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Title: Interactions of the Fumigant Methylisothiocyanate with Douglas-fir Wood and their Influence on Fumigant Effectiveness

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Experiments investigated how the fumigant methylisothiocyanate (MIT), Douglas-fir wood at various moisture contents (MC), and the wood decay fungus Poria carbonica Overh., interacted to govern overall fumigant effectiveness.

MIT decomposed in wood to form non-MIT residues at rates of about 0.16%, 0.9%, and 1.6% of the total bound MIT per week, in blocks fumigated at 0%, 12%, and 60% MC, respectively. Compounds formed during fumigation included N,N'-dimethylthiourea and 2,4-dimethyl-1,2,4-thiadiazolidine-3,5-dithione, which were toxic to P. carbonica, and elemental sulfur which showed minimal fungitoxicity. MIT not removed by extensive dry-aeration was rapidly volatilized at fungitoxic concentrations when wood was wetted.

The susceptibility of P. carbonica in Douglas-fir heartwood blocks to MIT vapors and the amount of MIT sorbed by wood were dependent on wood moisture content. At constant, low MIT vapor concentrations (less than 1 ug/cc air), wood at 10% MC bound 5 times more MIT, but required 4 times the exposure period to control P.

carbonica, than similarly treated wood above the fiber saturation point. Adsorption of MIT to wood was not substantially influenced by the amount of wood decay. Increasing wood moisture content from 10% to 30% during fumigation resulted in a rapid volatilization of previously bound MIT and an associated increase in fumigant fungitoxicity.

In wood at 0% MC, the equilibrium MIT adsorption/desorption ratio was low (0.2), but increased to about 0.94 above 18% MC. Partition coefficients (bound/vapor) for MIT adsorption to wood increased as wood moisture increased from 0% to 12% MC, and then decreased with increasing moisture content up to about 30% MC. Steady-state diffusion coefficients for MIT in Douglas-fir heartwood were over 300 times higher for longitudinal than transverse movement. Diffusion coefficients increased with wood MC, although increasing wood moisture contents from 22% to 80% MC reduced longitudinal MIT diffusion about 3 fold. Radial movement of MIT was about 7 times faster in Douglas-fir sapwood than in heartwood. Treatment with waterborne chromated copper arsenate (CCA) 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.

Interactions of the Fumigant Methylisothiocyanate with Douglas-fir Wood and their Influence on Fumigant Effectiveness

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Typed by Andrew Zahora

DEDICATED TO

My Wife

Ingrid McCutcheon Zahora

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INTRODUCTION

Large wood products, such as poles, pilings, and timbers, are commonly used under moist conditions that are conducive to growth of decay fungi. The products are usually pressure-treated with preservatives in accordance with established standards (Anonymous, 1987), providing a shell of protection against infection by decay organisms. Unfortunately, the preservative treated shell in Douglas-fir [Pseudotsuga menziesii (Mirb.) Franco] is often thin, and once bypassed, exposes a heartwood susceptible to rapid biological deterioration. Development of internal decay in Douglas-fir can be a problem whenever physical damage or seasoning checks penetrate the treated shell to expose untreated wood, or when preservative treatment methods do not kill fungi that become established in the living tree or during air seasoning. Once established, these decay organisms reduce the structural integrity of the wood, and often necessitate costly, early replacement.

An effective method for controlling internal decay in poles, piles, and other large wooden structural members involves the application of volatile fungicides or fumigants (Graham, 1973; Helsing et al. 1984; Morrell and Corden, 1986b). These fumigants are widely used by electric utility companies and wood product inspection companies in the United States to control internal decay in wood products (Goodell and Graham, 1983). Methylisothiocyanate (MIT), a volatile fungitoxicant, is an effective wood fumigant in pure form

(Zahora and Corden, 1985b). It is also a major fungitoxic component of Vorlex (20% MIT, 80% chlorinated C3 hydrocarbons), as well as a major volatile decomposition product of Vapam (a 32.7% solution of sodium N-methyldithiocarbamate) and a number of solid fumigants (Morrell and Corden, 1986b). Both Vapam and Vorlex are registered for use in wood by the U.S. Environmental Protection Agency and are effective in field applications (Helsing et al. 1984).

These fumigants are typically applied by drilling downward sloping holes in a spiral pattern around the pole and pouring the fumigant into the hole. The hole is then sealed with a wooden plug that traps the fumigant in the pole, where it diffuses through the wood to control decay fungi. Current treatment practices attempt to distribute the maximum amount of fumigant throughout the 4 quadrants of the pole without significantly influencing the poles strength.

Field and laboratory experiments have shown that MIT is highly toxic to decay fungi, readily moves through wood for up to 2.4 meters above the treatment site, and provides some residual protection for at least 5 years after treatment (Helsing et al. 1984; Zahora and Corden, 1985b). Although this fumigant is effective, specific information on MIT, decay fungus, and wood interactions that determine overall fumigant effectiveness under given environmental conditions are poorly understood. Without this information, treatment procedures cannot be optimized and decisions regarding drilling pattern, formulation, quantity of fumigant used, and retreatment schedules must be based on "rules of thumb" estimated from field experiments, rather than on a thorough understanding of interactions that determine chemical performance.

The major objective of this research was to obtain the basic data required to understand MIT-wood interactions and how they can be expected to govern overall fumigant effectiveness. Specific areas of interest were:

A) The physical interactions of fumigant and wood, including the rate of MIT diffusion through wood in longitudinal and transverse directions, and MIT sorption characteristics influencing overall MIT movement and persistence.

B) The rate of formation and fungitoxicity of the major MIT decomposition products formed in wood.

C) The fungitoxicity of MIT to the major Douglas-fir decay fungus Poria carbonica Overh., especially at low concentrations and over long exposures.

Of specific interest in these studies was the influence of wood moisture content on these various MIT-wood-fungus relationships.

LITERATURE REVIEW

The effectiveness of volatile chemicals for controlling soil pests has been known since the late 1800's, and many studies have been conducted on diffusion rates, influence of environmental factors, and relative toxicities of various soil fumigants (Goring 1962; Munnecke and Van Gundy 1979). Recently, a number of these fumigants have been studied for use in controlling fungi in wood. In 1959, Stabnikov reported that exposures of 30 g chloropicrin per cubic meter for 30 minutes effectively killed Coniophora cerebella in wood flooring. A few years later, Partridge (1961) also evaluated fumigants for control of the oak wilt fungus, Ceratocystis fagacearum, in oak logs for export. Partridge tested a number of volatile fungicides for penetration into small oak blocks and found that methyl bromide and chloropicrin effectively killed the oak wilt fungus. Two years later, Jones (1963) described a practical method of fumigating sawlogs up to 0.6 meter in diameter with methyl bromide, which effectively penetrated and eliminated the oak wilt fungus.

In 1962, Hand and Wetsch of the Bonneville Power Administration began studying the use of volatile fungicides for control of decay fungi and insects in wood utility poles (Belsher, 1968). Ricard et al. (1968) investigated the penetration of methyl bromide into Douglas-fir poles for control of incipient decay, and the use of ammonia and methyl bromide to form fixed ammonium bromide salts inside the wood for residual fungitoxicity. Hand et al. (1970) successfully controlled internal decay in Douglas-fir transmission

poles by pouring the agricultural fumigant Vapam into holes drilled into the poles and then sealing the holes with treated plugs. The effectiveness of fumigant treatments has been further investigated in Douglas-fir poles and piles by Graham (1973) and Helsing et al. (1984), in laminated timbers by Goodell et al. (1980), in waterfront timbers by Highley and Eslyn (1982), and in southern pine poles by Zabel et al. (1982), and has been recently reviewed by Morrell and Corden (1986b).

Chemicals Available

A large number of chemicals have been tested for fumigant activity against fungi in wood (Morrell and Corden 1986b). Methyl bromide was successfully used in a number of the initial wood fumigation studies (Partridge 1961; Jones 1963; and Ricard et al. 1968), but has not been studied to any degree for wood decay control since then. This is probably a result of its low odor, very high volatility, and high mammalian toxicity which make it difficult to safely use in the field, and the identification of safer fumigants that are equally effective and persist longer in wood (Graham, 1973).

The majority of current investigations into the control of wood decay fungi have concentrated on the use of four fumigants, chloropicrin (trichloronitromethane), Vapam , and Vorlex , which are currently registered with the U.S. Environmental Protection Agency for use in wood, and MIT (Graham and Corden 1980; Morrell et al. 1984; Helsing et al. 1984; Morrell and Corden 1986b). These fumigants were originally formulated for agricultural purposes and have characteristics that are less than ideal for application to

wood. All three registered fumigants are liquids which present potential application hazards including leakage from checks during treatment and spills that could contaminate personnel or the environment.

Although MIT is not registered for use in wood, it has been extensively studied for use in wood for a number of reasons. It is an effective fumigant providing excellent decay control (Helsing et al. 1984; Zahora and Corden 1985b; Morrell and Corden 1986b), and provides a concentrated formulation that is a solid and can be encapsulated for safe application (Zahora and Corden 1985a). Perhaps more importantly, it is a major volatile fungitoxicant resulting from a number of other fumigant applications, including two which are registered for wood use. MIT is a component of Vorlex (20%), a major fungitoxic decomposition product from Vapam treatment of wood (Zahora and Corden 1985b), and is also a major decomposition product of the solid chemicals Mylone and Tridipam, which offer potential for controlled release of fumigant in wood to tailor the treatment to the decay encountered (Morrell and Corden 1986a).

Fumigant Effectiveness

Fumigants can effectively move through wood to control decay fungi at sites distant from the site of application (Helsing et al. 1984; Morrell and Corden 1986b), but more information is needed on specific environmental, fumigant, and wood interactions that determine the overall effectiveness of fumigant treatments. Fumigants have been used for many years in soil, and fumigant interactions with and effectiveness in soils have been the subject of

several reviews (Goring 1967; Hamaker and Thompson 1972; Munnecke and Van Gundy 1979). These reviews stress that the effectiveness and rate of fumigant movement in soils are dependent on the soil, the fumigant, and how they interact under specific conditions.

Soil and wood are both porous solid substrates, and many of the basic concepts governing the movement and toxicity of fumigants in soils should also be applicable to wood. The parameters that govern fumigant effectiveness in soil include the soil composition and structure, which will determine the soil's pore structure available for vapor diffusion, its ability to reversibly bind fumigant, and the chemical sites available for covalent fumigant binding and decomposition. Fumigant characteristics, including volatility, sorption properties, and solubility in water will also be important. All of these factors will be influenced by environmental parameters such as temperature and moisture content. Specific information on fumigant interactions in soils that may provide insight into fumigant action in wood will be included in sections on fumigant diffusion and sorption, decomposition, and fungitoxicity below.

A. Diffusion and Sorption: The diffusion and sorption properties of a fumigant in wood will determine its range of effective movement and persistence, with strong sorption increasing the fumigant persistence, but decreasing the rate and range of fumigant diffusion.

In soils, the rate of fumigant diffusion is dependent on the continuity of air spaces and the distribution of the fumigant between the aqueous, vapor, and solid phases of the soil (Goring, 1962). Sorption of fumigants by soils increases with increasing soil

organic matter (Goring 1967) and decreasing soil moisture (Munnecke 1972), which often reduces a fumigants effectiveness by reducing its availability as a toxicant.

In wood fumigation for insect control, the use of fumigants with low wood sorption properties is beneficial since they allow quicker and better fumigant penetration and more rapid removal during subsequent aeration (Harris 1963). The selection of a fumigant with low wood sorption properties is less important for control of decay fungi in large wood structures as they need not be taken out of service for treatment, and the rate of fumigant penetration should be less critical. Furthermore, binding of fumigants to wood can prolong retention and residual fungitoxicity, which could greatly extend the duration that the fumigants would remain effective in the wood.

Numerous studies have investigated various aspects of fumigant sorption and movement through wood. The most general studies have investigated gross fumigant progress and persistence following standard fumigant applications to wood poles and piles (Scheffer and Graham 1975; Helsing et al. 1984; Morrell and Scheffer 1984; Morrell et al. 1986; and Highly 1987). These studies often used biological assays to detect the presence or absence of fumigant vapors over time at different distances from an initial treatment site. Results from these studies suggest that fumigants can move up to 1.2 meter longitudinally through wood and persist for up to 14 years for chloropicrin, and over 5 years for MIT.

More specific studies have used chemical analysis to quantify fumigant sorption and movement in wood. Cooper et al. (1974) found faster movement of chloropicrin through permeable Douglas-fir

heartwood than wood of low permeability, with wood decay facilitating fumigant movement. Goodell et al. (1980) found chloropicrin diffused through southern pine laminated timbers in a wave, moving up to 2 m from the treatment sites by 13 months. Studies of longitudinal movement of MIT vapors through Douglas-fir poles have produced conflicting results. Zahora and Corden (1985a) found MIT moved 0.3 m in 1 to 2 weeks, 0.6 m in 14 to 30 weeks, and 0.6 m above treatment holes after 49 weeks. Ruddick (1984) reported a more rapid movement of MIT, with vapors being detected at 0.6 meters above and below treatment holes in less than 5 weeks. He also reported that the rate of MIT movement through poles of 6 other Canadian conifers was generally better than chloropicrin.

