DIFFUSION AND SORPTION OF THE FUMIGANT METHYLISOTHIOCYANATE IN DOUGLAS-FIR WOOD[1]

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ABSTRACT

The influence of moisture content (MC) and conventional preservative treatment on methyliso-thiocyanate (MIT) sorption and diffusion were investigated in Douglas-fir wood. In wood at 0% MC, the ratio of equilibrium MIT adsorption to desorption concentrations was low (0.2), but it increased rapidly to about 0.94 above 18% MC. Partition coefficients (bound/vapor MIT) for MIT adsorption to wood increased with wood moisture from 0% to about 12%. At higher moisture contents, sorbed water apparently interfered with MIT sorption, and partition coefficients decreased with wood moisture content for both MIT adsorption and desorption.

Steady-state diffusion coefficients were dependent on wood moisture content, but were at least 200 times higher for longitudinal movement of MIT in Douglas-fir heartwood than for transverse movement. Diffusion coefficients increased with wood moisture content below the fiber-saturation point, apparently as a result of improved bound MIT diffusion. Increasing wood moisture content from 22% to 80% reduced longitudinal MIT diffusion almost threefold, but did not greatly influence tangential MIT diffusion. Radial movement of MIT was about seven times faster in Douglas-fir sapwood than in heartwood. Preservative treatment with waterborne chromated copper arsenate did not influence MIT sorption or diffusion in sapwood at 15% MC, but impregnation with P-9 Type A oil restricted MIT movement and may provide a barrier to fumigant loss.

Keywords: Methylisothiocyanate, fumigants, diffusion, adsorption, desorption, Douglas-fir.

INTRODUCTION

Because fumigants can effectively control internal decay in utility poles and other large wooden structural members (Helsing et al. 1984), they are seeing widespread use in the United States (Goodell and Graham 1983). Field results suggest that they effectively control decay fungi in pressure-treated utility poles for as long as 14 years (Helsing et al. 1984), but the specific fumigant and wood interactions that determine the effectiveness of a treatment are poorly understood. Current practices—the drilling pattern, formulation, quantity of fumigant used, and retreatment schedules—are based more on "rules of thumb" derived from field experiments than on an understanding of how fumigant, wood, and fungi interact to control internal decay.

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[1] This is Paper 2330 of the Forest Research Laboratory, Oregon State University, Corvallis, Oregon. Mention of commercial products does not constitute endorsement by Oregon State University.

TABLE 1. *Salts used for equilibrating Douglas-fir heartwood blocks and wafers to specific moisture contents for sorption and diffusion studies.*

Salt		Relative humidity[a]	Wood moisture content[b]
Type	Condition		
		------------------------------- % -------------------------------	
CaSO$_4$	Anhydrous	0	0–1
Mg(NO$_3$)$_2$	Saturated solution	55	7–9
NaCl	Saturated solution	76	11–13
NH$_4$H$_2$PO$_4$	Saturated solution	93	17–19
None	Distilled water	100	25–28

[a] From Winston and Bates (1960).
[b] Final moisture-content range observed in blocks and wafers.

Methylisothiocyanate (MIT), an effective wood fumigant, is a major fungitoxic component of Vorlex (20% MIT, 80% chlorinated C3 hydrocarbons) and a major volatile product of the decomposition of Vapam (sodium N-methyldithiocarbamate) and other solid fumigants (Morrell and Corden 1986). A basic understanding of MIT sorption and diffusion properties in wood is necessary for determining the rate and extent of effective fumigant movement and is required before fumigant treatments can be improved or tailored to specific conditions. Knowledge of fumigant diffusion rates will also help define the rate of fumigant loss from wood and provide the basis for accurate retreatment schedules.

This paper describes experiments investigating the sorption and diffusion properties of MIT in Douglas-fir heartwood and the influence of wood moisture content (MC) and standard preservative treatments on those properties.

