sup>/s) is the molecular diffusivity in water;  $r_{sw}$  (g/mL) is the internal wood solid-to-water ratio; and  $R$  is the internal retardation factor.

Since wood typically has irregular dimensions, including in our tests, we needed to evaluate the relative importance of longitudinal vs transverse uptake for our experiments. One can evaluate which direction of uptake should predominate in any given experiment by calculating diffusion

time scales:

$$\text{time scale} \approx \left(\frac{L}{2}\right)^2 \frac{1}{D_{eff}} = \left(\frac{L}{2}\right)^2 \frac{R}{\xi D_w} \quad (6)$$

using the measured thicknesses ( $L$ , cm) of the wood particles. Retardation factors,  $R$ , were estimated using measured equilibrium values of  $K_{wood}$  for the sorbate–sorbent combinations (Table 1), and measures of the water content of the saturated wood were used to calculate the internal solid-to-water ratio,  $r_{sw}$  (Douglas fir, Table 2). Retardation factors for Ponderosa pine were 5, 9, and 15, respectively, for benzene, toluene, and *o*-xylene. The factor  $\xi$  has empirically been found to have values between 0.01 and 0.025 for transverse diffusion into Douglas fir (16, 18). In general, transverse  $\xi$  values range between 0.01 and 0.06 for a variety of softwoods, including pine species (17, 18). Longitudinal  $\xi$  values range between 0.4 and 0.6 (17, 18). Combining these results with our knowledge of the diffusive length scales for our wood particle geometries and sorbate aqueous diffusivities, we found that transverse time scales (7–17 d for toluene,  $\xi = 0.01$ –0.025) were shorter than longitudinal time scales (29–48 d,  $\xi = 0.4$ –0.6) for Douglas fir sticks, while transverse (1–7 d,  $\xi = 0.01$ –0.025) and longitudinal (5–7 d,  $\xi = 0.4$ –0.6) time scales were comparable for Ponderosa pine chips. Therefore, only Douglas fir uptake kinetics were modeled since most of the sorption in our experiments should have occurred across the shortest transverse directions.

Using this insight, we applied available analytical solutions of the diffusion equation for transfer into solids from systems of fixed volume (eq 5.33, ref 25) to solve for the wood diffusivities,  $D_{expt}$ , which best fit our Douglas fir experimental time course data. In addition to the diffusion coefficient, these solutions are functions of the initial and final aqueous concentrations, the ratio of the dissolved-to-sorbed sorbate mass at equilibrium ( $\alpha$ , Table 2), and the characteristic length for diffusion. In light of our calculations of diffusive time scales, diffusion into cylindrical solids was assumed for the Douglas fir sticks with a characteristic length (0.1 cm) equal to half of the transverse thickness. Best-fit  $D_{expt}$  values were obtained by minimizing the sum of the square of the difference between the calculated and experimental aqueous concentrations over the time of greatest concentration change (e.g.,  $t = 10$ –1000 min, Figure 5). Our conceptualized model for wood diffusion was tested by comparing the best-fit values of  $D_{expt}$  in each case with  $D_{eff}$  values, estimated from theory (i.e., eq 5) (Table 2). The estimated *o*-xylene diffusion coefficient in Douglas fir wood compared favorably with the experimental value of  $6 \times 10^{-9}$  cm<sup>2</sup>/s. Benzene and toluene experimental diffusion coefficients were greater than the means of the calculated  $D_{eff}$  values by factors of 3 and 4, respectively (Table 2). This discrepancy between predicted and experimental wood diffusion coefficients may suggest that larger values of the factor  $\xi$  are appropriate for the sorbates used in our experiments. Values of  $\xi$  near 0.07 for Douglas fir would be necessary to have  $D_{eff}$  values in agreement with the observed wood diffusion coefficients ( $D_{expt}$ ). Larger values of the hindrance factor may indicate that nonpolar substances, especially in contrast to ionic counterparts, are able to move through more portions of wood media.

