

# Penetration of naphthalene, *n*-hexadecane, and 2,4-dinitrotoluene into southern yellow pine under conditions modeling spills and floods

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## Abstract

This paper investigates the penetration of three common contaminants into building grade southern yellow pine wood samples under the conditions experienced during chemical spills. Contaminants (*n*-hexadecane, naphthalene, and 2,4-dinitrotoluene) were applied in their <sup>14</sup>C-labeled forms to 5- to 9-cm-long pieces of southern yellow pine at ambient conditions. The impact of the following parameters on diffusivity was investigated: contaminant volatility and solubility in water, penetration direction compared to wood grain structure, and water saturation of wood under conditions characteristic of catastrophic floods. Water saturation (having a dramatic effect on diffusion rates) was studied under three conditions: wood pieces with ambient water concentration, those “post-soaked” with water after contamination, and those pre-soaked with water before contamination. Contaminant diffusivities in the ambient samples increased with increased contaminant volatility. For more water-soluble compounds, naphthalene and 2,4-dinitrotoluene, the diffusion rate was greater in post-soaked samples with diffusivities approaching 10<sup>-9</sup> m<sup>2</sup>/s, characteristic for their diffusion in bulk liquids. By contrast, *n*-hexadecane diffusion was hindered significantly in post-soaked samples. For all three contaminants, longitudinal and tangential penetration rates were similar, indicating that the rate-limiting step may be contaminant evaporation inside the wood tracheids or contaminant dissolution in water (diffusion being controlled by strong contaminant sorption in wood). Experiments with pre-soaked samples and those conducted under external capillary pressure showed different trends from non-pressurized post-soaked samples, indicating a possible switch in the rate-limiting steps for contaminant diffusion under these conditions.

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Contamination of building structural elements, which may be caused by spills or production/storage of chemicals, results in the retention of contaminants in wood over a period of years (Wilhelm and Bouchard 1989; Wilson et al. 1990). Penetration of chemicals into wood has been studied and modeled extensively, but only for relatively large chemical quantities (Comstock 1967, 1970; Petty 1975, 1978; Siau 1984, 1995) under conditions that are important for treating wood with preservatives, hardeners, and adhesives.

Penetration of relatively small quantities of chemicals into wood under atmospheric pressure is a separate problem. First, contaminant penetration into wood may be a combination of many different processes, including capillary effects. Darcy liquid flow, molecular diffusion and Knudsen diffusion (Comstock 1970, Petty 1975, Siau 1984), adsorption, and absorption (Mackay and Gschwend 2000, Tsuchikawa and Siesler 2003). Secondly, it occurs under poorly defined and changing conditions such as changes in available capillary

pressure and changes in the amount of entrained air in wood capillaries that are crucial for wood permeability (Comstock 1967; Petty 1978; Siau 1984, 1995). To our knowledge, no data have been reported regarding wood contamination under

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**Table 1.— Physical properties of model wood contaminants.**

| Parameter                                     | Naphthalene       | n-Hexadecane                      | 2,4-Dinitrotoluene                         |
|-----------------------------------------------|-------------------|-----------------------------------|--------------------------------------------|
| Boiling point (°C)                            | 218 <sup>a</sup>  | 287 <sup>a</sup>                  | 300 to 319 with decomposition <sup>b</sup> |
| Solubility in water at room temperature (g/L) | 0.03 <sup>c</sup> | $1.8 \times 10^{-6}$ <sup>d</sup> | 0.18 <sup>e</sup>                          |

<sup>a</sup> Aldrich Catalog Handbook of Fine Chemicals, 2003-2004. pp. 981, 1317.

<sup>b</sup> www.chem.unep.ch/irptc/sids/oecdsids/121142.htm accessed 09/27/05.

<sup>c</sup> Stephen and Stephen 1963.

<sup>d</sup> Beal and Betts 2000.

<sup>e</sup> Phelan and Barnett 2001.

atmospheric pressure by small amounts of contaminants, such as fuel oil hydrocarbons or nitroaromatic chemicals. The former are common wood contaminants in buildings (Wilhelm and Bouchard 1989, Wilson et al. 1990), whereas the latter (often called “energetics”) are contaminants abundant in military facilities (Burrows et al. 1989, Hanson et al. 2000, Zhang et al. 2001).