MATERIALS AND METHODS

Heartwood blocks and wafers used in the sorption and diffusion studies were cut from an unseasoned coastal Douglas-fir (*Pseudotsuga menziesii* [Mirb.] Franco) log that was 30 cm in diameter. The blocks, cut from clear outer heartwood where the curve of the growth rings was smallest, contained three to five growth rings per centimeter. Sapwood wafers, cut from an unseasoned old-growth Douglas-fir slab, contained six to seven growth rings per centimeter. Average specific gravity (oven-dry weight and green volume) of 10 heartwood wafers was 0.442 (±0.011) and that of 5 sapwood wafers was 0.439 (±0.006).

MIT sorption to Douglas-fir heartwood

The strength of MIT sorption to Douglas-fir heartwood was evaluated at different wood moisture contents by comparing equilibrium MIT sorption concentrations after previously fumigated (desorption) and nonfumigated (adsorption) blocks were combined in sealed vials.

First, Douglas-fir heartwood blocks were cut to volumes of 0.5 cm^3 (0.5 × 2.0 × 0.5 cm), 1.0 cm^3 (0.5 × 2.0 × 1.0 cm), 1.5 cm^3 (1.5 × 2.0 × 0.5 cm), and 3.0 cm^3 (1.5 × 2.0 × 1.0 cm). The blocks were oven-dried, weighed, and adjusted to one of six moisture contents: about 0, 8, 12, 18, 27, or 40%. Those adjusted to 40% MC were infiltrated with water under vacuum and air-dried to a weight representing an average 40% MC, although a moisture gradient probably existed within each block. All other blocks were equilibrated in humidity chambers (450

TABLE 2. *The volume of methylisothiocyanate (MIT) fumigated blocks and nonfumigated blocks combined in vials, and the percentage of fumigated wood in the adsorption-desorption study.*

Block type[a]	Vial contents								
	Volume of individual blocks (cm^3)								
Fumigated	0.5	1.0	0.5	1.0	1.5	1.5	1.0	3.0	3.0
Nonfumigated	3.0	3.0	1.0	1.5	1.5	1.0	0.5	1.0	0.5
	Percent MIT-fumigated wood								
	14	25	33	40	50	60	67	75	86

[a] Fumigated blocks were initially exposed to MIT vapors for 2 weeks before being combined with nonfumigated blocks in vials.

cm^3 wide-mouth glass jars) containing about 55 ml of salt solutions (Table 1). The sides of the jars were lined with filter paper to increase the solution surface-area, and the blocks were held away from the bottom and sides of the jar in nylon-screen baskets. All blocks were stored at 22 C for 9 to 10 days before wood moisture content was determined by weight. One-half of the blocks at each moisture content were placed in small jars and exposed to a saturated MIT atmosphere (about 35 μg MIT/ml air) for 2 weeks before use.

A preliminary sorption experiment was conducted to determine the effect of equilibration time on MIT sorption values. Five fumigated and five nonfumigated blocks (1.0 cm^3) at 0% MC were placed together in each of five small glass vials and stored at 22 C. Vials were sealed with Teflon®-lined screw caps and Parafilm®. Periodically, MIT concentrations in a vial were determined. MIT vapor concentration was determined by drilling a small hole through the jar cap, puncturing the Teflon® cap liner, and drawing 3 ml of vapor from the jar into a syringe containing 1 ml of ethyl acetate. Each block was then removed from the jar and extracted for 3 days in ethyl acetate. All ethyl acetate extracts were analyzed for MIT content by gas chromatography (Zahora and Morrell 1988).

In the main sorption experiment, five fumigated and five nonfumigated blocks of different relative volumes were combined for each wood moisture content (Table 2). By varying the relative amounts of fumigated and nonfumigated wood combined in each jar, a range of MIT concentrations was produced, with non-fumigated blocks absorbing and fumigated blocks desorbing to final equilibrium conditions. The block groups were sealed in small glass vials for at least 17 days. This time was deemed sufficient on the basis of the preliminary sorption experiment with blocks at 0% MC. The chambers were then sampled for MIT vapor content and MIT sorption concentration in each block in the same way as in the preliminary sorption experiment.

MIT diffusion through Douglas-fir wood

Diffusion coefficients were calculated for steady-state movement of MIT through Douglas-fir wood in longitudinal, radial, and tangential directions. In addition, the influences of wood moisture content and of conventional preservative treatment on the diffusion coefficients were evaluated.