Goodell et al. (1985) found that chloropicrin adsorption in Douglas-fir wafers continued to increase with time up to 15% by weight after 8 months, when the experiment was discontinued. The majority of this chloropicrin desorbed rapidly (within 4 days), but low levels remained even after extensive aeration. MIT sorption in wood has also been studied. Cooper (1986) reported that MIT had a stronger affinity for wood than chloropicrin, and suggested that MIT should therefore persist longer in wood. Zahora and Corden (1985b) found high concentrations of MIT sorbing to wood, which were dependent on wood moisture content, with about 1.5 times as much MIT sorbing to wood at 20% MC than at 40% MC. This MIT rapidly desorbed from wet wood after a short MIT exposure (Zahora and Corden 1985b), but desorbed very slowly from dry wood following a long MIT exposure (Zahora and Morrell, in press).

"Diffusion is the process by which matter is transported from

one part of a system to another as a result of random molecular motions" (Crank 1975). Diffusion in solids such as wood can be divided into two basic types, gaseous diffusion of vapor molecules through the gross void structure of wood, and sorption diffusion of sorbed molecules through the wood substrate itself (Bramhall 1979). In gaseous diffusion, the entire population of molecules is continuously migrating, but in sorption diffusion, only a small number of sorbed molecules will have sufficient energy at any time to break their bonds and migrate to new sorption sites. Fick's laws should be valid to describe both types of diffusion only if the force driving diffusion is expressed as a vapor pressure (or vapor concentration) gradient (Bramhall 1976; 1979).

Fick's first law describes diffusion in one dimension under steady-state conditions, where the rate of mass transfer of the diffusion substrate (flux) through a unit cross-sectional area is directly proportional to the concentration gradient measured normal to the section. This is mathematically expressed as

$$dq/dt = D(C)*(dC/dL)$$

where:
- dq/dt = the flux, or rate of fumigant movement past a point per unit cross sectional area,
- C = concentration,
- L = length of flow path, and
- $D(C)$ = diffusion coefficient as a function of vapor concentration.

The diffusion coefficient can be determined experimentally for fumigants in wood as

$$D(C) = m\ L\ /\ A\ C$$

where:
- $D(C)$ = diffusion coefficient (cm^2/min),
- m = rate of fumigant flow (ug/min),
- L = sample length in flow direction (cm),
- A = sample X-sectional area (cm^2), and

C = fumigant concentration difference over length L (ug/cm^3 air).

Although studies have not directly investigated diffusion coefficients for fumigants in wood, extensive work has been conducted on the diffusion of water through wood in relation to wood drying (Siau 1984). Bound-water diffusion coefficients show a strong dependence on wood moisture content below the fiber-saturation point (FSP) and increase exponentially with wood moisture content. This is believed to be a result of lower bond energies between water molecules and sorption sites at higher moisture contents. Water sorption in wood has also been extensively studied and reviewed by Skarr (1972). Water is believed to bind to wood mainly through hydrogen bonding to the carbohydrate fraction, and shows a hysteresis effect, apparently a result of swelling stresses. Similar information for fumigants in wood is not currently available.

B. Fumigant Decomposition: Fumigant decomposition in wood has received very little attention. Goodell et al. (1985) found that nonvolatile chlorinated residues remained at high concentrations (1.5% by weight) in Douglas-fir wafers exposed to saturated chloropicrin vapors for 8 months. These residues were not completely removed by extensive aeration, solvent extraction, or heating, and analyses suggested that these residues were covalently bound to lignin and phenolic extractives in wood (Goodell et al. 1986).

Vapam decomposition from its nonvolatile salt to produce active volatiles has also been investigated in wood. Vapam fungitoxicity has been attributed to the production of MIT (Morrell and Corden 1986b), which is produced at about 40% theoretical efficiency in wood

within a few hours after treatment (Zahora and Corden 1985a). This low conversion efficiency is apparently due to the acidic nature of wood. Vapam decomposition to nonvolatile residues in wood has also recently been investigated (Morrell 1987), with many of the products originally found in soils (Turner and Corden 1963) also produced in wood. Recent results also support the formation of carbon disulfide and carbonyl sulfide in wood fumigated with Vapam and MIT (Morrell 1987). The rate of MIT decomposition in wood and the products formed are unknown, but the rate can be expected to be slow based on the long-term persistence of vapors in wood after fumigant treatment (Helsing et al. 1984; Morrell 1987).

More extensive investigations have been conducted into the decomposition of fumigants and other chemicals in soils. In soils, toxicant loss can be attributed in large part to microbial activity, although hydrolysis and nucleophilic displacement with organic matter can also be very important (Goring 1967). Decomposition rates increase with increasing temperature, but, depending on the chemical, can either increase or decrease with soil moisture.

Vapam decomposes readily in soils, and many of the decomposition products have been previously identified (Turner and Corden 1963). Vapam breakdown appears to be an oxidative process, and is strongly influenced by soil acidity. At a pH of 9.5, only MIT and elemental sulfur are produced, but increasing quantities of a variety of other products are produced with increasing acidity, with only the release of carbonyl sulfide detected at a pH of 2.3 (Turner and Corden 1963; Goring 1962). The rate of Vapam decomposition increased with temperature and decreasing soil moisture content. Decomposition of

MIT has also been investigated by Smelt and Leistra (1974) and Gerstl et al. (1977). They found MIT decomposition to fit a first-order reaction rate equation, with a half-life in soils ranging from 3 to 10 days at 20°C, depending on soil type. Temperature greatly influenced decomposition, with rates decreasing to about one-half at 13°C and to about one-fourth at 4°C.

C. Fumigant Fungitoxicity: Dosage-response relationships in toxicological studies describe the response of organisms to a series of exposures to toxic chemicals. Whereas the concentration of nonvolatile toxicants remains relatively constant after an initial application, the concentration of vapor phase toxicants can change rapidly with time. Therefore knowledge of the duration of fumigant concentrations is needed to determine the fumigant dosage, which is often expressed as the cumulative product of concentration and time (CT). Theoretically the CT dose required for a specific level of toxicity should remain constant at any given temperature (Harris, 1963). Goring (1967) pointed out that this CT concept is logical only if the external concentration of toxicant is directly proportional to the concentration of toxicant in the organism, and that this internal concentration is inversely proportional to the time required for death. Any restriction on the diffusion of toxicant into the organism, or detoxification by the organism would invalidate these requirements. Deviations from the expected response to a CT product have been observed in soils by Munnecke et al. (1978), who found that 10 soil-borne fungi were uniformly more sensitive to methyl bromide at high concentrations and short exposures, than low concentrations for longer exposures. Goodell

(1981) observed the reverse relationship in wood, where Gloeophyllum saepiarium was more sensitive to chloropicrin at longer exposures than at shorter exposures with the same CT product.

Fumigant solubility in water is important for effective control since most soil microorganisms are surrounded by a water film which may protect them from direct action by the fumigant vapors (Munnecke and Van Gundy 1979). Fumigant toxicity to soil fungi generally increases with increasing soil moisture, which apparently reflects an inherent toxicant resistance by organisms in dry soils (Munnecke 1972). The influence of the moisture content of sclerotia and microsclerotia of soil fungi on the effectiveness of fumigants is dependent on the fumigant used (Munnecke et al. 1982). Chloropicrin fungitoxicity was greatly enhanced in propagules at 150% MC compared to propagules at 45% MC over a range of exposures. Conversely, the effectiveness of methyl bromide was less sensitive to moisture content, with moist propagules being more sensitive during short exposures and saturated propagules being more sensitive during longer exposures.

The fungitoxicity of fumigants to decay fungi in wood have also been investigated in a number of studies. Most of these studies have investigated the minimum lethal dose necessary to kill all the fungus used in the experiment. Cooper et al. (1974) reported CT values of about 20 to 40 ug x hr/ml for chloropicrin to kill Poria placenta in birch dowels. Even the lowest chloropicrin concentration tested (2.6 ug/ml) quickly killed the test fungus (9 hr), suggesting that much lower concentrations should be effective during longer exposures. Goodell (1981) determined minimum lethal chloropicrin CT values to

kill G. saepiarium and an unidentified Poria sp. in pine wafers. CT values remained fairly constant over exposure times ranging from 4 to 24 hr in the Poria sp. (10 to 15 ug x hr/ml), but decreased from about 13 to 1.5 ug x hr/ml for G. saepiarium as the length of exposure was increased from 4 to 24 hr. Cooper (1986) listed a number of minimum lethal CT values for 6 different fumigants, including chloropicrin and MIT, against two wood decay fungi in Douglas-fir heartwood blocks. The fumigant concentrations tested were high (5% to 20% of saturation) and generally gave variable results, with no consistent effect of fumigant concentration on toxic dosage.

Zahora and Corden (1985b) investigated the fungitoxicity of MIT to Poria carbonica in Douglas-fir heartwood by estimating the CT values necessary to kill 90% (CT_{90}) of the viable fungal propagules in small blocks. They found CT_{90} values to be dependent on wood moisture content during fumigation, as well as the length of fumigant exposure, which was tested up to 32 hr.

None of these studies investigated the toxicity of very low fumigant concentrations over long exposures, such as those that apparently remain for years in large wood structures after treatment with fumigants (Helsing et al. 1984; Morrell and Corden 1986b).

CHAPTER I
Decomposition of Methylisothiocyanate in Douglas-fir Heartwood

ABSTRACT

The formation of residues not removed by aeration during fumigation with methylisothiocyanate (MIT) was studied in blocks of Douglas-fir heartwood. Residue formation was influenced by wood moisture content (MC), and suggests that MIT decomposes in wood at about 0.16%, 0.9%, and 1.6% per week of the total bound MIT, in blocks fumigated at 0%, 12%, and 60% MC, respectively. N,N'-dimethylthiourea and 2,4-dimethyl-1,2,4-thiadiazolidine-3,5-dithione, which formed during fumigation, were toxic to the decay fungus Poria carbonica. Elemental sulfur was also formed, but showed minimal fungitoxic activity. Some MIT remained in fumigated wood even after extensive aeration under dry conditions. This MIT rapidly volatilized at fungitoxic concentrations when wood was wetted and may provide residual protection against fungal invasion.

INTRODUCTION

Fumigants are widely used in the United States to control internal decay in utility poles, marine piles, and other large wooden structural members (Goodell and Graham 1983; Graham 1973; Helsing et al. 1984; Morrell et al. 1984). Methylisothiocyanate (MIT), a volatile fungitoxicant, is an effective wood fumigant in pure form (Zahora and Corden 1985a). It also is a major fungitoxic component of Vorlex (20% MIT, 80% chlorinated C_3 hydrocarbons) and a major volatile decomposition product of Vapam (a 33% solution of sodium N-

methyldithiocarbamate) and a number of solid fumigants (Morrell and Corden 1986). Both Vapam and Vorlex are registered for use in wood by the U.S. Environmental Protection Agency and are effective in field applications (Helsing et al. 1984).

Although MIT effectively controls decay fungi, many questions remain about its ultimate fate in wood. Loss of fumigant activity can occur by diffusion out of the wood, decomposition to non-toxic or non-volatile products, or by strong binding to the wood. The rate of MIT loss by diffusion determines the safety of fumigant application in poorly aerated areas; losses from decomposition and strong binding may provide limited decay control if the products are fungitoxic. These losses will determine how long MIT treatments remain effective.

As an isothiocyanate, MIT can react with many chemical groups in wood, including water, alcohols, mercaptans, carboxylic acids, and amines (Assony 1961; Bridgart and Wilson 1971). Although MIT reacts slowly with these groups, this fumigant apparently remains in wood at least 5 years after treatment (Helsing et al. 1984), a period that may allow these chemical interactions to substantially influence fumigant effectiveness. Improved understanding of the ultimate fate of MIT in wood, including decomposition rates and the fungitoxicity of decomposition products, will help determine retreatment schedules and identify disposal hazards associated with fumigated wood. The influence of wood moisture content (MC) on MIT decomposition is particularly important. A wood moisture content above the fiber-saturation point (FSP) is required for active decay, but may also retard fumigant movement and increase MIT fungitoxicity in wood (Zahora and Corden 1985b).

This paper describes studies of the formation and fungitoxicity of MIT residues in Douglas-fir heartwood after fumigation and extensive aeration.

MATERIALS AND METHODS

Initial MIT Fumigation

Small blocks (0.8 cm grain direction x 1.0 cm x 3.0 cm) containing 3 to 6 growth rings per cm were cut from the heartwood of an unseasoned Douglas-fir (Pseudotsuga menziesii [Mirb.] Franco) log 30 cm in diameter. After the blocks were oven-dried (105°C for 24 hrs) and weighed, groups of 90 blocks were adjusted to either 0%, 12%, or 60% MC. Each group was enclosed in a glass jar containing excess solid MIT to produce a saturated MIT atmosphere (about 40 ug MIT/ml air). All jars were capped with a Teflon -lined screw-top and stored at 20°C. Ninety blocks were maintained under air-dry conditions as controls.

During fumigation, water condensed on the sides of jars containing 60% MC blocks. Final moisture contents of the blocks ranged from 36% to 93% (mean=55%, SD=14%). These blocks were all above the FSP of Douglas-fir and are referred to collectively as 60% MC blocks.

Forty-three blocks were removed from each jar after 15 weeks and after 36 weeks. Blocks were aerated in a fume hood for 36 weeks and 15 weeks, respectively, and then aerated further in a conditioning room at 20°C and 50% relative humidity (RH) for the periods specified in the experiments described below. Four blocks were removed from each jar after 30 weeks fumigation to determine the total

concentrations of MIT in the blocks during fumigation. These blocks were extracted for 2 weeks in 10 ml of ethyl acetate.