We attempted to assess the effect of sorbate hydrophobicity on wood diffusion coefficients by using benzene, toluene, and *o*-xylene in this experiment ( $K_{ow}$  varies by a factor of 10). Predicted retardation factors for Ponderosa pine and Douglas fir increased by factors of about 1.5 from benzene to toluene to *o*-xylene (Table 2). Together with differences in diffusivities, this implied that decreases by factors of 2 should have been observed in the wood diffusion coefficients from benzene to toluene to *o*-xylene. Benzene and toluene

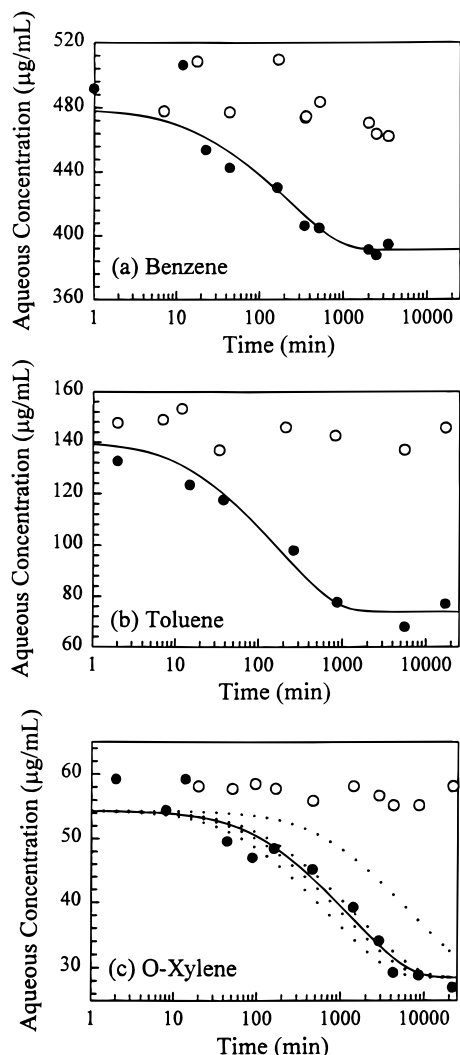


FIGURE 5. Decrease in aqueous sorbate concentration for Douglas fir sticks. Solid symbols are shown for wood-containing samples, and open symbols are for wood-free controls. Solid lines are best fits of the diffusion equation with experimental effective diffusivities reported in Table 2. Fits with alternate values of  $D_{\text{expt}}$  are shown as dotted lines in panel c where  $D_{\text{expt}}$  values are  $1 \times 10^{-8}$ ,  $0.7 \times 10^{-8}$ ,  $0.5 \times 10^{-8}$ , and  $0.1 \times 10^{-8}$  cm<sup>2</sup>/s, respectively, from left to right.

diffusion coefficients in Douglas fir were similar, although they were clearly greater than observed for *o*-xylene. Our data on the sorbate-to-sorbate variation in  $D_{\text{expt}}$  fitting parameter were too limited to clearly see hydrophobicity effects. Use of sorbates with a greater range of hydrophobicities would have improved our ability to detect the influence of sorbate hydrophobicity on wood uptake kinetics.

**Environmental Significance.** The results of this research can be used to make predictions of contaminant transport through wood-containing fill materials. Wood-water partition coefficients can be estimated with values of the wood fractional lignin content (about 30% for softwoods) and the reported  $K_{\text{lignin}} - K_{\text{ow}}$  free energy relationship. While the  $K_{\text{lignin}} - K_{\text{ow}}$  free energy relationship was developed for softwood lignins, it is likely also applicable to hardwood lignins. Hardwood lignins are formed from the same phenylpropanoid precursors but vary in the relative number of methoxy groups. There are about 0.95 methoxy groups per phenylpropanoid unit in softwoods (average 74% carbon) and 1.3–1.7 in hardwoods (69–71% C) (13).

Care must be taken when using wood-water partition coefficients to estimate solid-water partitioning to fill solids

composed of wood products. For example, municipal refuse is 30–60 wt % paper products (3). In the papermaking process, wood pulp is delignified to yield a finished product that may be less than 5% lignin by weight (13). The remaining mass is cellulose that exhibits virtually no sorption of organic contaminants. Thus, a measure of the lignin content of wood-derived fill materials would be required to predict sorbate partitioning accurately.

Further work is required to make accurate predictions of wood sorption kinetics. The model presented in this research enables order of magnitude estimates of wood diffusion coefficients to be made. A slowest case estimate of contaminant exchange with subsurface wood particles would assume transverse diffusion into the wood. Despite the physical hindrance and sorptive retardation of diffusion into wood, the time to equilibrium for wood particles of chip-sized dimensions appears fast (days) for the sorbates examined here relative to groundwater flow processes. However, years may be required to transfer to and from lumber with substantially greater thicknesses than the chips we investigated. Thus, prolonged site remediation via pump-and-treat technologies at industrial sites (26) may not be due to rate-limiting, diffusive exchange from chip-sized wood particles, but larger pieces of wood could be problematic.

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