Another aspect of the wood contamination problem is the differences in contaminant behavior for different water saturation scenarios. The worst case of this kind occurs during catastrophic floods, when fuel oil tanks and other sources may release their contents into flood waters where the contaminants are transported into wood structural elements of buildings. For the case of an immiscible fuel oil layer floating on top of flood water, there are four important scenarios that must be considered:

1. “Ambient” wood: the fuel oil contaminates wood structural members above the ultimate water line experienced during the flood, i.e., the floating oil layer contacts the wood structure and contaminates a section of the wood and then the water level (and thus the fuel oil level) recedes. This case is also comparable to point-source contamination due to spills.
2. “Post-soaked” wood: during rising water levels, the fuel oil contaminates wood structural members, then water soaks into the wood as the water level continues to rise.
3. Pressurized post-soaked wood: this is the same scenario as No. 2 (“post-soaked”) except that in this case the water level remains above the contamination zone for an extended period of time, providing capillary water pressure to facilitate diffusion of the fuel oil into the wood structural member.
4. “Pre-soaked” wood: the fuel oil layer forms on top of an existing body of water (for example, when the water level rises to the point of causing a fuel oil tank to rupture). As the water level drops, fuel oil contaminates the water-saturated wood structural members.

The influence of water on contaminant diffusivities assuming a proposed sorption-based diffusion model is described in this paper. Common building-grade southern yellow pine softwood (Kaiser 1999) was used with three model contaminants: *n*-hexadecane, naphthalene, and 2,4-dinitrotoluene (DNT). These were selected based on two criteria: 1) they are representative contaminants for fuel oil and “energetics,” two of the most common pollutants for wood-based building materials; and 2) they differ from each other in two basic physical properties affecting their penetration into wood: volatility and solubility in water (Table 1). We postulate that the main penetration path for contaminants into wood is via tracheids and

that the process can be described as sorption-based diffusion due to the large number of tracheids available for transport.

## Experimental

### Materials, reagents, and equipment

Southern yellow pine boards (sapwood) were cut into pieces of necessary size and the total pore volume of the wood was estimated by the amount of water absorbed by air-dry (“ambient”) specimens, see below. Only samples with a wood density of 0.35 to 0.10 g/cm<sup>3</sup> were utilized.

<sup>14</sup>C-labeled *n*-hexadecane (Sigma, St. Louis, MO), <sup>14</sup>C-naphthalene, and <sup>14</sup>C-DNT (American Radiolabelled Chemicals, St. Louis, MO) were used. Prior to application, labeled *n*-hexadecane was diluted 65-fold with non-labeled *n*-hexadecane for safety reasons, to generate lower disintegration per minute (DPM) rates. Labeled naphthalene and DNT were dissolved in a 10 percent w/v solution of *n*-octane and ethanol, respectively, and then diluted five times with non-labeled naphthalene or DNT also dissolved in a similar solution. These stock solutions yielded scintillation counting rates of  $2.22 \times 10^7$  (10.0),  $5.5 \times 10^4$  (25), and  $3.4 \times 10^4$  DPM/μL (15.3μCi/μL) for naphthalene, DNT, and *n*-hexadecane, respectively.

Radioactivity was monitored on a Beckman 6800 liquid scintillation counter (Beckman Coulter, Inc.; Fullerton, CA). Sample aliquots were placed in 26-mm-diameter plastic vials followed by the addition of 5 mL of Econo-safe scintillation cocktail (all from Research Products International Mt Prospect, IL). Radioactivity monitored in this manner was proportional to the amount of the chemical of interest.

### Mobility/penetration and retention study protocols

Wood specimens used for the mobility and penetration studies were standard-sized elongated blocks (Fig. 1) with dimensions of 7 by 20 by (50 to 90) mm (unless otherwise indicated). Samples were configured such that the largest side was cut perpendicular to the direction of the tracheids, i.e., cross-sectional specimens, or parallel to the direction of the tracheids with top and bottom surfaces being the tangential planes, i.e., parallel or tangential specimens (Fig. 1A). In both cases, the contaminant was applied with an Eppendorf-type pipette on the cut (smallest side) in order to study the longitudinal (applied to cross-sectional samples) and tangential diffusion (applied to parallel samples), through the largest-dimensioned side of the wood specimen (Fig. 1B). The aliquot sizes of the applied contaminants were: *n*-hexadecane, 5 μL of a 100-g/L solution in *n*-octane; naphthalene, 5 μL of a 100-g/L solution in *n*-octane; and DNT, 25 μL of a 170-g/L solution in ethanol. Only one contaminant was used for each series of experiments. Upon contaminant application, wood samples were set on a bench at room temperature for 5 minutes. This time was essential for contaminant absorption into the wood sample.