The extracts were analyzed by gas chromatography (GC) on a Varian 3700 Gas Chromatograph with a flame-photometric detector and a sulfur filter. A glass column (3 m x 4 mm inner diameter) packed with 10% Carbowax 20M on 80/100 Supelcoport solid support was operated under the following conditions: nitrogen flow rate, 75 cc/min; detector temperature 200°C; injector temperature 60°C or 200°C; column temperature, 135°C (isothermal) or 50°C programmed to 150°C. The lower injector and column temperatures were used to analyze extracts that decomposed to volatile sulfur compounds at higher temperatures. Identification and quantification of MIT and carbon disulfide (CS_2) were based on retention times and peak areas of standard solutions in ethyl acetate. Carbonyl sulfide (COS) was produced by reacting ammonium thiocyanate and dilute sulfuric acid; COS concentrations were estimated based on peak areas and COS sulfur content.

Analysis of MIT Fumigation Residues

The term "MIT residues" in this paper will refer to all products resulting from MIT fumigation of wood that are not removed by extended aeration. These residues will include MIT decomposition products deposited in the wood, MIT covalently bound to the wood substance, and MIT or its decomposition products that are sorbed to the wood with sufficient strength to prevent removal during aeration. Volatile MIT residues will refer to any products that are commonly found in the volatile state, although they may be strongly sorbed and

in a nonvolatile state in the wood. MIT residues remaining in blocks after fumigation and aeration were identified and quantified on the basis of block weight gain, total sulfur content, and specific fumigation residues.

A. Block Weight Gain- Six to 8 blocks from each treatment were analyzed for weight increases indicative of MIT residues not removed by aeration. Blocks were aerated in the conditioning room for 37 weeks (50% RH) and then exposed to 100% RH for 3 weeks in closed containers above distilled water. Blocks were weighed and sequentially equilibrated at 93%, 76%, and 55% RH above saturated salt solutions of ammonium phosphate, sodium chloride, and magnesium nitrate, respectively, to determine if MIT residues influenced wood equilibrium moisture contents (EMC) and to release any volatiles from the blocks dependent on high wood moisture content. Final oven-dry weights were determined by drying at 65°C for 3 days, followed by 70°C for 1 day in a closed container with anhydrous calcium sulfate. These weights were used to calculate EMC's and the mass of MIT residues remaining in the wood.

B. Total Sulfur Content- Total sulfur content (all compounds) remaining in blocks after 12 weeks aeration at 50% RH was determined for blocks from each treatment. Blocks were analyzed both before and after solvent extraction to determine whether the MIT residues were loosely deposited or tightly bound (possibly covalently) to the wood.

Eight blocks from each treatment group were ground in a Wiley mill (20 mesh screen); half of the material was extracted sequentially in room-temperature ethyl acetate (3 times in 25 ml, 18 hr each), room-temperature methanol (3 times in 25 ml, 18 hr each),

hot (85°C) water (3 times in 125 ml, 12 hr each), hot (65°C) 80% methanol (3 times in 125 ml, 18 hr each), and finally in acetonitrile (12 hr Soxhlet extraction). These extracts were saved for use in experiments described below. One-gram samples of ground blocks (extracted and nonextracted) were digested in 10 ml of concentrated nitric acid. These digests were analyzed for total sulfur content at the Oregon State University Plant Analysis Laboratory using a Jarrell-Ash ICAP-9000 inductively coupled plasma (ICP) spectrometer. Rates of formation of extractable and nonextractable MIT residues in the wood were estimated from the total sulfur contents.

Scanning electron microscopy (SEM) was used to investigate sulfur distribution within the wood cell-wall layers. A block initially fumigated for 36 weeks at 60% MC was split, evacuated, and carbon-coated for energy-dispersive X-ray scans under the SEM microscope.

C. Specific MIT Fumigation Residues- The extracts from blocks fumigated for 36 weeks were concentrated in a rotary evaporator and analyzed for specific MIT decomposition residues by high performance liquid chromatography (HPLC). Analyses were conducted on a Shimadzu HPLC using an Econosphere C-18 column (15 cm long, 4.6 mm ID, 3 um particle size), a detector wave length of 250 nm, and an elution rate of 1 ml/min. Each extract was analyzed using isocratic mobile phases of 100% methanol; 16% acetonitrile, 36% methanol, and 48% water; and 6.7% acetonitrile, 13.3% methanol, and 80% water. Identifications of decomposition products were based on comparisons of retention times with standards of known MIT decomposition products in the different mobile phases. Standards were made using N,N'-dimethylthiourea

(DMTU), 2,4-dimethyl-1,2,4-thiadiazolidine-3,5-dithione (DTD), and 4-methyl-5-methylimino-1,2,4-dithiazolidine-3-thione (MMTD) from Stauffer Chemical Co., Westport CT (reference numbers N773-A63, N1045-B63, N1044-A63, respectively) and sublimed sulfur.

Fungitoxicity of MIT Residues in Wood

A series of experiments were conducted to determine if residues produced in MIT-fumigated wood imparted any resistance to decay by Poria carbonica Overh., a major brown-rot fungus of Douglas-fir heartwood. These tests compared decay susceptibility of blocks containing all residues combined, specific extractable residues, and all nonextractable residues, with nonfumigated control blocks.

A. All Residues- The combined toxicity of all MIT residues in wood aerated 8 weeks at 50% RH was investigated using 10 blocks from each treatment. Blocks were infiltrated with water, sterilized using a reciprocal Tyndallization (Ricard 1971), adjusted to 60% MC, and inoculated with a water suspension of fragmented P. carbonica mycelium. The blocks were placed on glass rods over wet filter paper in petri dishes to maintain humidity. The plates were sealed with Parafilm and incubated for 10 weeks at 21-25°C to allow fungal colonization. Blocks were then exposed to a harsher decay treatment by transferring them to glass rod supports in petri dishes containing 2% malt agar medium and actively growing cultures of P. carbonica.

B. Specific Extractable Residues- The three decomposition residues identified in extracts of fumigated wood (DMTU, DTD, and sulfur) were tested for their influence on fungal colonization and subsequent decay of Douglas-fir heartwood blocks. Groups of 8 blocks

(0.5 cm grain direction x 2.5 cm x 2.5 cm) were oven-dried and infiltrated under vacuum with solutions of each test chemical to produce a range of concentrations. Water was used as the carrier for DMTU, and ethanol was used for DTD and sulfur. To remove ethanol, blocks were oven-dried at 70°C for 48 hr. All blocks were then infiltrated with sterile water under vacuum, adjusted to 70% MC, and inoculated with suspensions of fragmented P. carbonica mycelium. After 12 weeks, the blocks were observed with a dissecting microscope (30X) for fungal growth, oven-dried, and weighed to determine weight loss.

C. Nonextractable Residues- Eight blocks from each treatment (24 week aeration) were extracted in methanol (36 hr), water (60 hr), and acetonitrile (36 hr) in a Soxhlet apparatus, and then dried (72°C for 48 hr) and weighed to determine initial oven-dry weights. These blocks were infiltrated with water under vacuum, autoclaved (15 min at 15 psi), and Soxhlet-extracted for 24 hr in water to remove any water soluble compounds produced by autoclaving. The blocks were adjusted to 70% MC and inoculated with a suspension of fragmented P. carbonica mycelium.

After 6 weeks, P. carbonica was poorly established on control blocks and not established on treated blocks; Penicillium sp. also contaminated some blocks. To resterilize blocks and subject them to a harsher decay treatment, they were autoclaved (10 min, 15 psi) and placed on glass rods above 2% malt agar in petri dishes inoculated with P. carbonica. After 10 weeks incubation at 21-25°C, fungal mycelium was scraped off the blocks, and the blocks were oven-dried to determine weight loss caused by decay.

Release of Volatiles from Fumigated and Aerated Wood

The fungitoxicity studies suggested that fumigated blocks aerated at 50% RH would release fungitoxic concentrations of volatile chemicals when wetted. This was further supported by GC analyses of headspace vapors above aerated blocks that were kept dry or wetted to 100% MC; COS and MIT were found only after the wood was wetted.

The influence of moisture content on the release of volatile sulfur compounds from MIT-fumigated wood was investigated further using a block from each treatment. After aeration for 27 weeks at 50% RH, blocks were ground in a Wiley mill (20 mesh screen), and immediately sealed in 25-ml jars. After 2 hrs, headspace gases were analyzed by GC to determine if grinding released volatile sulfur compounds. The ground wood was then aerated for 3 days at 50% RH to allow newly released volatiles to dissipate. Subsamples (0.25 g) were then extracted in ethyl acetate (7 days) to determine the initial levels of extractable, volatile sulfur compounds. Wood was either extracted dry, or after addition of an equal weight of water, to determine if water influenced extraction results.

The remaining ground wood (0.6 g) was wetted to about 100% MC and loosely packed into glass columns (5.5 mm ID x 20 cm long). A humidified air flow of 30 ml/hr was passed through the columns, and the air flows were monitored by GC for volatile sulfur compounds for 3 days. The wood was removed from the columns, extracted in ethyl acetate (7 days), and analyzed by GC to quantify the extractable, volatile MIT residues remaining.

RESULTS AND DISCUSSION

Initial MIT Fumigation

Low levels of CS_2 (20 to 60 ug/g wood) and COS (16 to 240 ug/g wood), and high concentrations of MIT (28 to 31 mg/g wood) were detected in blocks during fumigation. The lowest concentrations of COS and CS_2 were found in blocks fumigated at 0% MC, suggesting that water influences MIT decomposition to form these products.

Blocks fumigated at 12% and 60% MC were distinctly yellowed, while those exposed at 0% MC appeared unchanged. The surface of blocks fumigated for 36 weeks at 60% MC contained many clear to yellowish crystals. Crystals were common on the external surfaces of blocks, but were never observed internally by SEM. Most crystals were prismatic, but plate-like crystals were also observed. Melting points ranged between 117 and 122^{o}C. Crystals dissolved in methanol and analyzed by HPLC produced a large peak corresponding to sulfur, along with a number of smaller, unidentified peaks. Energy-dispersive X-ray scans using SEM found high sulfur content in all cell wall layers.

MIT Fumigation Residues

A. Block Weight Gain- Wood moisture content during fumigation greatly influenced the mass of MIT residues not removed by extensive aeration (Table I.1). Block weights did not increase significantly when fumigated at 0% MC, but blocks gained significant weight as wood moisture content and length of exposure to MIT increased. These weight gains represent the deposition of all MIT fumigation residues,

Table I.1. Mass of MIT residues in Douglas-fir heartwood blocks after fumigation in a methylisothiocyanate-saturated atmosphere[a].

Wood MC During Fumigation	Block Weight Gain (mg/g Oven Dry Wood)[b]	
	15-week Exposure	36-week Exposure
0%	0.3 (1.4)	0.0 (1.5)
12%	5.9 (1.4)	12.5 (2.2)
60%	6.4 (1.0)	20.2 (1.2)

[a] After fumigation, blocks were aerated for 37 weeks (50% relative humidity), wetted to the fiber saturation point (3 weeks), and then dried at 70°C.

[b] Values are the means (standard deviations) of 6-8 blocks. Weight changes were corrected for a 0.8 mg average weight loss in controls.

including both extractable and nonextractable compounds.

The slight influence of high wood moisture content during fumigation (36 weeks) on EMC of blocks during desorption (Table I.2) is probably a function of the increased deposition of residues in the wood. A similar pattern of increased moisture content at high RH and decreased moisture content at low RH was also observed in blocks fumigated 15 weeks. All influences on EMC were minor and should not substantially influence water behavior in wood.

B. Total Sulfur Content- MIT fumigation greatly increased the total sulfur content of blocks, indicating that high concentrations of MIT residues remain in wood after extensive aeration (Table I.3). Total sulfur content of blocks increased with increasing wood moisture content and exposure time. Much of this sulfur was extractable, especially in wood at higher moisture contents. Nonextractable sulfur residues were present at low concentrations in wood fumigated at 0% MC. In wood fumigated at 12% and 60% MC, the nonextractable sulfur content was much higher; concentrations depended only on the length of fumigation and were independent of wood moisture content. These nonextractable residues may result from covalent reactions of MIT with alcohol groups in the wood to form carbamothioates (Assony 1961).

C. Specific MIT Fumigation Residues- HPLC of extracts of wood fumigated for 36 weeks found the decomposition products DMTU, DTD, and elemental sulfur, as well as MIT (Table I.4). Concentrations of these decomposition products depended on wood moisture content during fumigation; minimal concentrations were formed in wood fumigated at 0% MC, and much higher concentrations in wood fumigated at 12% and

Table I.2. The influence of wood moisture content (MC) during fumigation on subsequent desorption equilibrium moisture contents (EMC).[a]

Wood MC During Fumigation	Desorption EMC (%) at Relative Humidity			
	100%	93%	76%	55%
Controls	27.4	23.6	16.1	11.6
0%	27.8	23.7	16.1	11.3[b]
12%	28.3	23.8	16.0	11.2[b]
60%	30.6[b]	24.8[b]	16.2	11.3[b]

[a] Blocks of Douglas-fir heartwood at each moisture content were exposed to a methylisothiocyanate-saturated atmosphere for 36 weeks and aerated extensively.

[b] Significantly different from controls at a=0.01 by least significant differences of means.

Table I.3. Average sulfur content of methylisothiocyanate (MIT)-fumigated Douglas-fir heartwood blocks before and after solvent extraction.[a]

Fumigation Conditions		ug Sulfur/g Oven-dry Wood[b]		
Exposure Duration	Wood MC[c]	Total Residues	Nonextract. Residues	Extractable Residues
Control	--	40 (11)	41 (15)	0
15 Week	0%	300 (14)	180 (2)	120
	12%	1240 (20)	810 (43)	430
	60%	2190 (91)	810 (67)	1380
36 Week	0%	800 (80)	520 (42)	280
	12%	4680 (230)	1770 (38)	2920
	60%	7770 (300)	1780 (130)	5990

[a] Sulfur contents were determined by ICP analysis of acid-digested wood, after blocks were exposed to an MIT-saturated atmosphere for 15 or 36 weeks and aerated extensively.

