STEADY-STATE DIFFUSION OF CHLOROPICRIN IN DOUGLAS-FIR HEARTWOOD[1]

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ABSTRACT

The effects of moisture content, flow direction, concentration, and temperature on the diffusion of chloropicrin in Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) heartwood were investigated. Diffusion coefficients were strongly affected by wood moisture content. Coefficients for radial and tangential diffusion at the fiber-saturation point were twice as high as those at the oven-dry condition. Longitudinal diffusion coefficients, however, increased only 12.5% when the moisture content was increased over the same range. Longitudinal diffusion coefficients were about three orders of magnitude higher than those in the transverse directions, while there was no significant difference between radial and tangential diffusion coefficients. Diffusion coefficients were independent of concentration, showing the validity of Fick's law of diffusion in characterizing the flow of the fumigant in wood. Diffusion coefficients were always higher at 35 C than at 20 C; however, the difference was not statistically significant, suggesting that the flow of the fumigant is not a temperature-activated process.

Keywords: Diffusion, chloropicrin, fumigant, heartwood, Douglas-fir.

INTRODUCTION

While large timbers and poles can provide excellent service life when properly treated and handled, some of them will develop deep checks that penetrate beyond the treated shell and permit the development of internal decay. Internal decay can be arrested by application of liquid fumigants to holes drilled into the wood (Morrell and Corden 1986). These chemicals volatilize and diffuse up and down from the point of application. Because of their excellent activity and long-term protection against reinvasion by decay fungi, fumigants are widely used to control internal decay of utility poles and marine piling in the United States (Goodell and Graham 1983).

Four fumigants are registered for wood application in the United States; three are based on methylisothiocyanate (MITC) as a primary fungitoxic ingredient and one, chloropicrin, is based on trichloronitromethane. Chloropicrin, which contains 96% active ingredient, is the most effective of these compounds, providing over 20 years of residual protection to Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) utility poles (Morrell 1989). Field trials have demonstrated the degree of chloropicrin movement in a variety of wood species (Goodell et al. 1980; Highley and Eslyn 1982; Ruddick 1984; Morrell and Scheffer 1985; Cooper

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1986). Although fumigants have been used to arrest decay in utility poles and other large timbers for over 20 years, relatively little is known about the basic movement of chloropicrin in commercial wood species. In the laboratory, Cooper et al. (1974) noted that chloropicrin moved more slowly through inland than coastal Douglas-fir heartwood and developed rough longitudinal diffusion coefficients that described this process. Subsequent research suggested that chloropicrin interacted chemically with phenolic components in wood (Goodell et al. 1986) and that this reaction residue was resistant to acetone extraction (Daniel and Goodell 1989). While these results demonstrate the effectiveness of chloropicrin as a wood fumigant, their application towards improving the performance of this chemical are limited. We have recently developed a computer model that simulates the movement of MITC through Douglas-fir heartwood (Zahora et al. 1988). In an effort to extend this model to chloropicrin, the data on the effects of wood moisture content, temperature, and chemical concentration on chloropicrin diffusion were developed.

MATERIALS AND METHODS

Sample preparation and experimental variables

Douglas-fir heartwood disks 54.2 mm in diameter were obtained from air-dried boards. Tangential- and radial-flow samples were cut to a nominal 2.2-mm thickness, while longitudinal-flow samples were sawn to a nominal 20-mm thickness. To ensure unidirectional flow, the edges of the samples were coated with several layers of epoxy before being inserted in the experimental set-up. The samples that were tested in the dry condition were first dried in an oven set at 103 ± 2 C for at least 24 hours; the samples tested in the wet condition were exposed to saturated atmosphere in a 3-liter glass vessel for at least one week prior to the experiment. At the end of each test, the moisture content (MC) of the samples was found to have mean values of 1.18% and 24.04% for the dry and wet conditions, respectively. Moisture content did not vary by more than 2% from those observed before the samples were introduced in the diffusion apparatus. The study was performed as a two-factor factorial experiment in a completely randomized design with moisture content (oven-dry and fiber-saturation point), and direction of flow (radial, tangential, and longitudinal) as the variables. Each variable was tested on four wafers for a given orientation.