The procedure was different in the following sets:

1. In the experiments under “post-soaked” conditions, wood samples were submerged into a beaker containing a sterile aqueous medium (3.8 g/L of sodium chloride in distilled water). To ensure no fungal biodegradation of the contaminant, 5 mM sodium azide was added to the solutions.
2. In the experiments under pressurized “post-soaked” conditions, uniaxial external pressure was generated by placing the contaminated face of the 7-mm-thick wood unto the hori-

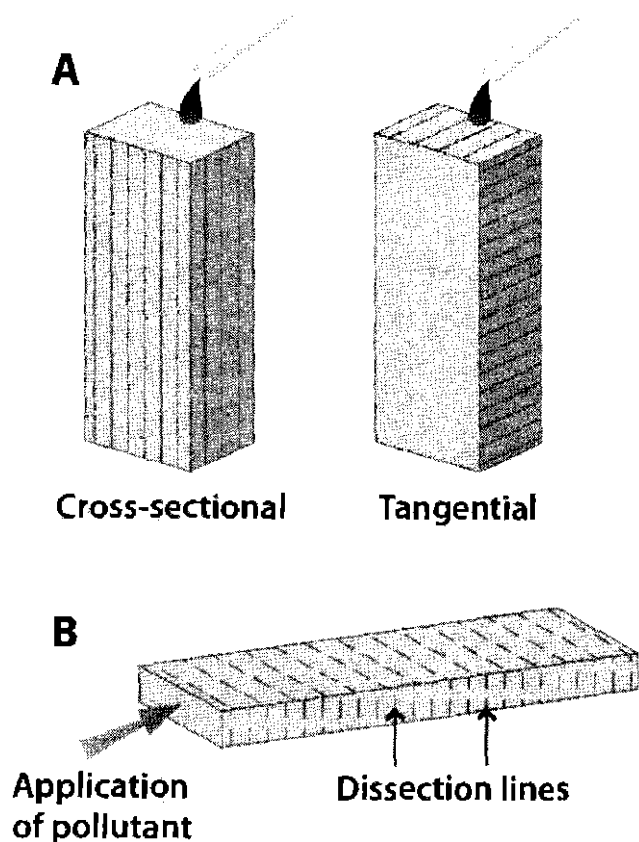


Figure 1. — Schematics of the direction of application and diffusion of the pollutants, and sectioning of the contaminated wood samples. A) Application of pollutants on cross-sectional and parallel (tangential) surfaces of the wood blocks to start longitudinal and tangential pollutant penetration, respectively. The tracheid orientation is shown as close spaced lines. Pollutants (5  $\mu$ L) were applied on the top of the wood sample as shown. B) Sectioning of wood samples in the diffusion studies. The point of pollutant application is shown as a large arrow; dissection lines are shown on the side of the wood sample. Each section between the cuts was 5-mm-thick.

zontal surface of agar slabs (3.8 g NaCl plus 20 g agar per L of distilled water was sterilized in an autoclave and cast in Petri dishes to the thickness of 5 to 10 mm). Then the Petri dishes with wood samples were immediately covered with lids and sealed with parafilm. Only selected experiments with *n*-hexadecane as a contaminant were conducted with such specimens.

3. In the experiments under “pre-soaked” conditions, wood specimens were submerged in the aqueous medium prior to the contaminant application.

Following contaminant application, samples were covered with aluminum foil and stored at 23°C and an approximate relative humidity of 70 percent.

After incubation, wood specimens were removed and cut into 5-mm-thick sections (Fig. 1B) except for the samples described in No. 3, which were cut in two halves (3.5-mm-thick sections). The resulting wood pieces were ground to obtain particles not exceeding 1 mm in either dimension using a coffee grinder and then extracted with 10 mL of 2-propanol. Then the radioactivity of 0.5-mL aliquots of these solutions was

counted. To calculate the overall contaminant retention, the radioactivities of all of the wood pieces were summed and the resulting value was compared with the initial radioactivity.

#### Extraction of model contaminants from wood

Contaminants were extracted from wood samples using 2-propanol, which was found to extract all three chemicals consistently under all wood/water content conditions. To verify accuracy, aliquots of contaminants were applied on wood specimens (7 by 20 by 10 mm), and the resulting samples were set on the bench for 3 months. These samples were then incubated with 10 mL of 2-propanol on an orbital shaker. For *n*-hexadecane and DNT, the extraction was complete in 3 days (72 hr) yielding  $70 \pm 5$  percent recovery regardless of the sample's age. Due to strong sorption of contaminants into the wood specimens, complete solvent extraction is not likely in a single-stage process. Determination of diffusion coefficients involved normalization of each 5-mm-thick section to the total of all such sections obtained upon cutting the wood sample (Fig. 1B) to account for the incomplete extraction.