[b] Values are means (standard deviations) of duplicate blocks. Extractable residues calculated as difference between total and nonextractable residues.

[c] MC, moisture content.

Table I.4. Concentrations of methylisothiocyanate (MIT) residues extracted from of Douglas-fir heartwood blocks.[a]

Wood MC During Fumigation	Fumigation Residue (ug/g Oven-dry Wood)[b]				
	DMTU	DTD	MIT	Sulfur	Total as S
Controls	0	0	0	2	2
0%	2	0	67	13	43
12%	1750	102	140	360	1020
60%	6000	840	170	2170	4540

[a] Blocks were fumigated in an MIT-saturated atmosphere for 36 weeks at the moisture content (MC) indicated and extensively aerated (19 weeks) before analysis.

b Values are the average of two replicates that, except for MIT concentrations, were very similar.

60% MC. Although wood at 12% MC is well below the FSP of Douglas-fir, and free water should not be present, substantial amounts of these MIT-water reaction products (Bridgart and Wilson 1971) were formed. Even after 19 weeks aeration, significant amounts of MIT were extracted, suggesting that some MIT was tightly sorbed to wood components and not easily removed by dry aeration. This is also supported by the results of Zahora and Morrell (In press).

Both DMTU and DTD are highly soluble in ethyl acetate and methanol, but only about one-third of each compound was removed by ethyl acetate extraction, with the rest removed by methanol. These decomposition products may have been deposited in the cell walls, so that the greater wood-swelling ability of methanol (Rowell 1983) improved extraction.

Decomposition products identified from the extracts (Table I.4) accounted for only part of the total extractable sulfur removed from these blocks (Table I.3). This was expected, since MIT reacts with a large number of chemical groups, but only a few standards for known MIT decomposition products were available for HPLC peak comparisons.

Rate of MIT Residue Formation

The rate of MIT residue formation in Douglas-fir heartwood blocks was estimated based on the deposition of MIT residues not removed by extensive dry aeration. Blocks were fumigated under saturated MIT vapor conditions which produced constant MIT concentrations throughout the fumigation (about 30 mg MIT/g wood). Based on the observed increase in block sulfur content (excluding extractable MIT) after fumigation for 36 weeks (Table I.3) MIT

residues were formed at about 0.16%, 0.93%, and 1.6% of the total MIT in each block per week in wood at 0%, 12%, and 60% MC, respectively. Nonextractable sulfur residues were produced at a rate of 0.36% of the sorbed MIT per week in wood fumigated at 12% or 60% MC.

Similar rates of MIT residue formation in wood fumigated at 12% and 60% MC (1.1%, and 1.8% of the total MIT in each block per week, respectively) were also calculated based on the observed increase in block weights after fumigation for 36 weeks (Table I.1). Weight increase data was apparently not sensitive enough to detect MIT residues in wood at 0% MC. If MIT decomposition is functionally defined to include all MIT losses due to chemical reactions occurring in blocks (breakdown, covalent binding), then these rates can be used as rough estimates of average MIT decomposition rates in wood under test conditions. The rates represent minimum rates of MIT decomposition as they do not account for formation of volatile MIT decomposition products, such as CS_2 or COS, that would be lost during aeration.

Although MIT apparently decomposes slowly in wood, the long time that fumigants remain in poles (Helsing et al. 1984) may permit deposition of substantial MIT residues. Wood in contact with the ground is generally at 12% MC and above; at these moisture contents, MIT fumigation deposited extractable residues at rates dependent on wood moisture content and nonextractable residues at rates independent of wood moisture content in the blocks. Decomposition may influence fumigant effectiveness by reducing fumigant concentrations in wood, but the residues formed may also provide decay control.

Fungitoxicity of MIT Residues in Wood

A. All Residues- MIT fumigated blocks aerated for 8 weeks (50% RH) and then wetted, sterilized and inoculated with P. carbonica hyphal fragments were resistant to infection and decay, and fungal growth was observed only on control blocks. After further exposure to actively growing cultures of P. carbonica for 6 weeks, only control blocks and blocks fumigated for 15 weeks at 0% MC were colonized. Even though there was no direct wood-agar contact, the P. carbonica colonies were killed in all other plates, except one containing blocks fumigated for 36 weeks at 0% MC. Although these blocks were aerated extensively under dry conditions, volatile fungitoxicants apparently were released when the wood was wetted.

B. Specific Extractable Residues- All three MIT decomposition products tested inhibited the ability of P. carbonica hyphal fragments to colonize and decay blocks (Table I.5). The most fungitoxic, DTD, prevented visible growth on wood at concentrations above 0.24 mg/g oven-dry wood. Although DMTU was less toxic, requiring 4.8 mg/g oven-dry wood to prevent fungal growth, it was also produced in much higher concentrations (Table I.4). On the other hand, sulfur was slightly fungitoxic at all concentrations tested. The inability of the high sulfur concentrations to inhibit fungal growth beyond that observed at lower concentrations is probably a function of the low solubility of sulfur in water.

The decay hazard in this test was relatively mild, as the fungus had to colonize and decay wood without external nutrients. This resulted in low weight losses even in controls, but probably more

Table I.5. Influence of methylisothiocyanate (MIT) decomposition products on the ability of Poria carbonica to decay Douglas-fir heartwood blocks.[a]

MIT Decomposition Product[b]	Concentration mg/g OD Wood	Fungal Growth	Block Weight Loss (%)[c]	Weight Loss[d]
DMTU	4.8	-	0.32 (0.11)	13
	1.1	+	1.19 (0.20)	49
	0.21	++	2.41 (0.41)	99
	0.00	++	2.44 (0.37)	100
DTD	0.93	-	0.30 (0.05)	16
	0.46	-	0.36 (0.06)	20
	0.24	-	0.63 (0.09)	35
	0.12	++	2.03 (0.17)	52
	0.03	++	3.64 (0.61)	94
	0.00	++	3.89 (0.95)	100
Sulfur	1.2	+	1.15 (0.16)	63
	0.62	+	1.02 (0.15)	56
	0.23	+	1.15 (0.17)	63
	0.12	+	1.41 (0.37)	36
	0.00	++	3.89 (0.95)	100

[a] Blocks at 75% MC were inoculated with a suspension of mycelial fragments and spores and incubated for 12 weeks at 21-25°C.

[b] DMTU, N,N'-dimethylthiourea. DTD, 2,4-dimethyl-1,2,4-thiadiazolidine-3,5-dithione. DTD was about 90% DTD and 10% MMTD (4-methyl-5-methylimino-1,2,4-dithiazolidine-3-thione when infiltrated into blocks.

[c] Figures represent means (standard deviations) of 8 blocks.

[d] Weight loss as a percent of weight loss in control blocks.

closely approximates actual decay hazards.

C. Nonextractable Residues- MIT fumigation residues remaining in blocks after solvent extraction can also impart some decay resistance to the wood (Table I.6). Although all blocks were colonized, blocks fumigated at high moisture contents, which resulted in high concentrations of sulfur residues, lost substantially less weight. The decay hazard in this test was severe, as the fungus had an external carbon source (malt agar). Although MIT decomposition residues remaining after aeration may increase the wood nitrogen content, they did not increase rates of wood decay, but instead provided some decay protection.

Release of Volatiles from Fumigated and Aerated Wood

Release of volatile sulfur compounds after blocks were wetted was similar in blocks fumigated for 15 and 36 weeks, but concentrations were lower in the former. Only results from blocks exposed for 36 weeks are described below.

Grinding dry-aerated blocks released volatile sulfur compounds into the air. MIT was released at 0.46, 0.15, and 0.07 ug/g oven-dry wood, and CS_2 was released at 0.23, 0.55, and 0.09 ug/g oven-dry wood from blocks fumigated at 0%, 12%, and 60% MC, respectively, but release of COS was not detected. Even after 3 additional days of dry aeration, substantial amounts of MIT, CS_2, and COS were extracted from the ground wood when water was added to wood before extraction (Table I.7). When dry wood was extracted, COS and CS_2 were not detected, and the concentration of MIT in each block was about one-fourth that found when water was added.

Table I.6. Influence of non-extractable MIT fumigation residues on the ability of Poria carbonica to decay Douglas-fir heartwood blocks.[a]

Fumigation Conditions				
Exposure Duration	Wood MC	Residues (ug S/g wood)[b]	Block Weight Loss (%)[c]	Weight Loss[d]
Control	--	0	23.8 (1.9)	100
15 Week	0%	140	20.3 (1.2)	85
	12%	770	15.2 (3.2)	64
	60%	770	13.2 (2.1)	55
36 Week	0%	480	11.8 (1.2)	50
	12%	1730	8.3 (3.4)	35
	60%	1740	8.4 (4.0)	35

[a] Blocks weighing about 1 g were decayed for 10 weeks above malt agar inoculated with P. carbonica.

[b] Concentration of sulfur in wood from Table I.5 gives a relative estimate of MIT fumigation residues in blocks.

[c] Means (standard deviations) from 8 replicate blocks.

[d] Weight loss as a percent of weight loss in control blocks.

Table I.7. Extractable concentrations of methylisothiocyanate (MIT) residues in dry-aerated wood before and after aeration for 3 days at 100% moisture content (MC).[a]

Wood MC During Initial Fumigation	Volatile Content (ug/g Oven Dry Wood)[b]					
	COS		CS_2		MIT	
	Pre	Post	Pre	Post	Pre	Post
0%	10	7	7	0	190	1
12%	2	4	4	2	140	8
60%	8	4	4	3	210	23

[a] Blocks at each moisture content were exposed to an MIT-saturated atmosphere for 36 weeks and then extensively aerated.

[b] Volatile contents were measured in ground wood that was wetted to 100% MC, and then extracted immediately in ethyl acetate (Pre), or aerated for 3 days at 100% MC before extraction (Post).

The release of MIT and CS_2 after grinding suggests physical sorption of these compounds to the wood. The higher concentrations extracted from wetted ground wood may result from the water swelling the wood structure to enhance solvent accessibility, but the presence of COS only in wetted wood suggests that chemical reactions involving MIT decomposition products and water may also produce these volatile compounds.

The rate of MIT release from ground blocks wetted to 100% MC was influenced by wood moisture content during fumigation (Fig. I.1). High rates of MIT release were initially observed in wood fumigated at 0% MC, but these rates decreased rapidly and MIT concentrations fell below the detector sensitivity (0.05 ug MIT/hr/g wood) after 2 days. The rates of MIT release were initially slower in wood fumigated at higher moisture contents, but these rates were maintained longer. COS and CS_2 were also initially released from wetted wood, but rapidly declined below detectable concentrations and are not discussed further here.

Concentrations of extractable MIT were greatly reduced after 3 days of wet aeration, especially in wood initially fumigated at 0% MC (Table I.7). Dry aeration (50% RH) for 33 weeks did not remove all volatile MIT residues from the blocks. Because wet wood is required for active fungal growth and decay, this moisture content dependent release offers a potentially beneficial reservoir for fumigant control of decay fungi.

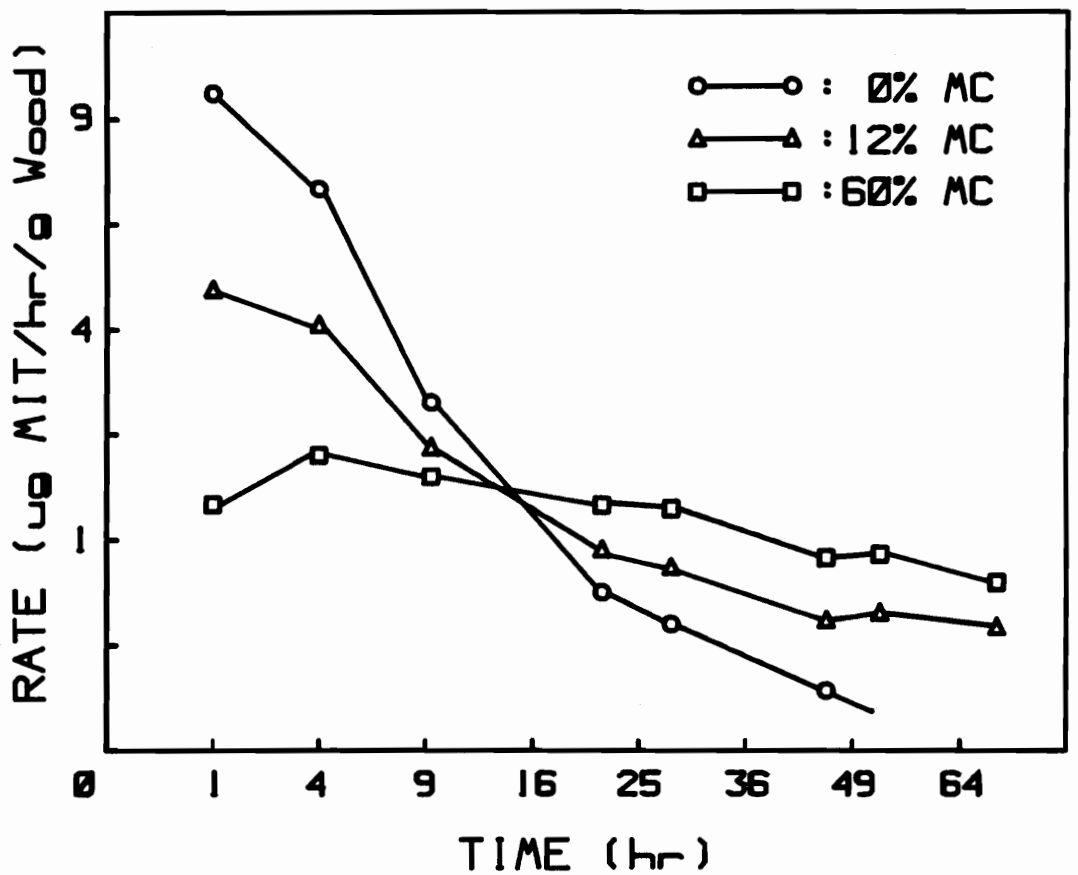

Figure I.1. Rate of methylisothiocyanate (MIT) release over time from ground blocks of Douglas-fir heartwood moistened to 100% moisture content (MC) and aerated at a flow rate of 30 ml/hr. Blocks at 0%, 12%, and 60% MC were fumigated for 36 weeks and then aerated extensively (34 weeks at 50% relative humidity).