A modified diffusion-cup apparatus (Siau 1984) was designed to allow direct measurement of fumigant loss through a given surface area (Fig. 1). The cups measured 4.9 cm in diameter (air volume about 90 cm^3). Solid MIT produced an atmosphere in the upper cup that was saturated with MIT vapors (about 35
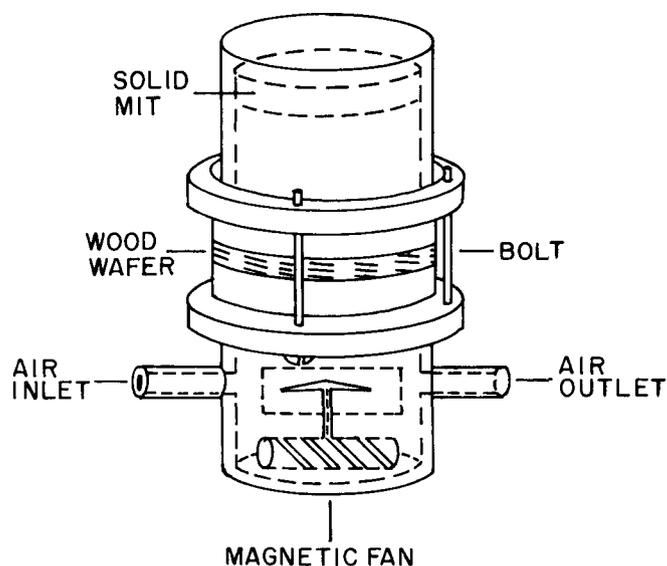
FIG. 1.   A modified diffusion-cup apparatus for studying diffusion of methylisothiocyanate (MIT) through sections of Douglas-fir wood.

μg/ml air). The bottom cup contained air inlet and outlet ports through which a steady air flow could pass. A fan attached to a magnetic stir bar in the bottom cup thoroughly mixed the air. The rate of MIT flow through the blocks was calculated from measurements of air flow and MIT vapor concentrations in the air exiting the bottom cups.

Douglas-fir heartwood wafers were cut 1.5 cm thick for longitudinal and 0.5 cm thick for radial and tangential diffusion experiments. Thick wafers were used for longitudinal diffusion studies to ensure that diffusing MIT would cross multiple cell walls. Thinner wafers were required for transverse diffusion experiments to ensure measurable MIT movement across the blocks and to restrict equilibration times. The different thicknesses preclude accurate comparisons of longitudinal and transverse diffusion coefficients, but should provide information on the relative importance of longitudinal and transverse diffusion. The end-grain surfaces of longitudinal wafers were surfaced with a microtome knife; radial and tangential wafers were sanded smooth in the direction of the grain with 180-grit sandpaper. Groups of five wafers were conditioned to one of four moisture contents (about 14%, 22%, 40%, or 80%) for each diffusion direction. Wafers were conditioned to 14% or 22% MC by placing them over saturated solutions of NaCl or $NH_4H_2PO_4$, respectively, and to 40% or 80% MC by infiltration with water under vacuum, followed by aeration to the weight associated with the desired moisture content. The final weights again represent an average wafer moisture content that may have varied substantially within a wafer. The edge of each diffusion wafer was then sealed with an acrylic-latex coating, and the wafers were stored in closed containers over distilled water for at least 1 week before use in diffusion experiments.

Douglas-fir sapwood wafers (0.5 cm thick) were used to test the influence of conventional preservative treatments on radial MIT diffusion rates. Five wafers

each were treated to refusal with P-9 Type A oil and a 2.5% waterborne chromated copper arsenate (CCA) solution, and five were left untreated. These wafers were equilibrated at 76% relative humidity over a saturated NaCl solution at 23–25 C for at least 1 month before use.

The diffusion surface area was 18.9 cm² for radial and tangential diffusion experiments, but was restricted to 12.2 cm² for longitudinally oriented wafers by placing steel washers between the wood wafers and diffusion cups. A thin layer of Dow Corning high-vacuum grease was used to seal the wafers to the metal cup (or washers) before the wafers were tightly bolted into the cup apparatus. The edges of the blocks were then further sealed with Teflon tape and molten paraffin.