To assure consistent recovery, 4-day extraction of all three contaminants was conducted throughout this study. For naphthalene, high volatility (Table 1) resulted in only  $50 \pm 7$  percent recovery in ambient samples. However, significant contaminant evaporation occurred only for 1 day, after which evaporation appeared to be negligible, and  $50 \pm 10$  percent recovery was maintained throughout the duration of the experiment. Post-soaked sample results were similar ( $70 \pm 10\%$  recovery, regardless of the sample's age).

#### Calculation of contaminant diffusion coefficients

Diffusion coefficients were calculated using Fick's first Law of diffusion. Integration of its differential equation using the boundary conditions characteristic for point-source diffusion results in the following equation (Jost 1960, Cussler 1997):

$$-\ln \left( \frac{C}{C_0} \right) = \frac{x^2}{4Dt} + \frac{1}{2} \ln (\pi Dt) \quad [1]$$

where  $C/C_0$  = ratio of the contaminant amount recovered in the given cut piece of wood to the initial contaminant amount applied on the wood sample ( $C_0$ );  $x$  = distance from the point of contaminant application for the given piece;  $t$  = time between the contaminant's application and its extraction;  $D$  = contaminant's diffusion coefficient.

If the contamination profiles are quantified in a series of samples while holding time constant (wood samples cut and extracted at a specific experimental duration time), this equation represents a straight line ( $\ln (C/C_0)$  vs.  $x^2/40$ ). The slope yields  $[-1/D]$  while  $[-1/2 \ln(\pi Dt)]$  is the y-intercept. Wood sections containing less than 1 percent of the total radioactivity were not taken into account because of the potentially high impact of stochastic factors.

The diffusion coefficients were also estimated by using a “differential” method, i.e., plotting the penetration distance vs. the square root of time, based on the following equation (Crank 1975, Cussler 1997):

$$x_{rms} = x_0 + \sqrt{4Dt} \quad [2]$$

where  $x_{rms}$  = root-mean-square average distance of penetration;  $x_0$  = depth of penetration upon the contaminant's application. The penetration distance is defined as the distance between the point of application and the 5-mm cut section in

which the contaminant's concentration was at least 3 percent of the total.

Statistical variation in the calculated diffusion coefficients was quantified as the standard deviation of the mean for the slope of the straight line. In the case of the differential method, since the slope yielded a  $2D^{1/2}$  value, relative errors were adjusted correspondingly.

## Results and discussion

### Contaminant absorption and retention in wood

For all three contaminants studied, both in ambient and post-soaked wood, the process of wood penetration can be described as a two-phase process: 1) fast physical absorption of the liquid phase into the wood subsurface area; followed by 2) long-term contaminant diffusion through the bulk of the wood. The first phase was similar for all three contaminants regardless of the sample water content: 5  $\mu$ L aliquots of contaminants applied on wood in this work visually disappeared in 3 to 5 seconds. Five minutes after contaminant application, penetration profiles were similar for all contaminants as long as aliquots of a similar volume were used. For 5- $\mu$ L aliquots, 5 to 8 percent of the contaminants reached the second 5-mm section (as shown in **Figure 1B**, i.e., 5 to 10 mm from the surface), and trace amounts were detected in the third 5-mm section (i.e., 10 to 15 mm from the surface) in 5 minutes.

Five minutes after *n*-hexadecane application, washing the sample with distilled water for 3 days resulted in leaching of only 0.05 to 0.5 percent of the applied radioactivity on either cross-sectional or parallel surfaces. Similarly, 15 to 20 percent of the initial amount of DNT and 30 to 40 percent of naphthalene were recovered in the surrounding aqueous medium during the first 2 days of application (includes evaporation into the headspace for naphthalene), and then the total amount of radioactivity in the wood remained nearly constant for the duration of the experiments (commensurate with the solubility of all three contaminants in water, see **Table 1**). This experiment illustrates that contaminated wood cannot be cleaned using pump-and-treat methods, even for relatively water-soluble contaminants, such as naphthalene and DNT.

It is noteworthy that near naphthalene aliquots of the same size completely evaporated within 1 hour, whereas naphthalene contained in wood samples after absorption lasted for months ( $50 \pm 10\%$  recovery was maintained throughout the duration of the experiment), despite naphthalene's significant volatility. This observation is evidence that naphthalene is entrained within wood and difficult to remove.