CONCLUSIONS

Chemical reactions of MIT in Douglas-fir heartwood to form residues not removed during aeration may be significant in determining the overall effectiveness of this fumigant. MIT residue formation will reduce internal fumigant concentrations, but may also provide residual protection against recolonization by decay fungi.

Formation of solvent-extractable residues increases with increasing wood moisture content during fumigation. Residues include DMTU, DTD, and sulfur, as well as MIT not removed by aeration. DTD and DMTU are both fungitoxic to Poria carbonica at concentrations found in fumigated blocks. DMTU and DTD offer the potential for long term residual protection in fumigated products, depending on the concentrations deposited in wood by MIT decomposition. These products are formed at the highest concentrations in wet wood, where their ability to prevent re-establishment of decay is most needed.

Formation of nonextractable MIT residues is independent of wood moisture contents above 12%, and offers limited residual protection by reducing the rate of weight loss caused by decay. Wetting fumigated wood aerated under dry conditions releases fungitoxic concentrations of MIT at rates dependent on initial fumigation conditions. This effect offers a residual fumigant pool that is not readily volatilized until wet wood conditions conducive to decay are present.

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CHAPTER II
Diffusion and Adsorption of the Fumigant Methylisothiocyanate in Douglas-fir Wood

ABSTRACT

The influence of moisture content (MC) and conventional preservative treatment on methylisothiocyanate (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 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% MC. 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 over 300 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 contents from 22% to 80% MC reduced longitudinal MIT diffusion about 3 fold, but did not greatly influence tangential MIT diffusion. Radial movement of MIT was about 7 times faster in Douglas-fir sapwood than in heartwood. Preservative treatment with waterborne chromated copper arsenate (CCA) 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.

INTRODUCTION

Fumigants can effectively control internal decay in utility poles and other large wooden structural members (Helsing et al., 1984). As a result, these chemicals are seeing widespread use in the United States (Goodell and Graham, 1983). Methylisothiocyanate (MIT), an effective wood fumigant, is a major fungitoxic component of Vorlex (20% MIT, 80% chlorinated C_3 hydrocarbons) and a major volatile decomposition product of Vapam (sodium N-methyldithiocarbamate), as well as a number of solid fumigants (Morrell and Corden, 1986).

Although field results suggest that fumigants will effectively control decay fungi in pressure treated utility poles for up to 14 years (Helsing et al., 1984), the specific MIT/wood interactions which determine the effectiveness of this fumigant treatment are poorly understood. Current fumigant treatment practices, including the drilling pattern, formulation, quantity of fumigant used, and retreatment schedules, are based more on "rules of thumb" estimated from field experiments than on an understanding of how the fumigant, wood, and fungi interact to control internal decay. A basic understanding of MIT sorption and diffusion properties in wood is necessary to accurately estimate retreatment schedules and to determine the rate and extent of effective fumigant movement.

Fumigant diffusion rates will also help define the rate of fumigant loss from wood. Information on MIT interactions with and movement through wood are required before fumigant treatment practices can be improved or tailored to specific treatment

conditions.

This paper describes experiments investigating the sorption and diffusion properties of MIT in Douglas-fir heartwood, and examines how wood moisture content influences these properties.

MATERIALS AND METHODS

All heartwood blocks used in these studies were cut from an unseasoned coastal Douglas-fir (Pseudotsuga menziesii [Mirb.] Franco) log 30 cm in diameter, and contained 3-5 growth rings/cm. Blocks were cut from clear wood from the outer heartwood where the curve of the growth rings was smallest. Sapwood blocks were cut from an unseasoned old growth Douglas-fir slab and contained 6-7 growth rings/cm. The specific gravity (oven-dry weight and green volume basis) of 10 heartwood wafers averaged 0.442 (+/- 0.011) while that of 5 sapwood wafers averaged 0.439 (+/- 0.006).

MIT Binding to Douglas-fir Heartwood

The strength of MIT sorption to Douglas-fir heartwood blocks was evaluated at different wood moisture contents (MC) by comparing equilibrium MIT sorption concentrations from both the adsorption and desorption directions.

Douglas-fir heartwood blocks were cut to volumes of 0.5 cm^3 (0.5 x 2.0 x 0.5 cm), 1.0 cm^3 (0.5 x 2.0 x 1.0 cm), 1.5 cm^3 (1.5 x 2.0 x 0.5 cm), and 3.0 cm^3 (1.5 x 2.0 x 1.0 cm). The blocks were then oven dried, weighed, and adjusted to either 0, 8, 12, 18, 27, or 40% MC. Blocks were adjusted to 40% MC by infiltrating with water under vacuum and air drying to their desired weight. This 40% MC

represents an average moisture content for the blocks, which probably has a moisture gradient through the block. All other blocks were equilibrated in humidity chambers (450 cc wide-mouth glass jars) containing about 55 ml of salt solutions (Table II.1). The sides of the jars were lined with filter paper to increase solution surface area and blocks were held in nylon screen baskets that were raised away from the bottom and sides of the jar. Blocks were stored at 22°C for 9 to 10 days and then weighed to determine wood moisture content. One-half of the blocks at each moisture content were removed and exposed to a saturated MIT atmosphere (excess solid MIT, about 35 ug MIT/ml air) in small jars for 2 weeks before use.

A preliminary experiment was conducted to determine the influence of equilibrium time on MIT sorption values. Groups of 5 fumigated and 5 nonfumigated blocks (1.0 cm^3) at 0% MC were placed into each of 5 small glass vials and stored at 22°C. Vials were sealed with Teflon -lined screw-caps and Parafilm . Periodically, the concentration of MIT in the air and in each block in a vial was 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 then analyzed for MIT content by gas chromatography (Zahora and Morrell, in press).

In the main experiment, groups of 5 fumigated and nonfumigated blocks of different relative volumes were combined as outlined in Table II.2 for each wood moisture content. The relative amounts of

Table II.1. Salts used to equilibrate Douglas-fir heartwood blocks to specific moisture contents for sorption and diffusion studies.

Salt	Condition	Relative Humidity (%)[a]	(%) Wood Moisture Content[b]
$CaSO_4$	Anhydrous	0	0 - 1
$Mg(NO_3)_2$	Saturated Solution	55	7 - 9
NaCl	" "	76	11 -13
$NH_4H_2PO_4$	" "	93	17 -19
None	Distilled Water	100	25 -28

[a] From Winston and Bates (1960).

[b] Final moisture content ranges observed in adsorption.

Table II.2. Pair combinations of wood block sizes used to produce a range of final methylisothiocyanate (MIT) vapor concentrations for adsorption/desorption equilibrium studies.

	Relative Volumes of Blocks (cm^3)								
Desorption[a]	0.5	1.0	0.5	1.0	1.5	1.5	1.0	3.0	3.0
Adsorption[a]	3.0	3.0	1.0	1.5	1.5	1.0	0.5	1.0	0.5
Percent MIT[b]	14	25	33	40	50	60	67	75	86

[a] Desorption blocks initially fumigated with MIT for 2 weeks were combined with nonfumigated adsorption blocks in closed containers to equilibrate.

[b] The percentage of total wood in each vial that was initially exposed to MIT vapors.

fumigated and nonfumigated wood combined in each jar were varied to produce a range of equilibrium MIT vapor concentrations, with blocks either adsorbing (nonfumigated blocks) or desorbing (fumigated blocks) to the desired vapor concentration. The paired block groups were sealed in small glass vials and equilibrated for at least 17 days. The chambers were then sampled for MIT vapor content and MIT sorption concentration in each block as described above.

MIT Diffusion Through Douglas-fir Wood

Steady-state diffusion coefficients for movement of MIT through Douglas-fir wood in longitudinal, radial, and tangential directions were calculated in this study. In addition, the influences of wood moisture content and preservative treatment on these diffusion coefficients were evaluated. The diffusion apparatus was designed to directly measure fumigant loss through a given surface area using a modified diffusion cup (Siau, 1984) apparatus (Fig II.1). In this apparatus, the wood section to be tested was sandwiched between two stainless steel cups. The upper cup contained solid MIT to produce a saturated MIT vapor atmosphere (about 35 ug MIT/ml air), and the bottom cup contained air inlet and outlet ports, through which a steady air flow could pass. The cups measured 4.9 cm in diameter (air volume about 90 cc) and a fan attached to a magnetic stir bar was placed in the bottom cup to thoroughly mix the air. The rate of MIT flow through the blocks was calculated from measurements (at equilibrium) of air flow and MIT vapor concentrations in the air exiting the bottom cups.

Douglas-fir heartwood wafers were cut to thicknesses of 1.5 cm

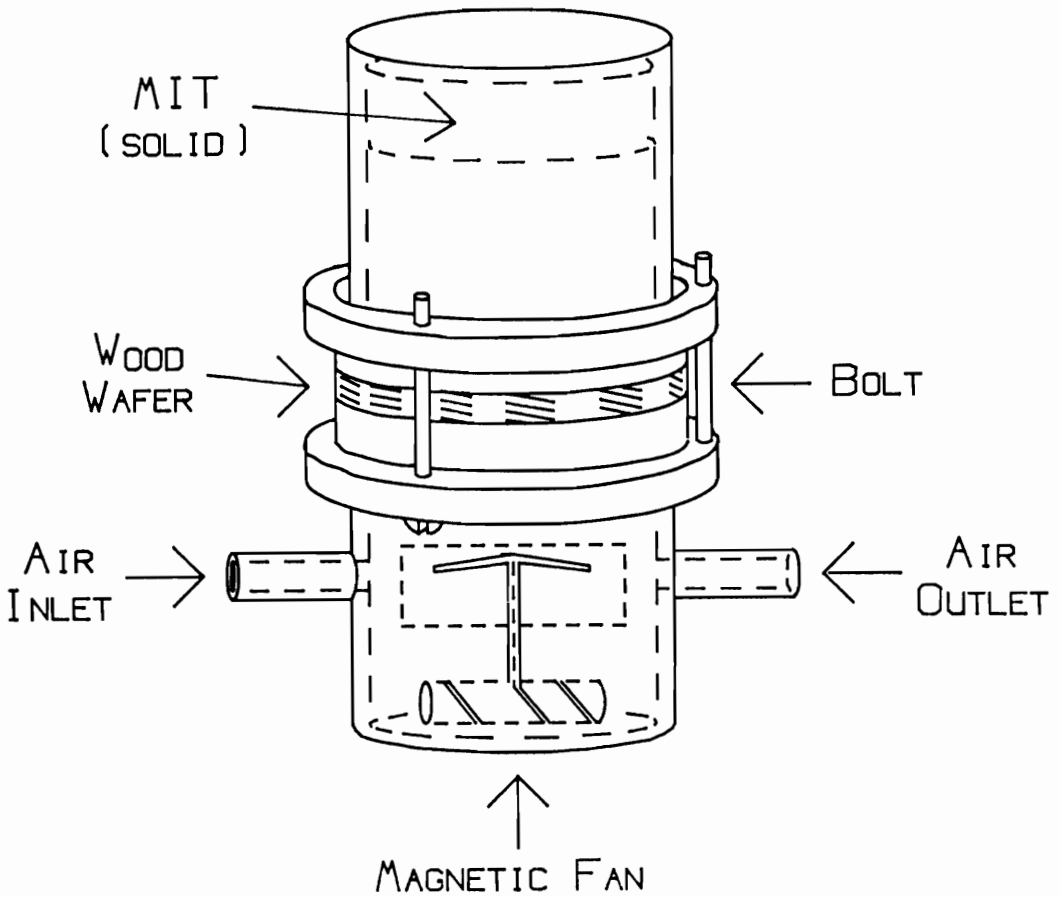

Figure II.1. Modified diffusion cup apparatus used to study the diffusion of methylisothiocyanate (MIT) through sections of Douglas-fir wood. See text for description.

for longitudinal, and 0.5 cm for radial and tangential diffusion experiments. The end grain surfaces of longitudinal diffusion wafers were surfaced with a microtome knife, while the radial and tangential wafers were sanded smooth in the grain direction with 180 grit sand paper. Groups of 5 wafers were initially conditioned to one of 4 moisture contents (about 14%, 22%, 40%, or 80% MC) for each diffusion direction. Wafers were conditioned to 14% or 22% MC by placing over saturated solutions of NaCl or $NH_4H_2PO_4$, respectively, while the 40% or 80% MC blocks were infiltrated with water under vacuum, then aerated to the desired moisture content. These higher moisture contents again represent the average wood moisture content, which may vary substantially within the wafers. The edge of each diffusion wafer was then sealed with an acrylic latex coating, and wafers were "equilibrated" for at least 1 week before use in diffusion experiments.