Five replicate wafers were monitored simultaneously for each wood moisture content and diffusion direction in the apparatus. To minimize wafer drying during the diffusion experiment, the air flowing to the cups was bubbled through the same salt solutions (or water) initially used to adjust the wafers to their test moisture contents. All diffusion cups were maintained at 21.5 C (±0.5 C) in a temperature-controlled chamber. MIT vapor concentrations were determined by withdrawing a selected volume of vapor into a 5-ml airtight syringe containing a known volume of ethyl acetate, shaking the syringe to extract MIT into the ethyl acetate, and analyzing the ethyl acetate for MIT content by gas chromatography. The ratio of sampled vapor to ethyl acetate depended upon the concentration of MIT in the air flow.

Steady-state diffusion coefficients were calculated according to Fick's first law, by means of the equation

$$D(C) = mL/A \, \Delta C$$

where

$D(C)$ = diffusion coefficient (cm³/min)
m = rate of MIT flow (μg/min)
L = sample length in flow direction (cm)
A = sample cross-sectional area (cm²)
ΔC = MIT concentration difference over length L (μg/cm³ air).

Each set of diffusion cups was sampled until MIT vapor concentrations exiting the apparatus remained steady over a 24-hour period at one airflow rate; then the airflow rate was changed. The initial airflow rates through the bottom diffusion cups were high, about 60 and 30 ml/min for longitudinal and transverse diffusion, respectively. Flow rates were then decreased to about one-fourth of those rates, then increased to previous levels. This allowed diffusion coefficients for given blocks to be checked at different times, across different concentration gradients (different MIT concentrations in the bottom cups), and from both adsorption and desorption directions.

RESULTS AND DISCUSSION

MIT sorption in Douglas-fir heartwood

Fumigated (desorption) and nonfumigated (adsorption) blocks at 0% MC that were placed in the same container stabilized at a constant ratio of sorbed MIT (adsorption/desorption) after 3 weeks of equilibration (Table 3). As the equili-

TABLE 3.   *Influence of equilibration time on methylisothiocyanate (MIT) sorption ratio (adsorption/desorption) in Douglas-fir heartwood blocks at 0% moisture content.*[a]

		mg MIT/g wood[b]		
Time (weeks)	MIT (μg/ml air)	Adsorption	Desorption	Sorption ratio
1.3	7.54	1.87	9.79	0.19
3	5.72	1.62	7.77	0.21
6	4.66	1.47	6.95	0.21
10	3.07	0.85	4.27	0.20
24	—	0.54	2.57	0.21

[a] Equal volumes of wood saturated with MIT vapor and unfumigated wood were combined in vials for each time period.
[b] Sorption data represent the average of five replicate blocks. Coefficients of variation for the means ranged from 3 to 13%.

bration period lengthened, MIT sorption and vapor concentrations in the vials slowly decreased. The rate of decrease was substantially faster than the 0.16% per week that can be attributed to MIT decomposition (Zahora and Morrell 1988) and may reflect the escape of MIT vapors through the Teflon®-lined screw caps and Parafilm® wrapping. This slow loss of MIT allowed nonfumigated (adsorption) blocks to desorb MIT and may have prevented the establishment of true equilibrium conditions, but it did not appear to influence the ratio of sorbed MIT, which remained constant at about 0.2 in the two types of blocks. The relationships between equilibrium MIT concentrations of fumigated and nonfumigated blocks combined in the same vial will be referred to here as the adsorp/desorp ratio.

The adsorp/desorp ratios for MIT in the Douglas-fir blocks were strongly dependent on wood moisture content (Fig. 2). Although the adsorp/desorp ratios varied among replicate vials (different MIT concentrations) for each wood moisture content, strong correlations were found when MIT adsorption and desorption concentrations were regressed over the range of concentrations tested (Table 4). These regressions were forced through the origin to minimize the influence of extreme adsorption values on the calculated slope, which represented the adsorp/desorp ratio. Adsorp/desorp ratios increased rapidly from about 0.2 in wood at 0% MC to more than 0.9 in wood at 18% MC. Above 18% MC, increased wood moisture content did not significantly influence the sorption ratio, which stabilized at about 0.94.