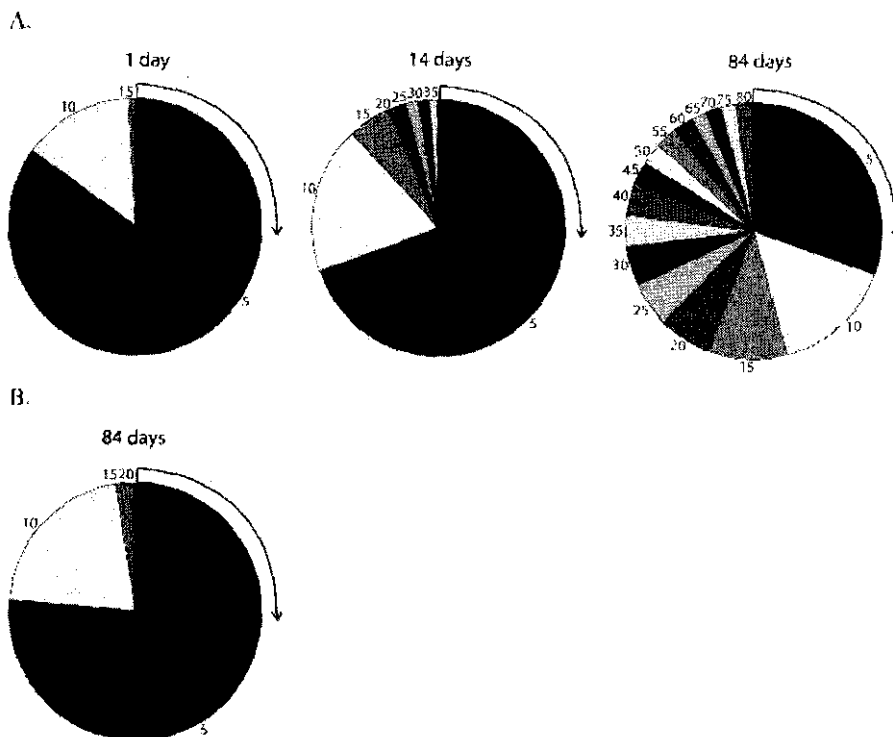


Figure 2. — Distribution of <sup>14</sup>C-labeled *n*-hexadecane in 7- by 20- by 80-mm wood samples upon long-term incubation. From the beginning of the arrow around a pie chart in a clockwise fashion, each segment represents the normalized pollutant concentration in that 5-mm-thick wood section, starting from the first one, upon which the contaminant was applied. The distance (mm) from the point of application to the end of each section in which the pollutant was found is shown as numbers around the pie chart, next to the corresponding segment. A) Ambient cross-sectional wood: B) Post-soaked cross-sectional wood.

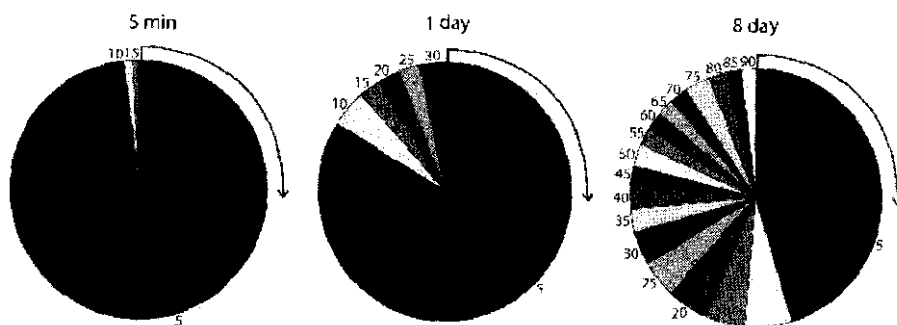
### Contaminant profiles in ambient and post-soaked wood

Wood contamination profiles for *n*-hexadecane and naphthalene are presented in **Figures 2** and **3**, respectively (DNT not shown). Once the first physical absorption phase was completed in the first 5 to 10 minutes after contaminant application, further penetration of the contaminants into wood tracheids was much slower. The diffusion rates and contamination profiles were strongly dependent on the type of contaminant and whether the wood was submerged in water.

***n*-Hexadecane** — Contamination profiles were similar for longitudinal and tangential penetration (not shown). The *n*-hexadecane content in the nearest to the surface 5-mm section of ambient wood samples decreased steadily until it reached the end of the specimen (8 cm) in 40 days (**Fig. 2A**). By contrast, for post-soaked wood, contaminant penetration was significantly slower and virtually stopped in 20 days. Maximum penetration depth into post-soaked wood in 3 months (same depth as measured after 2 weeks) equaled 1.5 to 2 cm (3 to 4 5-mm sections, **Fig. 2B**).