Fifteen Douglas-fir sapwood wafers (0.5 cm thick) were used to test the influence of preservative treatments on radial MIT diffusion rates. Five wafers each were treated to refusal with P-9 oil, with a 2.5% waterborne chromated copper arsenate (CCA) solution, or were left untreated. These wafers were equilibrated at 76% RH (over a saturated NaCl solution) for at least 1 month prior to use.

The diffusion surface area was 18.9 cm^2 for radial and tangential diffusion experiments, but was restricted to 12.2 cm^2 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 where the metal cup (or washers) contacted the sections to provide a good seal when 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 wood 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 humidified by bubbling 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^{o} (+/- 0.5^{o}C) in a temperature controlled chamber. MIT vapor concentrations were determined by withdrawing a selected volume of vapor into an 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 vapor sampled to ethyl acetate was varied depending on the concentration of MIT in the air flow.

Steady-state diffusion coefficients were calculated based on Fick's first law, using the equation

$$D(C) = m\ L\ /\ A\ C$$

where: $D(C)$ = Diffusion Coefficient (cm^2/min)
m = Rate of MIT flow (ug/min)
L = Sample length in flow direction (cm)
A = Sample X-sectional area (cm^2)
C = MIT concentration difference over length L (ug/cm^3 air).

Each set of diffusion cups was sampled until the MIT vapor concentrations exiting the apparatus remained steady over a 24 hr period at one air flow rate, then the air flow rate was changed. The initial air flow rates through the bottom diffusion cups were high, about 60 or 30 ml/min for longitudinal and transverse diffusion experiments, respectively. Flow rates were then decreased to about

1/4th this rate, then increased back to their previous levels. This allowed the diffusion coefficients to be checked in the same blocks 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 Binding in Douglas-fir Heartwood

Fumigated (desorption) and nonfumigated (adsorption) blocks at 0% MC placed in the same container stabilized at a constant ratio of sorbed MIT (adsorp/desorp ratio) after 3 weeks of equilibration (Table II.3). As the equilibration period was increased, MIT sorption and vapor concentrations in the vials slowly decreased. This rate of decrease was substantially faster than the 0.16% that can be attributed to MIT decomposition (Chapter I) and may reflect the escape of MIT vapors through the Teflon -lined screwcaps 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 did not appear to influence the ratio of sorbed MIT in these two types of blocks, which remained constant at about 0.2. The relationship between MIT concentrations when fumigated and nonfumigated blocks were combined in this experiment will be referred to as the adsorp/desorp ratio.

The adsorp/desorp ratios in the Douglas-fir blocks (Fig. II.2) were calculated over a range of MIT concentrations at each moisture content, depending on the relative volumes of fumigated and

Table II.3. Influence of equilibration time on methylisothiocyanate (MIT) "adsorption/desorption" ratios in Douglas-fir heartwood blocks at 0% moisture content.[a]

Time (Weeks)	ug MIT/ ml air	mg MIT/g wood[b] Adsorption	Desorption	Adsorp/Desorp 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 MIT vapor saturated and nonfumigated wood were combined in vials for each time period.

[b] Sorption data represents the average of 5 replicate blocks. The coefficients of variation for the means ranged from 3 to 13%.

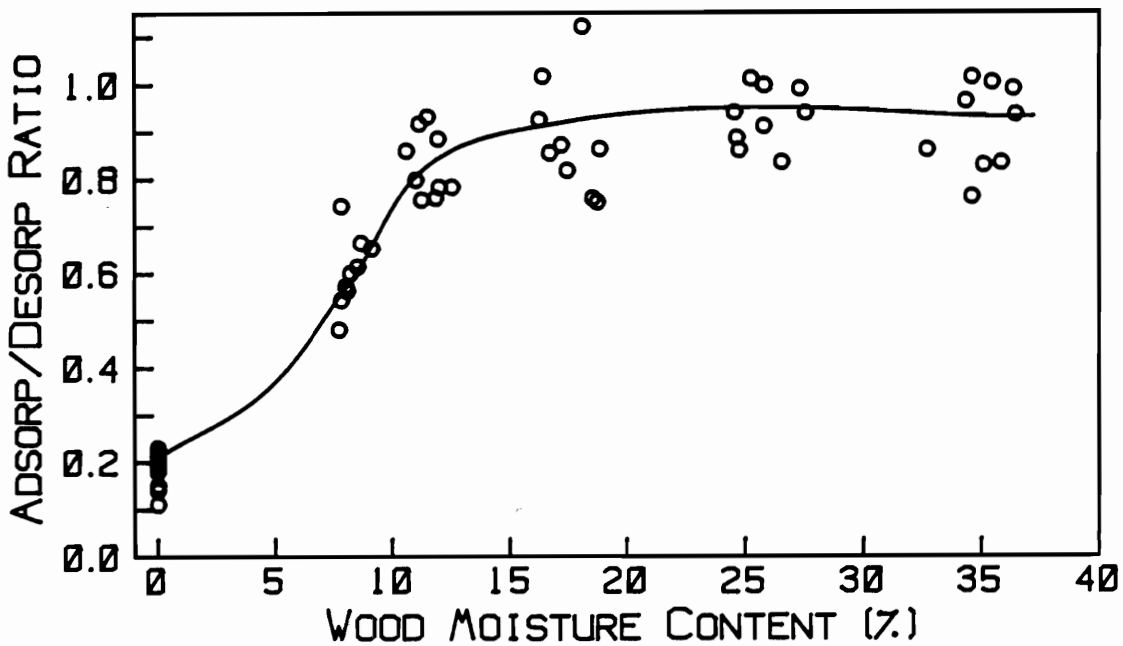

Figure II.2. The relationship between wood moisture content and the ratio of sorbed methylisothiocyanate when fumigated (desorp) and nonfumigated (adsorp) Douglas-fir blocks were combined in small sealed containers for over 17 days. Each point represents the ratio of the average MIT concentrations in 5 desorp and 5 adsorp blocks. Different volumes of fumigated and nonfumigated wood were combined to determine the ratio over a range of MIT vapor and sorption concentrations.

nonfumigated wood combined in the replicate vials. Although the adsorp/desorp ratios varied between replicates for each wood moisture content, strong correlations were found when MIT adsorption and desorption concentrations were regressed over the range of concentrations tested (Table II.4). These regressions were forced through the origin to minimize the influence of extreme adsorption values on the calculated slope, which represents the adsorp/desorp ratio at that moisture content. Adsorp/desorp ratios increased rapidly from about 0.2 in 0% MC wood to over 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 concentrations (vapor and sorption) often did not follow the expected pattern based on the relative amounts of fumigated and nonfumigated wood initially combined in each vial, suggesting that some vials were more susceptible to fumigant loss than others. Although these losses probably prevented a true equilibrium from being established, they did not appear to influence the adsorp/desorp ratios, which should reflect the relative strength of MIT sorption, as well as the ease of desorption and movement through wood at different moisture contents. Poor correlations were found between adsorp/desorp ratios and MIT vapor or wood sorption concentrations (r^2 = 0.001 to 0.53) within each wood moisture content grouping. This suggests that these ratios are independent of MIT concentration over the range of concentrations tested (Table II.4).

MIT partition coefficients describing the relative proportion of MIT sorbed to wood vs that in the air ([ug MIT/g wood]/[ug MIT/cc

Table II.4. Influence of wood moisture content (MC) on the relative concentrations of methylisothiocyanate (MIT) in fumigated (desorp) and nonfumigated (adsorp) blocks sealed in vials and equilibrated at a range of MIT vapor concentrations.

Wood MC (%)	Vapor range ug MIT/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 slope of regression lines for MIT adsorp vs desorp concentrations (forced through origin). Values followed by the same letter do not statistically differ (a=0.05).

[b] Sampling was delayed until 13 weeks after the start of the experiment and escaping vapors resulted in lower MIT vapor concentration ranges.

air]) were also influenced by wood moisture content (Fig. II.3). Partition coefficients varied greatly between replicates using different proportions of fumigated and nonfumigated wood, possibly as a result of poor accuracy in measuring MIT vapor concentrations in the jars. However, average partition coefficients suggest a trend where MIT sorption slowly increases as wood moisture content decreases from 35% to 12% MC, 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 1100), then rapidly decreased to about 300 at 0% MC.

For comparative purposes, sorption of MIT in wood will be briefly compared to that for water, which has been extensively studied (reviewed by Skaar, 1972). Wood contains less available sorption sites for MIT than for water, becoming fully sorbed at about 30 mg (0.41 mmol) MIT (Chapter I)) versus 300 mg (16.7 mmol) water per g oven dry wood under vapor saturation conditions (22^{o}C). Water has an adsorption/desorption ratio of about 0.82 in Douglas-fir at a given RH (Spalt, 1958), which is believed to result from swelling stresses. As wood adsorbs water, compressive stresses are formed which reduce water sorption at constant vapor concentrations. MIT is reported to swell wood about 40 percent that of water (Rowell, 1983), but shows lower adsorp/desorp ratios at low moisture content. These lower ratios with less 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. This suggests that MIT sorption sites are limited in

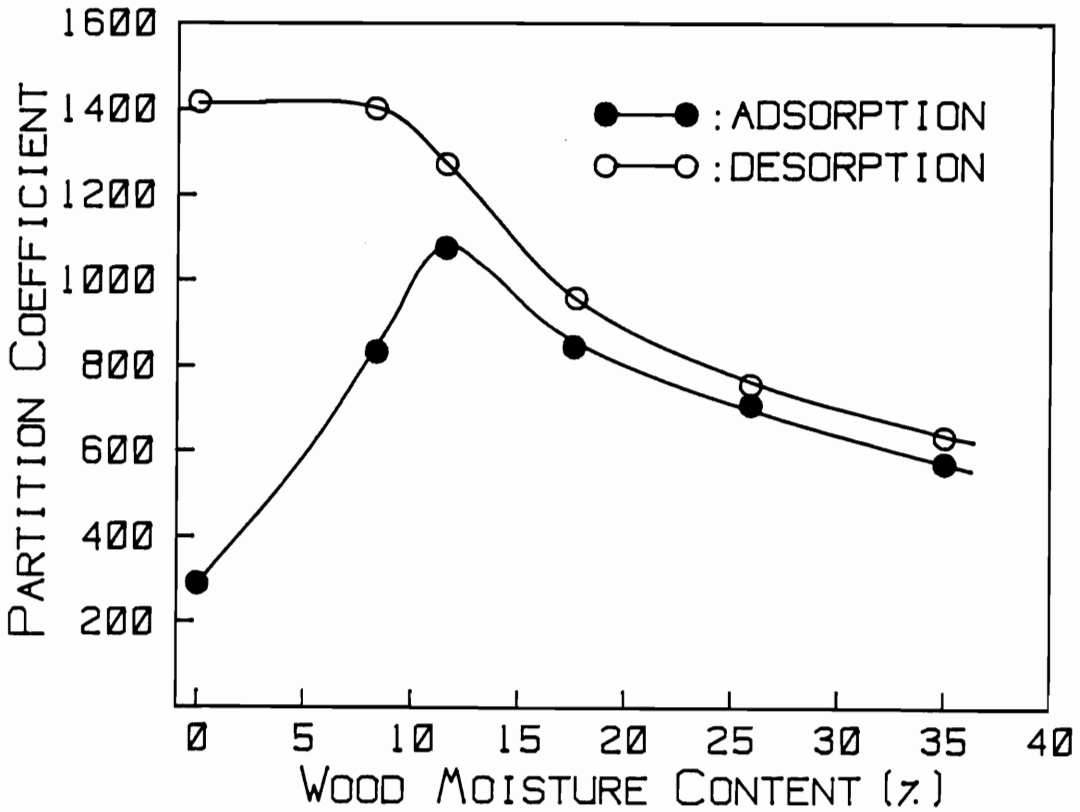

Figure II.3. Relationship between the moisture content of Douglas-fir heartwood blocks and MIT partition coefficients for wood adsorbing and desorbing fumigant. Partition coefficients describe the relationship between sorbed MIT (per g oven dry wood) and vapor concentrations of MIT (per cc air) at equilibrium.

dry wood, but once the sites are filled, MIT is strongly bound and not easily desorbed. As wood moisture contents increased to about 12% MC, adsorp/desorp ratios increased primarily through an increase in adsorption partition coefficients. This increase may result as water swells the wood and increases MIT access to adsorption sites, but does not appear to interfere with the ability of MIT to desorb. As wood moisture content is 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, allowing less MIT to bind at a given MIT vapor concentration during both adsorption and desorption.

MIT Diffusion Through Douglas-fir Wood:

Heartwood: Diffusion coefficients for steady-state movement of MIT through Douglas-fir heartwood were strongly influenced by wood moisture content, and were over 300 times higher in the longitudinal than transverse directions (Table II.5). These diffusion coefficients include the combined effects of both bound and vapor diffusion components. In calculating these coefficients, it was assumed that the air was saturated with MIT (35 ug MIT/cc air) at the surface of the wood in the upper diffusion cup. This figure represents the average saturated MIT vapor concentration measured under test conditions, but does not account for any concentration gradients formed between the solid MIT and the upper surface of the wood sample. This slight inaccuracy was compensated for by measuring diffusion coefficients over large concentration gradients (>10 ug

Table II.5. Diffusion coefficients describing the rate of methyl-isothiocyanate movement through Douglas-fir heartwood wafers.