Final MIT vapor and sorption concentrations often did not follow the pattern expected from the relative amounts of fumigated and nonfumigated wood initially combined in each vial. Some vials may have been more susceptible to fumigant loss than others. Although such losses probably prevented true equilibrium from being established, they did not appear to affect the adsorp/desorp ratios, which reflect the ease of desorption and movement through wood and the relative strength of MIT sorption at different moisture contents. Poor correlations ($r^2 = 0.001$ to 0.53) were found between adsorp/desorp ratios and MIT vapor or wood sorption concentrations within each moisture content grouping, suggesting that these ratios are independent of MIT concentration over the range tested (Table 4).

MIT partition coefficients describing the relative proportion of MIT sorbed to wood versus that in the air [(μg MIT/g oven-dry wood)/μg MIT/cm³ air)] were also influenced by wood moisture content (Fig. 3). These partition coefficients are kept in a format (cm³/g) that is not dimensionless for ease of understanding. To
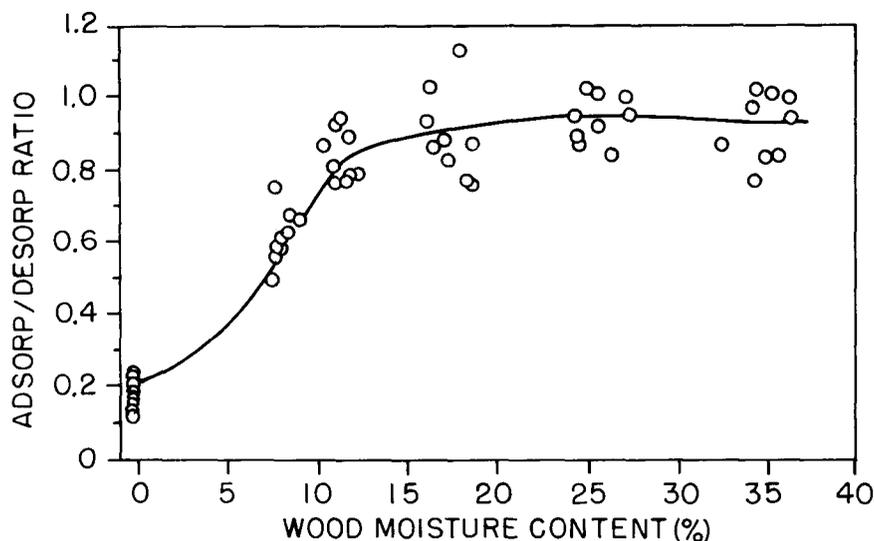
FIG. 2. The relationship between wood moisture content and the equilibrium ratio of sorbed methylisothiocyanate (MIT) in unfumigated (adsorp) and fumigated (desorp) Douglas-fir blocks combined in sealed containers for 17+ days. Each point represents the ratio of the average MIT concentration in five fumigated blocks to that in five unfumigated blocks.

make them dimensionless, they would have to be multiplied by the density of wood substance at the given moisture content. This would create a coefficient that would require knowledge of the volume of wood substance used, which is harder to measure or understand than the equivalent dry weight. Partition coefficients varied greatly between replicates having different proportions of fumigated and nonfumigated wood, possibly as a result of inaccurate measurement of MIT vapor concentrations in the jars. However, the average partition coefficients suggest a trend in which MIT sorption slowly increases as wood moisture content decreases from 35% to 12%, with desorption values slightly higher than adsorption values. Whereas desorption partition coefficients leveled off at about 1400 below 10% MC, adsorption was highest at 12% MC (about 1,100), then rapidly decreased to about 300 at 0% MC.