**Naphthalene**. — The longitudinal contamination pattern in ambient wood resembled that obtained for *n*-hexadecane, but the diffusion was faster (not shown). In just 1 day, only 40 percent of the total wood-entrained naphthalene was recovered in the 5-mm wood section nearest the application surface. By this time, 10 5-mm sections of the wood sample contained measurable quantities. The effect of wetting the wood

A.



B.

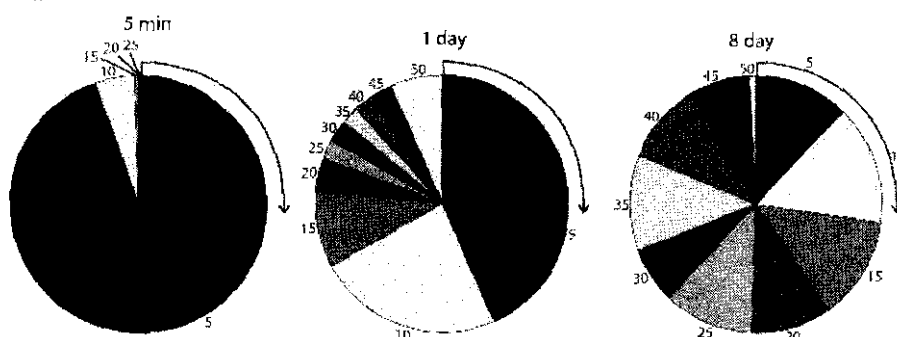


Figure 3. — Distribution of  $^{14}\text{C}$ -labeled naphthalene in wood samples upon long-term incubation. From the beginning of the arrow around a pie chart in a clockwise fashion, each segment represents the normalized pollutant concentration in that 5-mm-thick wood Section, starting from the first one, upon which the contaminant was applied. The distance (mm) from the point of application to the end of each section in which the pollutant was found is shown as numbers around the pie chart, next to the corresponding segment. A) Post-soaked parallel (tangential) wood, 7 by 20 by 90 mm; B) Post-soaked cross-sectional wood, 7 by 20 by 50 mm.

samples was opposite to that for *n*-hexadecane diffusion, resulting in even faster naphthalene penetration in this post-soaked wood. This could be associated with naphthalene's moderate solubility in water (Table 1). However, in addition to slightly speeding up the penetration rates, water also significantly speeds up the establishment of an even distribution of the contaminant. In 8 to 14 days, the distribution of naphthalene in post-soaked wood was almost uniform (Fig. 3B), whereas this was not the case for ambient wood. Apparently, inundation of wood tracheids with water causes desorption of naphthalene from earlier occupied sites, thus increasing its mobility.

Naphthalene tangential penetration in post-soaked wood in sections 2 to 10 (5 to 50 mm from the point of application, Fig. 1B) was continuous and similar to that in longitudinal penetration (a nearly uniform distribution was achieved in 8 to 14 days), but the amount of naphthalene in the first 5-mm tangential penetration section was disproportionately high for up to 3 to 4 weeks of incubation (Fig. 3A). Apparently, strong preferential sorption of naphthalene occurs on some near-surface sites. Anomalies like this one are listed in Table 3 (see the footnote).

These observations indicate that contaminant penetration beyond the initial 5-minute interval can be described as sorption-based diffusion. In this diffusion model, both contaminant mobility and the length of the diffusion path are less in-

portant than the rate of desorption from sites in wood, which is the rate-limiting step. The observed preferential subsurface absorption of fast moving chemicals, naphthalene (Fig. 3A) and DNT (not shown) during tangential penetration is likely due to the presence of long tracheids parallel to the surface and interconnected with the surface (Siau 1984, 1995; MacKay and Gschwend 2001). The surface area within the tracheids immediately available for contaminant sorption in the tangential direction is much greater than for longitudinal penetration. The flow of aqueous medium created in post-soaked wood results in desorption of weakly adsorbed contaminant molecules while leaving the strongly adsorbed molecules behind.

#### ***n*-Hexadecane contaminant profiles in pre-soaked wood**

To further model flood conditions and verify the hypothesis that sorption-based diffusion is the dominant transport mechanism, penetration hydrocarbons into pre-soaked, i.e., water-submerged, wood samples was investigated. Changing the order of application (water followed by *n*-hexadecane) results in a reversal of the trends for contaminant penetration into wood. The contaminant penetration in pre-soaked wood (not shown) is much faster than in the ambient wood, whereas in post-soaked wood it is much slower. When the contaminant is applied first, *n*-hexadecane does not reach the opposite end of the wood sample even in a few months (Fig. 2B), whereas when the wood is totally saturated with water, it does so in just a few hours. However, the contaminant distribution never becomes uniform because a significant fixation of *n*-hexadecane remains in the 5-mm section nearest to the surface where the pollutant was applied.