Wood Moisture Content (%)	Diffusion Coefficients by flow direction[a]		
	Longitudinal	Radial	Tangential
13 -16	1.4 (0.1)	0.0019 (0.0004)	0.00047[b] (0.00021)
21 -24	2.3 (0.2)	N.A.	0.0038 (0.0003)
35 -47	1.7 (0.2)	0.0062 (0.0007)	0.0043 (0.0002)
73 -91	0.84 (0.10)	N.A.	0.0040 (0.0006)

[a] Diffusion coefficients (cm^2/min) were calculated using ug MIT per cc air as the concentration gradient. Figures represent the means and standard deviations (in parenthesis) of combined results from 5 replicate blocks sequentially equilibrated at a series of flow rates in the diffusion apparatus.

[b] Diffusion coefficients in these blocks were still slowly increasing after 14 days in the apparatus, when the experiment was discontinued.

MIT/cc air), where a small inaccuracy in the MIT concentration would not substantially influence the diffusion coefficient.

Longitudinal diffusion coefficients in wood at 15% MC calculated over MIT vapor gradients ranging from 32 ug MIT/cc air (flow of 122 cc/min at 3.1 ug MIT/cc air) down to 11 ug MIT/cc air (flow of 5.3 cc/min at 24 ug MIT/cc air) did not vary significantly. This suggests that longitudinal diffusion coefficients are independent of MIT concentration, at least over this range of vapor gradients. Radial and tangential diffusion coefficients were calculated using air flow rates from 32 to 7 cc/min, at 0.01 to 1.0 ug MIT/cc air, depending on wood moisture content. These flows did not alter the MIT vapor gradients (34 to 35 ug MIT/cc air) sufficiently to detect an influence of MIT concentration on diffusion coefficients, but did allow verification of diffusion coefficients under different flow conditions.

Bound water diffusion coefficients increase exponentially with wood moisture content, probably as a result of lower bond energies between water molecules and sorption sites at higher moisture contents (Siau, 1984). A similar relationship between MIT concentration and bound MIT diffusion may be obscured by the large MIT vapor diffusion component in longitudinal diffusion.

Wood moisture content influenced diffusion coefficients differently in the longitudinal and transverse directions (Table II.5), probably as a result of the relative importance of the vapor and bound components of diffusion. Douglas-fir heartwood tracheids average about 140 times longer than their lumen diameters (Krahmer, 1961), providing long channels for uninterrupted vapor diffusion.

The vapor diffusion component should therefore be very important in determining overall longitudinal MIT diffusion through Douglas-fir, with the bound component involved only in the relatively few cell wall crossings over a given distance. In the transverse directions, the bound vapor diffusion component should become more important since large numbers of cell walls must be crossed, with only short vapor spaces in between.

Longitudinal MIT diffusion coefficients increased by about 65% as wood moisture increased from 15 to 22% MC. This moisture content increase below the fiber-saturation point (FSP) should not interfere with MIT vapor diffusion through the cell lumens. The increased bound water may improve bound MIT diffusion by interfering with MIT sorption sites to facilitate MIT desorption and subsequent movement (Fig. II.3). MIT diffusion coefficients decreased substantially as wood moisture content was increased above the FSP. These moisture content changes should not influence bound MIT diffusion, but probably reflect free water in the tracheid lumens restricting MIT vapor movement.

Tangential MIT diffusion coefficients increased almost 8 fold as wood moisture content increased from 15 to 22% MC, reflecting a high dependence on bound diffusion, which could be influenced by increased sorbed water. Wood moisture above the FSP did not substantially reduce tangential MIT diffusion coefficients. This is not unexpected, as increased free water in the cell lumens should not restrict bound diffusion, which should be more important than vapor diffusion in determining overall transverse MIT diffusion.

MIT diffusion coefficients were larger radially than

tangentially, and showed a smaller relative increase as wood moisture increased from 15 to 40% MC. The larger radial values could result from ray cells allowing greater vapor diffusion, thus increasing overall MIT diffusion, and reducing the relative importance of wood moisture influences on bound MIT diffusion. While tangential MIT diffusion coefficients stabilized after 4 days in blocks at 22% MC, they were still slowly increasing after 14 days in blocks at 15% MC, suggesting bound MIT diffusion may be very slow to reach equilibrium under dry conditions. This effect was not observed in radial and longitudinal diffusion, probably because bound diffusion was less important in determining these overall MIT diffusion coefficients.

Sapwood: Diffusion coefficients for radial movement of MIT were about 7 times higher in Douglas-fir sapwood (Table II.6) than in heartwood (Table II.5). This increased diffusion probably reflects lower levels of pit aspiration or encrustation in the sapwood.

Treatment of Douglas-fir sapwood to refusal with P-9 Type A oil retarded MIT diffusion. Whereas MIT diffusion coefficients equilibrated at 0.014 cm^2/min in untreated sapwood after 3 days in the diffusion apparatus, diffusion coefficients in oil-impregnated sapwood were only about 0.007 cm^2/min after 20 days, and were still slowly increasing (about 6% per day). MIT was very soluble in the P-9 Type A oil, with wafers impregnated with about 530 mg oil/g wood containing over 100 mg MIT/g wood more than in wafers without oil. Oil-borne preservative treatments apparently retard MIT movement by both reducing the equilibrium diffusion coefficient and slowing the establishment of equilibrium conditions.

Treatment of sapwood with CCA did not appear to influence MIT

Table II.6. Influence of preservative treatments on radial diffusion and sorption of methylisothiocyanate (MIT) in Douglas-fir sapwood wafers equilibrated at 76% RH (about 15% MC).

Preservative Treatment Type	(kg/m^3)	Sorption[a] (mg MIT/g wood)	Diffusion[b] Coefficient
None	---	16 (2)	0.014 (0.002)
P-9 oil	245	121 (20)	0.007 (0.002)[c]
CCA	16	14 (1)	0.014 (0.001)

[a] The average (standard deviation) MIT sorption at an average MIT vapor concentration of 18 ug/cc air (35 to <1 ug/cc air across the wafer length).

[b] Average (standard deviation) diffusion coefficients (cm^2/min) were calculated using ug MIT/cc air as concentration gradient.

[c] Diffusion coefficients were still slowly increasing even after 20 days in the apparatus, when the experiment was discontinued.

diffusion coefficients or sorption. CCA microdistribution in wood follows closely with that of lignin (Daniel and Nilsson, 1987), suggesting that CCA may fix primarily to lignin. The strong influence of water, and the lack of influence of CCA preservative treatment on MIT sorption and diffusion, suggests that MIT reacts mainly with the carbohydrate portion of wood.

CONCLUSIONS

The information obtained on MIT interactions with and movement through wood at different moisture contents can be used to predict the performance of MIT fumigations of wood poles in service.

MIT diffuses over 300 times faster longitudinally than transversely, suggesting fumigant treatment patterns should provide much smaller lateral than longitudinal spacing between treatment holes to provide complete fumigant penetration of poles. MIT sorbs at high concentrations in dry wood (<15% MC) and diffuses slowly. As the wood moisture content increases to about the FSP, less MIT is sorbed to the wood, and MIT steady-state diffusion coefficients increase (especially in the tangential direction). This suggests that fumigation of low moisture content wood (dry climates) may require more fumigant and provide slower control than wood under more humid conditions. Wood moisture contents above the FSP restrict longitudinal MIT diffusion, but cause only minimal influence on transverse MIT diffusion. MIT should adequately penetrate active decay pockets that may have high moisture contents.

Untreated or CCA treated sapwood shells did not restrict radial MIT movement, but treatment with oil-borne preservatives

significantly restricted fumigant movement. This suggests that MIT should perform better in oil-borne than in water-borne treated products, especially in the pole shell and outer heartwood.

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CHAPTER III
The Fungitoxicity and Adsorption of Methylisothiocyanate in Douglas-fir Heartwood at Different Wood Moisture Contents

ABSTRACT

High concentrations of the fumigant methylisothiocyanate (MIT) will effectively control decay fungi in large wood structures, but the fungitoxicity of low MIT concentrations and the influence of wood moisture content (MC) on its performance are not well understood. Wood moisture content greatly influenced the susceptibility of the decay fungus Poria carbonica in Douglas-fir heartwood to MIT vapors and the amount of MIT sorbed by the wood. At constant, low MIT vapor concentrations (less than 1 ug/cc air), wood at 10% MC bound 5 times more MIT, but required 4 times the exposure period to control P. carbonica, than similarly treated wood above the fiber saturation point. Adsorption of MIT to wood was not substantially influenced by the amount of wood decay. Increasing wood moisture content from 10% to 30% during fumigation resulted in a rapid volatilization of previously bound MIT and an associated increase in fumigant fungitoxicity.

INTRODUCTION

Volatile fumigants can effectively control internal decay in large wooden structural members and extend their service lives (Graham 1973, Goodell et al. 1980, Zabel et al. 1982, Helsing et al. 1984). Methylisothiocyanate (MIT) is a volatile fungitoxic component of the fumigant Vorlex (20% MIT, 80% chlorinated C-3 hydrocarbons) and a volatile decomposition product of the fumigant Vapam (a 32% water solution of sodium N-methyldithiocarbamate) in wood (Zahora and Corden, 1985a). Both of these fumigants are registered with the U.S. Environmental Protection Agency for application to wood. MIT is also a decomposition product of a number of solid fumigant formulations (Morrell and Corden, 1986) and can be used in pure form for decay control (Zahora and Corden, 1985a).

Residual MIT vapors can be detected in wood poles and pilings for at least 5 years after initial fumigant treatments (Helsing et al. 1984). Although MIT effectively controls wood decay fungi, limited information is available on MIT interactions and fungitoxicity in wood during long exposures at low fumigant concentrations. At high fumigant concentrations (above 2 ug MIT/ml air) and short exposure times (less than 32 hr), wood moisture content greatly influenced both the fungitoxicity and sorption of MIT in wood (Zahora and Corden, 1985b). Wood blocks at 20% moisture content (MC) bound about 50% more MIT than wood blocks above the fiber-saturation point (FSP), but required twice the fumigant dosage to control the decay fungus Poria carbonica Overh. These experiments were limited to high MIT concentrations over short exposure periods,

and did not investigate the effect of wood moisture content on MIT binding and fungitoxicity during long fumigant exposures at low concentrations. These interactions may be very important in determining the overall effectiveness of fumigant treatments.

This report describes the toxicity of long exposures at low MIT vapor concentrations to P. carbonica in Douglas-fir heartwood blocks, and how wood moisture content influences fungal susceptibility and MIT sorption properties. The results should help to determine the most effective fumigant treatment conditions and to better define fumigant retreatment schedules for continued control of decay fungi in wood products.

MATERIALS AND METHODS

Fungitoxicity Studies

The fungitoxicity of MIT in wood was investigated using previously described techniques (Zahora and Corden 1985b), which were modified to accommodate longer fumigation periods. These general methods will be briefly outlined, along with more detailed descriptions of required modifications.

Sample Preparation

Groups of 30 coastal Douglas-fir (Pseudotsuga menziesii [Mirb] Franco) heartwood blocks (0.5 cm grain direction by 2.5 cm square) were oven-dried, weighed, infiltrated with water, and sterilized by autoclaving for 20 min (15 psi). Blocks were then adjusted to 75% MC

by aeration under sterile conditions in a laminar flow hood and inoculated with an aqueous suspension of fragmented P. carbonica mycelium. Blocks were placed on glass rods above wet filter paper (humidity source) in petri plates, and incubated for 4 to 7 months at 22-25°C. The blocks were adjusted through aeration to about 10%, 20%, 40%, or 70% MC at least 1 week prior to use in fumigation experiments, based on a 5% decrease in block weight loss due to decay. The initial moisture contents of the blocks were estimated by comparing the wet and oven-dry weights of small pieces of each block (0.5 cm by 0.8 cm square) removed just prior to fumigation.

Fumigation Apparatus

Blocks adjusted to the desired moisture contents were fumigated in a continuous flow apparatus that produced an air stream containing constant MIT vapor concentrations (Zahora and Corden 1985b). Fumigation experiments were conducted using MIT vapor concentrations ranging from 0.70 to 0.05 ug/cc air, as well as control experiments where MIT was not present in the air flow. The air stream was split to flow into 3 identical fumigation chambers at a rate of 15 cc/min/chamber.

Fumigation chambers (450 cc jars) were modified to control the relative humidity (RH) surrounding blocks to prevent drying during fumigation. The desired humidity was maintained within the jars by lining the sides of the jars with filter paper, which was either wetted with water (40% and 70% MC blocks), saturated NaCl solution (20% MC blocks), or left dry (10% MC blocks). The jars also contained magnetic stirring fans for air circulation and wire mesh

supports to hold blocks above the bottom of the jars.

Fungitoxicity Estimates

The prefumigation fungal population densities were estimated by cutting six radial sections (1.5 cm by 0.5 cm by 60 um) from each block with a microtome. The wood sections were homogenized for 1 minute (20,000 rpm) in 16 ml of water, which was added to 60 ml of potato-dextrose-agar (50°C). The final wood-medium suspension contained 2 ppm benomyl and 1% agar (pH 4.5) and was distributed between 5 petri plates. Plates were incubated at 20-24°C and resulting P. carbonica colonies counted.

Groups of 5 blocks were fumigated together in chambers for each wood moisture content and MIT vapor concentration tested. During fumigation, the blocks were periodically removed and sampled as above to estimate the surviving P. carbonica population in each block, and then returned to the fumigation chambers. The number of microtomed sections removed was increased to 8 or 10 as the length of fumigation increased, to improve assay sensitivity. Fumigant fungitoxicity was expressed as the percent reduction in the P. carbonica population during fumigation, and was based on the maximum population density measured in each replicate block.