The effects of fumigant concentration and temperature (20 and 35 C) on diffusion rate were evaluated only on dry samples. Chemical levels were established by placing chloropicrin in chambers with differing surface areas. Greater surface area exposed more chloropicrin to volatilization, increasing airborne levels. Chloropicrin was placed in a 16-mm × 125-mm culture tube for the first concentration level; for the second level, the chemical was placed in a 40-mm × 85-mm wide-mouth bottle. Gas chromatographic analyses of the gas stream at steady-state revealed concentration values of 6.56 and 16.66 μg/ml at 20 C and 35 C, respectively, with the culture tube; the corresponding values were 36.84 μg/ml and 102.66 μg/ml, respectively, with the wide-mouth bottle.

Diffusion apparatus

Wood specimens were clamped between two stainless-steel diffusion cells (Fig. 1A, B), each with an inside diameter of 48.9 mm, and provided with a gas inlet and outlet. The edges of the wood were liberally coated with a silicone-rubber caulk to prevent chloropicrin loss at the cell-specimen interface. The assembly, stainless-steel coils, and chloropicrin container were immersed in a thermostatted water bath to maintain the temperature at 20 or 35 C (Fig. 2).

Compressed air was passed through a hydrocarbon trap, a moisture trap, and a chloropicrin container before entering diffusion cell A (the high-concentration side), while compressed air passed through identical traps was allowed to flow into diffusion cell B. Before

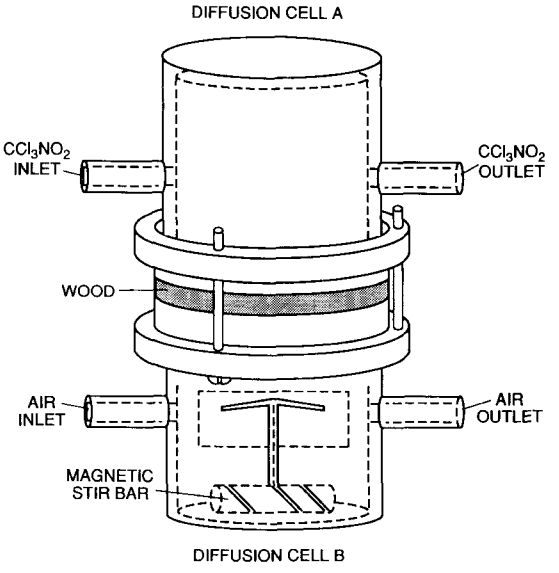

FIG. 1. Wood and diffusion-cell assembly used to study the steady-state diffusion of chloropicrin in wood.

entering the diffusion cell, each gas stream went through several turns of stainless-steel coil immersed in the water bath to bring the gas to equilibrium temperature. Chloropicrin that diffused through the wood from cell A to cell B was carried away by the chloropicrin-free air stream, which later went through a calibrated and correlated flowmeter.

The flow in each line was controlled with a needle valve. A zero total pressure drop was maintained across the specimen. Pressure was monitored by connecting each cell to a leg of a U-tube manometer containing a low-density silicone oil dyed with sudan red oil-soluble pigment. The actual total pressure (1.18 mmHg in excess of atmospheric pressure) was measured using a manometric gage containing the same low-density oil connected to cell B.

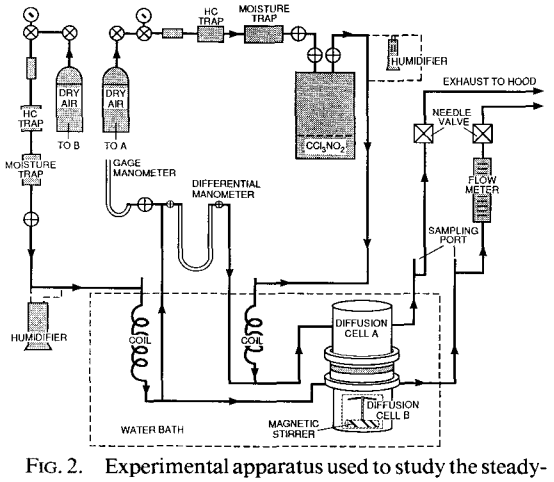

FIG. 2. Experimental apparatus used to study the steady-state diffusion of chloropicrin in wood.

Gas sampling and analyses

Chloropicrin concentrations were assessed by regular sampling of air streams exiting from both cell A and cell B. For each analysis, 0.5 ml of air was withdrawn from the exit tube with a gas-tight syringe containing 5 ml of hexane. Samples were withdrawn so that they bubbled through the hexane. The syringe was plugged and the barrel was rotated to disperse the hexane and enhance trapping of volatile chloropicrin. Six μl of the hexane extract was then analyzed for chloropicrin using a Varian 3700 Gas Chromatograph equipped with a ^{63}Ni electron capture detector. Operating conditions were: flow rate (N_2) = 50 ml/min, injection temperature 110 C, column temperature 90 C, and detector temperature 110 C. Concentrations were quantified by comparisons with standards containing known concentrations of chloropicrin.