#### **Contaminant diffusion coefficients in wood**

These coefficients were calculated based on Equation [1] as shown in Figure 4 (the "integral method") for the tangential penetration of naphthalene into ambient wood samples and are listed in Table 2. The diffusion coefficients are similar for different incubation times but statistically different for varied penetration depths, exhibiting a biphasic behavior. The values show that the near-surface diffusion (within 5 to 10 mm from the surface) is slower than diffusion within the bulk structure of the wood, which is consistent with diffusivity values of borates in wood, i.e., of water-soluble chemicals under similar conditions (Ra et al. 2001).

The diffusivity values obtained for various contaminants, their application with respect to the tracheid directions, and different cases of water saturation (Table 3) reveal a few trends. The most conspicuous of them is the similarity of longitudinal and tangential mobilities. In combination with a

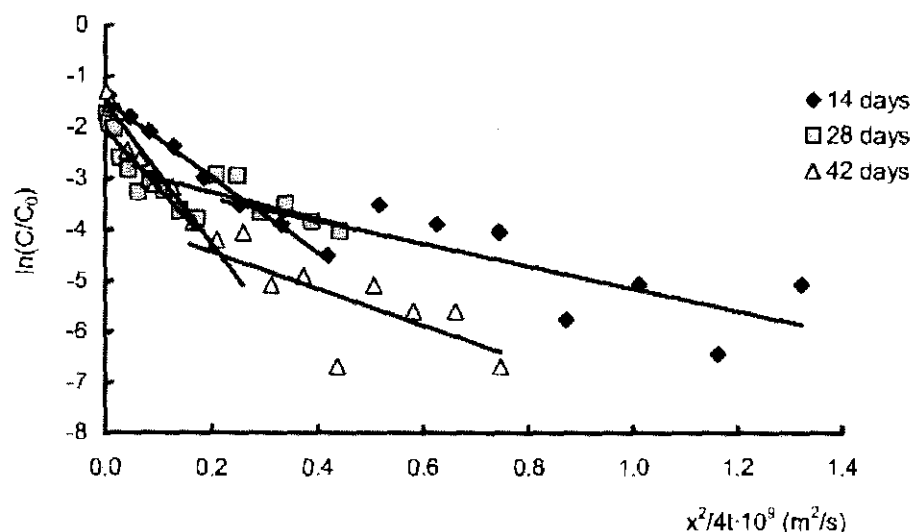


Figure 4. — Determination of diffusion coefficients. The data of naphthalene diffusion in ambient parallel (tangential) wood are presented. Diffusion coefficients were determined as  $-1/\text{slope}$  values.

Table 2. — Naphthalene diffusion coefficients in parallel (tangential) ambient wood (determined using the data in Fig. 4 based on Eq. [1]: the slope =  $1/D$ ).

|                | Near-surface          |                       | Deep penetration      |                       |
|----------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                | D                     | SD <sup>a</sup>       | D                     | SD                    |
| (days)         | (m <sup>2</sup> /s)   |                       |                       |                       |
| 4 <sup>b</sup> | $1.4 \times 10^{-10}$ | $0.2 \times 10^{-10}$ | ND <sup>c</sup>       | ND                    |
| 8 <sup>b</sup> | $5.0 \times 10^{-11}$ | $1.5 \times 10^{-11}$ | $5.0 \times 10^{-10}$ | $1.7 \times 10^{-10}$ |
| 14             | $1.4 \times 10^{-10}$ | $0.3 \times 10^{-10}$ | $5.0 \times 10^{-10}$ | $0.7 \times 10^{-10}$ |
| 28             | $1.0 \times 10^{-10}$ | $0.2 \times 10^{-10}$ | $2.0 \times 10^{-10}$ | $0.6 \times 10^{-10}$ |
| 42             | $1.0 \times 10^{-10}$ | $0.2 \times 10^{-10}$ | $2.5 \times 10^{-10}$ | $1.2 \times 10^{-10}$ |

<sup>a</sup>SD = standard deviation.

<sup>b</sup>The graphs for low incubation times are not shown in Figure 4 because of the order of magnitude scale difference for the  $x^2/4t$  factor.

<sup>c</sup>ND = not determined because of low penetration depth.

strong dependence of diffusivity values in ambient wood on contaminant volatility (e.g.,  $D_{\text{DNT}} < D_{n\text{-hexadecane}} < D_{\text{naphthalene}}$ , Table 3 first row), its relative independence on wood tracheid alignment (and, thus, on diffusion path) indicates that contaminant desorption (evaporation or dissolution) may be the rate-limiting step.