TABLE 4. *Influence of wood moisture content (MC) on relative concentrations of methylisothiocyanate (MIT) in fumigated (desorp) and unfumigated (adsorp) blocks sealed together in vials and equilibrated at a range of MIT vapor concentrations. Ratios followed by the same letter do not differ statistically (α = 0.05).*

Wood MC (%)	MIT vapor range (μg/ml air)	Adsorp/desorp ratio[a]	
		Ratio	r^2
0–1	1–10	0.21A	0.98
7–10	3–19	0.58B	0.95
11–13	2–17	0.83C	0.96
16–20	1–13[b]	0.92D	0.87
24–28	2–12[b]	0.95D	0.99
31–46	4–28	0.93D	0.96

[a] Calculated as the slope of regression lines (forced through origin) for MIT concentrations in fumigated and unfumigated blocks.
[b] Escaping vapors due to sampling delay until the 13th week of the experiment resulted in lower MIT vapor concentrations.
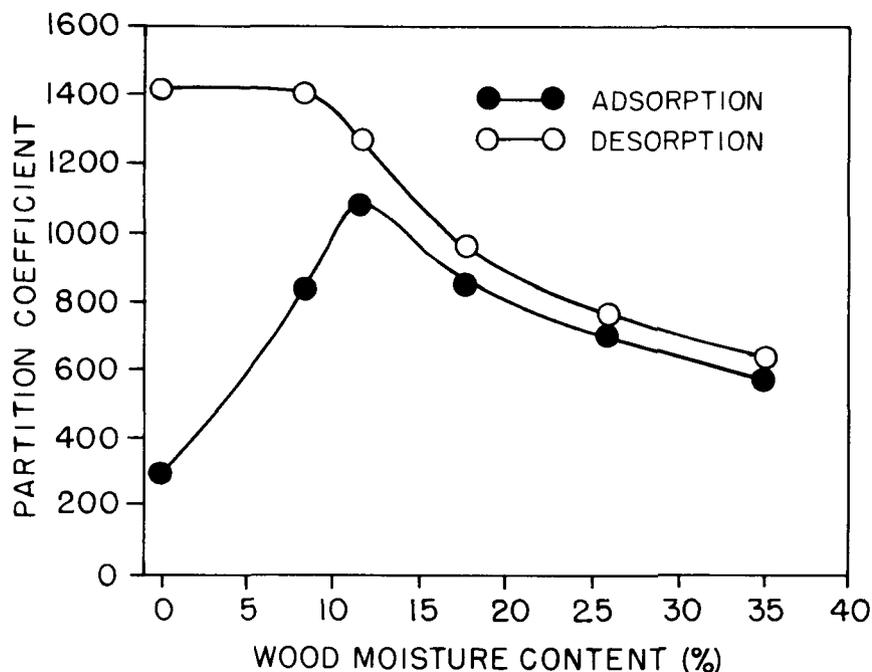
FIG. 3. The relationship between the moisture content of Douglas-fir heartwood blocks and the MIT partition coefficients for blocks adsorbing and desorbing fumigant. Partition coefficients describe the relationship at equilibrium between MIT sorbed per g oven-dry wood and vapor concentrations of MIT per cm³ air.

Sorption of water in wood has been extensively studied (review by Skaar 1972). Wood contains fewer sorption sites for MIT than for water, becoming fully sorbed at about 30 mg (0.41 mmol) MIT (Zahora and Morrell in preparation) versus 300 mg (16.7 mmol) water per g oven-dry wood under vapor-saturation conditions (22 C). It is not known if the sorption sites are common to both water and MIT. Water has an adsorption/desorption ratio of about 0.82 in Douglas-fir at 32 C (Spalt 1958), probably as a result of swelling stresses. As wood adsorbs water, compressive stresses are formed that reduce water sorption at constant vapor concentrations. Swelling of wood by MIT is reported to be about 40% that of water (Rowell 1983), but MIT shows lower adsorp/desorp ratios at low moisture content. The lower ratios and swelling suggest that these chemicals sorb differently.

At 0% MC, the MIT adsorp/desorp ratio was very low (0.2), with equivalent differences in adsorption and desorption partition coefficients. MIT sorption sites may be limited in dry wood, but once the sites are filled, MIT is strongly bound and not easily desorbed. As wood moisture increased from 0 to 12%, the adsorp/ desorp ratio increased as adsorption partition coefficients became larger, while the desorption coefficients remained unchanged. This may result from water swelling the wood and allowing better MIT access to adsorption sites, but the water does not appear to interfere with the capacity of MIT to desorb. As wood moisture content increased further, both adsorption and desorption partition coefficients decreased, while the adsorp/desorp ratios remained constant at about 0.94. The higher concentrations of bound water apparently interfere with MIT sorption,