The diffusion coefficient (D) of chloropicrin in wood was calculated with Fick's law of diffusion.

$$D = \left[\left(\frac{1}{A}\right)\left(\frac{dq}{dt}\right)\right] \Big/ \left(\frac{dc}{dx}\right) \qquad (1)$$

where A is the area (cm^2) perpendicular to the direction of the flow, dq/dt is the rate of transfer (g/s), and dc/dx is the concentration gradient [g/cc (cm)]. The value of A was assumed to be equal to the area of the diffusion-cell mouth; no edge-effect corrections were made. The rate of transfer of chloropicrin through the sample was calculated by combining the flow rate measurement and the calculated CCl_3NO_2 concentration at cell B. The concentration gradient was determined by dividing the differ-

TABLE 1. *Effect of wood moisture content on tangential, radial or longitudinal steady-state diffusion coefficients of chloropicrin in Douglas-fir heartwood.*

Moisture content	Flow direction	Diffusion coefficient,[a] cm^2/s
Oven-dry	Tangential	$5.1855 \cdot 10^{-6}$ ($0.9234 \cdot 10^{-6}$)
	Radial	$5.1530 \cdot 10^{-6}$ ($1.1960 \cdot 10^{-6}$)
	Longitudinal	$7.3788 \cdot 10^{-3}$ ($0.2906 \cdot 10^{-3}$)
Fiber-saturation point	Tangential	$9.4305 \cdot 10^{-6}$ ($0.1551 \cdot 10^{-6}$)
	Radial	$9.8236 \cdot 10^{-6}$ ($0.5673 \cdot 10^{-6}$)
	Longitudinal	$8.3088 \cdot 10^{-3}$ ($0.1261 \cdot 10^{-3}$)

[a] Values are the mean (and standard deviation) of four replicates.

ence between the surface concentrations by the thickness of the material.

RESULTS AND DISCUSSION

The mean D values at different MC and flow direction levels are shown in Table 1. An analysis of variance revealed that the two factors, together with their interaction, were significant at the 1% probability level. The interaction effect was caused mainly by the difference in tangential and radial diffusion at the two MC levels.

Mean analysis with Tukey's studentized range test showed that D was strongly affected by wood MC. Coefficient values for diffusion in the transverse directions were almost doubled when MC increased from oven-dry to fiber-saturation. The effect of MC on diffusion in the longitudinal direction was less dramatic, but an increase of 12.5% was still observed when MC was raised from 0 to 24%.

The results indicate that the fumigant interacts with reactive sites in wood. The dipole moment of chloropicrin is approximately the same as that for water, hence secondary bonding should be possible between the chloropicrin molecules and the hydroxyl groups in wood (Goodell et al. 1986). The bonding energy between the sorption site and the chloropicrin molecule in oven-dry wood should be relatively high. As MC increases, the water molecules interact with the hydroxyl groups, decreasing the number of reaction sites and reducing the bonding energy between wood and fumigant. Because the force of attraction between the sorption sites and the chloropicrin molecules decreases rapidly with increased distance, the mobility of the fumigant molecules rises with increases in the polymolecularity with which water is held in those sorption sites. Hence, fumigant flow should increase with increase in moisture content, as observed in this study.

Diffusion coefficients include the combined effects of both bound and vapor diffusion components. The relative contributions of these two components may have been responsible for the differences observed in the effect of MC on diffusion coefficients in transverse and longitudinal directions. In the former, the bound diffusion component is more important because more cross-walls have to be transversed per unit length; in the latter, the vapor diffusion component is expected to predominate. In this study, no attempt was made to separate the bound and vapor diffusion components or to determine how these are affected by MC. Inferences can, however, be made from results of past studies on moisture diffusion in wood. In those investigations, it had been demonstrated that bound water diffusion in the hygroscopic range increases exponentially with MC, while water vapor diffusion in the cell lumen remains more or less constant at low values of MC, then decreases with further increases in MC (Siau 1984). Hence, if the results are extended to fumigant flow, it is expected that the increase in the value of D—as MC increases from the oven-dry condition to the fiber-saturation point—should be higher in the transverse directions (80 to 90% increase) than in the longitudinal direction (12.5% increase).