Confirming this hypothesis, contaminant mobilities in water-submerged (post-soaked) wood samples increase with their solubility in water and the rates of naphthalene and DNT diffusion into wood reach  $10^{-9}$  m<sup>2</sup>/s, which is characteristic for non-restrained diffusion in liquids (Siau 1984, 1995; Cussler 1997; Mackay and Gschwend 2000). This result is consistent with the observation made by Ra et al. (2001) that water-soluble borates have greater diffusivities in moist wood.

The complexity of the wood-water transport system also influences diffusivity (Table 3). Slightly higher numerical values of tangential (rather than longitudinal) diffusivities were observed for fast-moving contaminants such as naphthalene and DNT (the latter in post-soaked wood only where it moves fast). This effect can be explained if the preferential near-surface sorption in the tangential direction (discussed earlier) is taken into account. If the “leaders” move faster while strongly bound molecules are left behind, a non-

equilibrium situation occurs, resulting in a superposition of two different profiles. This assessment is supported by abnormally high values of DNT and naphthalene diffusion coefficients in post-soaked wood ( $>10^{-9}$  m<sup>2</sup>/s, i.e., faster than in the bulk liquids) under these conditions (Table 3).

The occurrence of two different diffusion profiles can be explained, from the standpoint of wood structure, by the combination of two processes: the first being sorption-based contaminant diffusion in the tracheids whereas the second, slower step is due to penetration into the cell wall/absorption. Significant adsorption (perhaps combined with some adsorption on the surface of tracheids) may explain a few other observed effects, such as slow diffusion

of *n*-hexadecane in post-soaked wood (water would force this non-polar chemical into the walls where it would remain practically immobile). It also explains the occurrence of two different diffusion coefficients for different penetration depths observed for mobile contaminants (i.e., those with high diffusivities, Tables 2 and 3). This may be attributed to preferential contaminant sorption near the surface (when the bulk of the contaminant is still in one piece) followed by penetration of its scattered molecules controlled by the rates of its desorption/absorption. Note that this effect is consistently observed in samples contaminated parallel to the tracheids (tangential penetration), where the difference between the near-surface and deep-penetration diffusivities is more pronounced for post-soaked wood. This is expected for sorption-based diffusion.

The analysis of diffusivity values for *n*-hexadecane and naphthalene when the order of contaminant and water application is varied (Table 3) confirms that filling the wood tracheids with water prior to the contaminant's application (pre-soaked wood) results in faster (by a few orders of magnitude) rather than slower diffusion of hydrophobic chemicals, such as naphthalene and *n*-hexadecane; the diffusivity values in pre-soaked wood are abnormally high ( $10^{-8}$  to  $10^{-7}$  m<sup>2</sup>/s), thus indicating the influence of non-equilibrium factors.

Note that a significant fraction of *n*-hexadecane, the least water-soluble of the model contaminants, in pre-soaked wood remains immobile (Table 3, footnote). This is similar to the case of fast-moving chemicals in post-soaked wood, which is also characterized by abnormally high diffusivities and the accumulation of contaminant near the surface. Both effects are consistent with sorption-based diffusion because the application of water results in saturating non-specific adsorption sites and creates a physical barrier for the contaminant diffusion into the cell walls (thus forcing its unhindered unidirectional diffusion along the tracheid). Yet, only a fraction of *n*-hexadecane remains mobile, whereas the bulk of it gets adsorbed/absorbed near the surface either due to the occurrence of the chemical as a continuous phase or the presence of more hydrophobic/specific sites, like lignin exposed when the wood samples were cut. This creates a non-equilibrium situ-



ous-source application of bulk amounts of contaminants should be described as an unrestrained rather than sorption-based diffusion process (because at a large contaminant/wood ratio all of the surface adsorption sites and accessible spaces between the tracheids become saturated without using up the bulk of the contaminant).

The significance of this experiment for flood damage is that for pressurized post-soaked conditions in flooded basements, longitudinal diffusion of poorly water-soluble hydrocarbons significantly exceeds tangential penetration, whereas under ambient, atmospheric pressure conditions, wood contamination does not appear to depend upon this variable.

### Conclusions

The results of this study show that for the penetration of small quantities of organic contaminants into wood, characteristic of spills and/or floods, the presence of water and the order/mode of water's application compared to the organic contaminant have a substantial impact on diffusion. Similarity in diffusivity was observed for longitudinal and tangential penetration in non-pressurized wood samples. The most likely physical description of the contamination process is sorption-based diffusion, i.e., adsorption/absorption on/into the tracheid walls, and desorption from those sites, with the latter being the rate-limiting step.

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