TABLE 2. *Effect of chemical concentration and temperature on steady-state diffusion coefficients of chloropicrin in oven-dry Douglas-fir heartwood measured in the transverse and longitudinal directions.*

Concentration	Temperature, °C	Diffusion coefficient, cm^2/s	
		Transverse[a]	Longitudinal[b]
Low	20	5.1693×10^{-6}	7.3788×10^{-3}
		(0.9893×10^{-6})	(0.2906×10^{-3})
	35	5.7525×10^{-6}	8.6575×10^{-3}
		(0.8277×10^{-6})	(0.1259×10^{-3})
High	20	5.3620×10^{-6}	8.4760×10^{-3}
		(0.8765×10^{-6})	(0.1145×10^{-3})
	35	5.5002×10^{-6}	8.6392×10^{-3}
		(0.9220×10^{-6})	(0.7641×10^{-3})

[a] Values are the mean (and standard deviation) of eight replicates.
[b] Values are the mean (and standard deviation) of four replicates.

Similar effects were noted with diffusion of MITC in Douglas-fir heartwood (Zahora and Morrell 1989). Tangential MITC diffusion coefficients increased almost 8 times as MC increased from 15 to 22%. Longitudinal MITC diffusion coefficients increased only by about 65% over the same MC range. Interestingly, at a given moisture level, diffusion coefficients for MITC were 3 to 4 times greater longitudinally and 5 to 10 times greater radially or tangentially than for chloropicrin. These differences reflect the relative interactions each chemical has with the wood. Chloropicrin apparently undergoes more interactions with wood than MITC. Previous studies have suggested that chloropicrin binds to phenolic materials (Goodell et al. 1986), but no such interactions have been noted with MITC (Zahora and Morrell 1989).

Longitudinal diffusion coefficients were significantly different from those in the radial and tangential directions; the values in the two transverse directions were not statistically different from each other. Longitudinal diffusion coefficients for oven-dry wood were 1,400 times higher than the transverse values; at the fiber saturation point, the longitudinal-to-transverse ratio was about 800. A similar trend was observed by Cooper et al. (1974) in a study on the unsteady-state diffusion of chloropicrin in Douglas-fir heartwood, except that the longitudinal-to-transverse ratio calculated in that work is two orders of magnitude lower than the value obtained here. Variations between our study and earlier studies most probably reflect differences in experimental apparatus as well as improvement in analytical techniques over the intervening years. The different diffusion rates in longitudinal and transverse directions reflect the relative importance of the bound and vapor diffusion components. Douglas-fir heartwood tracheids are about 140 times longer than their lumen diameter (Krahmer 1961); thus a longer uninterrupted path is provided for vapor flow in the longitudinal direction.

Radial diffusion of moisture in wood is generally higher than tangential diffusion, presumably due to the ray cells allowing greater vapor flow in the radial direction. Differences in the rate of movement in the two transverse directions were not observed in this study, suggesting that the ray cells of Douglas-fir did not influence the transfer of chloropicrin radially to the degree that the bound diffusion effect obscured the vapor flow component.

T-tests of longitudinal diffusion coefficients showed that values in oven-dry wood did not differ significantly with concentration at 35 C but they did differ at 20 C. The reasons for these differences are unclear. Tangential and radial coefficients did not differ significantly with chloropicrin concentration at either temperature (Table 2). These results indicate that chloropicrin diffusion in wood is independent of concentration within a range of chemical levels that could occur with fumigant treatment, supporting the use of Fick's law to characterize fumigant movement in wood. Previous studies with MITC reached similar conclusions with that chemical (Zahora and Morrell 1989).

Comparisons between diffusion coefficients at 20 or 35 C showed that higher temperatures resulted in slightly higher diffusion coefficients; however *t*-tests indicated that those differences were not significant at the 1% probability level. The lack of significant effects suggests that chloropicrin diffusion through

Douglas-fir heartwood is not a temperature-activated process.

SUMMARY AND CONCLUSIONS

Steady-state diffusion of chloropicrin through Douglas-fir heartwood was strongly affected by moisture content and wood orientation but unaffected by changes in chemical concentration or temperature. Chloropicrin diffusion coefficients were generally smaller than those found with MITC, suggesting that the former chemical interacted with the wood. Although such interactions initially slow fumigant distribution, they result in longer retention times within the wood and may help to explain the excellent protection this chemical affords.

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