After 7 days fumigation, small pieces of wood (0.5 cm x 0.8 cm square) were removed to estimate wood moisture content and the amount of MIT adsorbed by the blocks. These wood samples were weighed, then extracted in 2 ml of ethyl acetate for 7 days. Extracts were analyzed for MIT content on a Varian 3700 gas chromatograph (GC) equipped with a flame-photometric detector and a sulfur filter. A 3

m long by 4 mm (ID) glass column packed with 10% Carbowax 20M on 80/100 Supelcoport solid support was used at injector and detector temperatures of 200°C, oven temperature of 170°C, and a nitrogen flow rate of 75 cc/min. MIT concentrations were determined by comparing MIT peak areas with those obtained using standard solutions of MIT in ethyl acetate.

MIT Adsorption in Douglas-fir Heartwood

MIT adsorption to the Douglas-fir heartwood blocks used in these fungitoxicity experiments was greatly influenced by wood moisture content, with higher MIT concentrations binding to wood below than above the FSP. This was expected based on previous sorption studies (Chapter II above; Zahora and Corden 1985b), but was further studied here under the specific conditions used in the fumigation experiments. This experiment investigated the concentrations of adsorbed MIT in blocks at a range of moisture contents after a 1 week exposures at a constant MIT vapor concentration, and if wood decay by the brown rot P. carbonica would influence the amount of MIT adsorbed to wood.

Forty-two Douglas-fir heartwood blocks (0.5 cm grain direction by 2.5 cm by 0.8 cm) were inoculated with P. carbonica and incubated at 20-25°C for at least 6 months. Blocks were then oven-dried, and their weight losses due to decay determined. These blocks, along with 42 sound (undecayed) blocks were divided into 7 groups of 6 decayed and 6 sound blocks for fumigation in the previously described fumigation apparatus. This apparatus could accommodate 4 groups of blocks at a time. In the first fumigation, groups of blocks were

adjusted (based on weight) to either 10%, 20%, 40%, or 70% MC, and fumigated at 0.25 ug MIT/ml air in the apparatus. Water was placed in the bottom of fumigation chambers to maintain humidity for 40 and 70% MC blocks, and saturated NaCl solution for 20% MC blocks. After 7 days, blocks were removed, weighed, and extracted in 5 ml of ethyl acetate for 7 days. Total MIT adsorption was then determined by GC analysis of the ethyl acetate extracts. The fumigation was repeated using similar groups of blocks that were equilibrated at 0%, 55%, and 93% RH, using anhydrous $CaSO_4$, or saturated solutions of $Mg(NO_3)_2$, or $NH_4H_2PO_4$, respectively. These saturated solutions were also added to the fumigation chambers to maintain humidity during fumigation.

The influence of moisture content on MIT adsorption by P. carbonica mycelium was also tested. Fungus was scraped from the surface of decaying Douglas-fir blocks, and about 0.25 g were loosely wrapped in tissue and equilibrated at either 55%, 93%, or 100% RH. The fungal mycelium was then fumigated, weighed, and extracted as described above, to determine moisture content and MIT adsorption.

RESULTS AND DISCUSSION

Fungal Sampling Considerations

Fungal population densities before fumigation varied greatly between blocks, ranging from about 100 to over 5000 colonies per 6 microtomed sections sampled. Periodically during fumigation, small subsamples were sequentially removed from each block to estimate surviving fungal population densities. Ideally, blocks would have a uniform fungal population density throughout, and a change in

population density would reflect the influence of fumigant treatment. Unfortunately, fungal population densities were not uniform and fluctuated in successive subsamples, which could result in apparent increases in fungal populations during fumigation. This effect was apparent during short MIT exposures at low moisture contents (limited fungal kill), where maximum fungal populations densities in replicate blocks were not always observed at zero time. As a result, the following graphs (Fig. III.1 and III.2) should have greatest accuracy at low survival estimates (below 60% survival).

In addition to fungal density variations within the blocks, wood moisture content changes during fumigation also influenced fungal population estimates (Fig. III.1). In the absence of MIT, fungal populations fluctuated, but remained high throughout an 18 day sampling period in wood at 63-87% MC, which is well above the FSP of Douglas-fir (28% MC). However, fungal survival estimates decreased substantially when block moisture contents were either increased or decreased through the FSP during the sampling period (Fig. III.1). Drying of blocks from 84% to 16% MC caused fungal populations to decrease to less than 5% of their original level, but did not completely kill the fungus. Increasing wood moisture contents by exposing blocks at 17% MC to 100% RH caused a rapid decrease in fungal recovery (about 80% reduction), which then slowly increased over time, probably as the fungus started actively growing.

The physiological reasons for these population decreases were not investigated. Drying of wood below the FSP may reduce fungal populations through hyphal death, possibly associated with formation of resting structures such as chlamydospores. The decrease in fungal

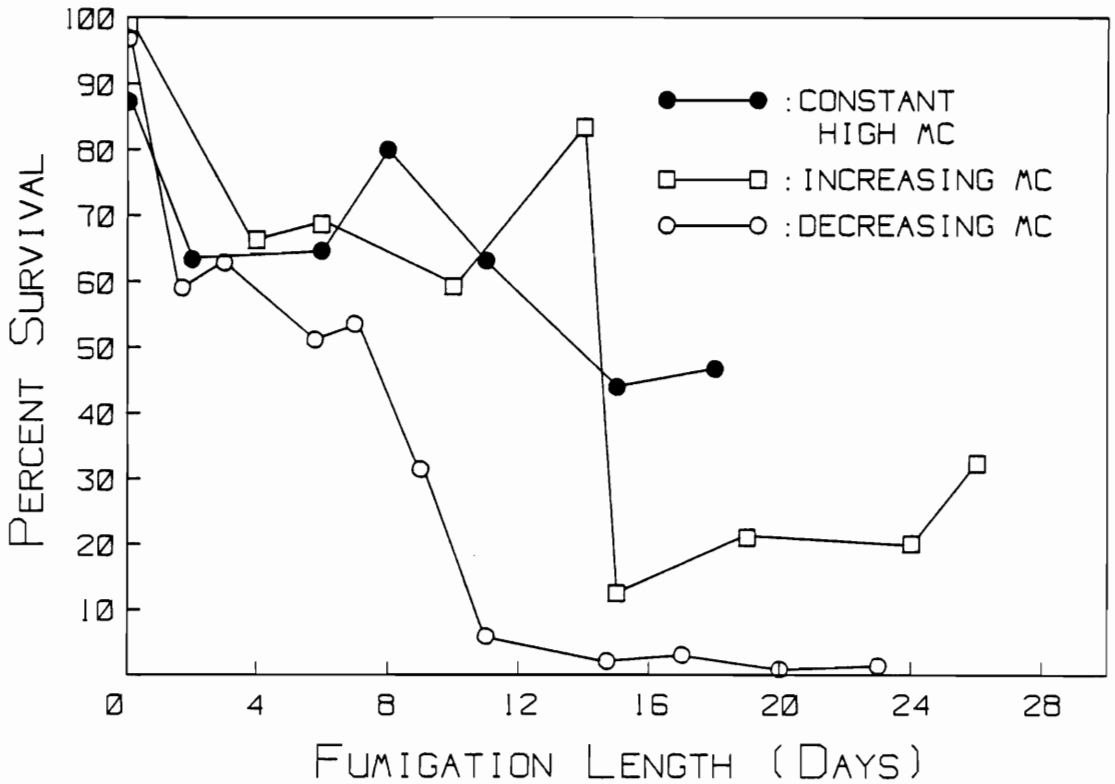


Figure III.1. Influence of wood moisture content (MC) on the observed P. carbonica populations estimated in Douglas-fir heartwood blocks in the absence of fumigant. Blocks were either maintained at 63-87% MC throughout the sampling period (constant high MC), increased from 17% to 27% MC at day 14 by exposing to 100% RH (increasing MC), or dried from 84% (initial MC) to 43% (day 9 MC) to 17% MC (day 10 MC) (decreasing MC) during exposure in the fumigation chambers. Each point represents the average fungal survival in 5 replicate blocks expressed as the percent of the maximum population density measured in each block.

populations when dry wood was exposed to 100% RH was unexpected. This decrease may result from previously dry (dormant) fungus becoming metabolically active and susceptible to toxic wood extractives, or more sensitive to the fragmentation resulting from sampling procedures. Although estimates of fungal survival varied with the sample position in the block, and changes in block moisture content during fumigation, distinct influences of fumigation on P. carbonica survival could be determined.

MIT Fungitoxicity at Constant Wood Moisture Content

Poria carbonica was more sensitive to low MIT vapor concentrations in Douglas-fir heartwood blocks above than below the FSP (Figure III.2). In wood fumigated at 0.72 ug MIT/cc air, over 2.5 times the exposure length was required to control P. carbonica in wood at 14-16% MC than in wood above the FSP (Figure III.2A). A similar but more pronounced relationship was observed in wood fumigated at 0.25 ug MIT/cc air (Figure III.2B), where over 4 times the exposure period was required for decay fungus control in the drier wood. Because of the long exposure times required to kill P. carbonica in dry wood, only blocks above the FSP were fumigated at 0.10 (Figure III.2D) and 0.05 ug MIT/cc air.

The exposure time (days) required to kill 98 percent of the P. carbonica propagules in replicate blocks was estimated for each wood moisture content at 0.70 and 0.25 ug MIT/cc air (Table III.1). Significantly longer exposures were required for 98 percent kill in blocks below than above the FSP, and for blocks at 9% than at 15% MC. Differences in wood moisture contents above the FSP did not

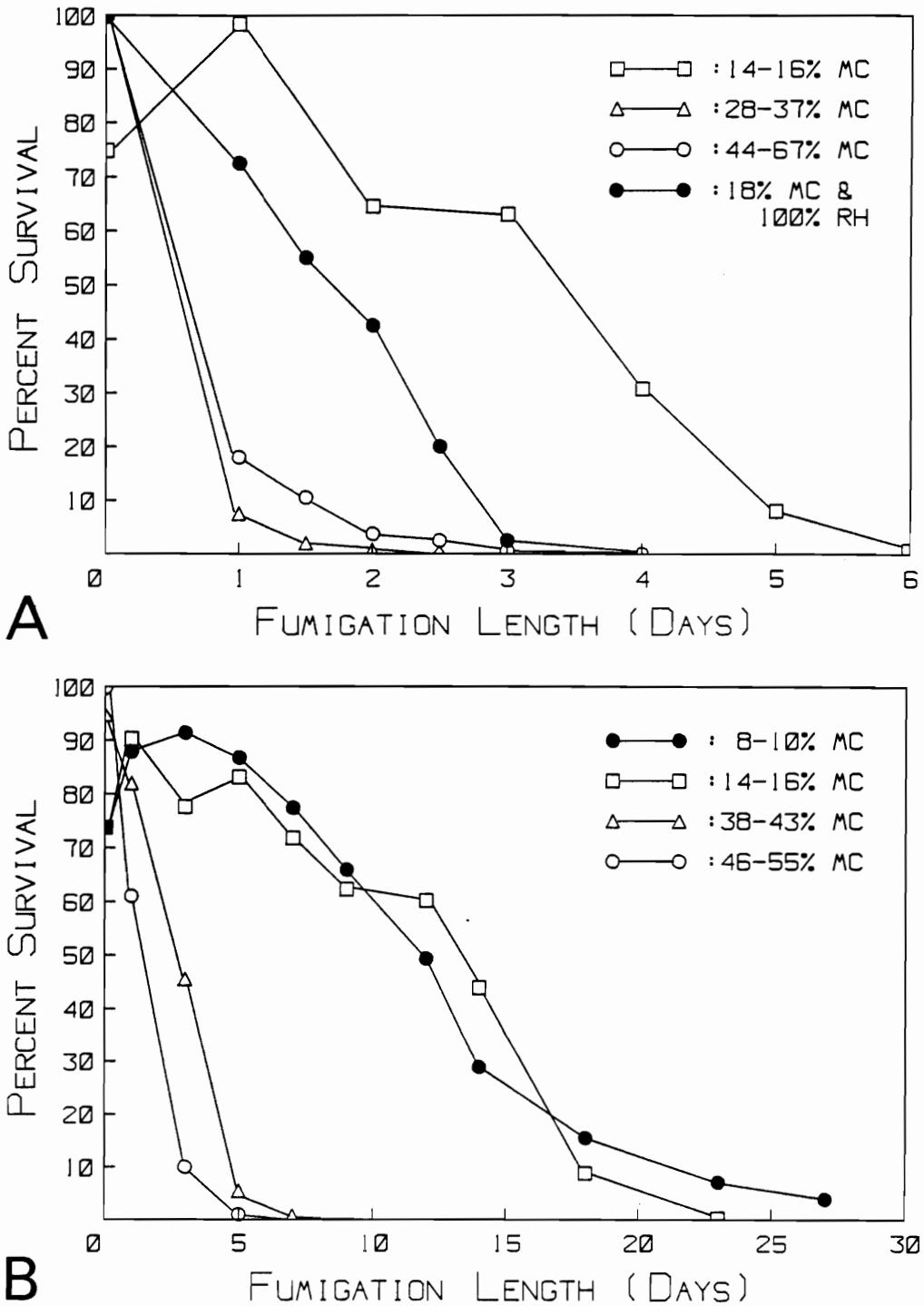
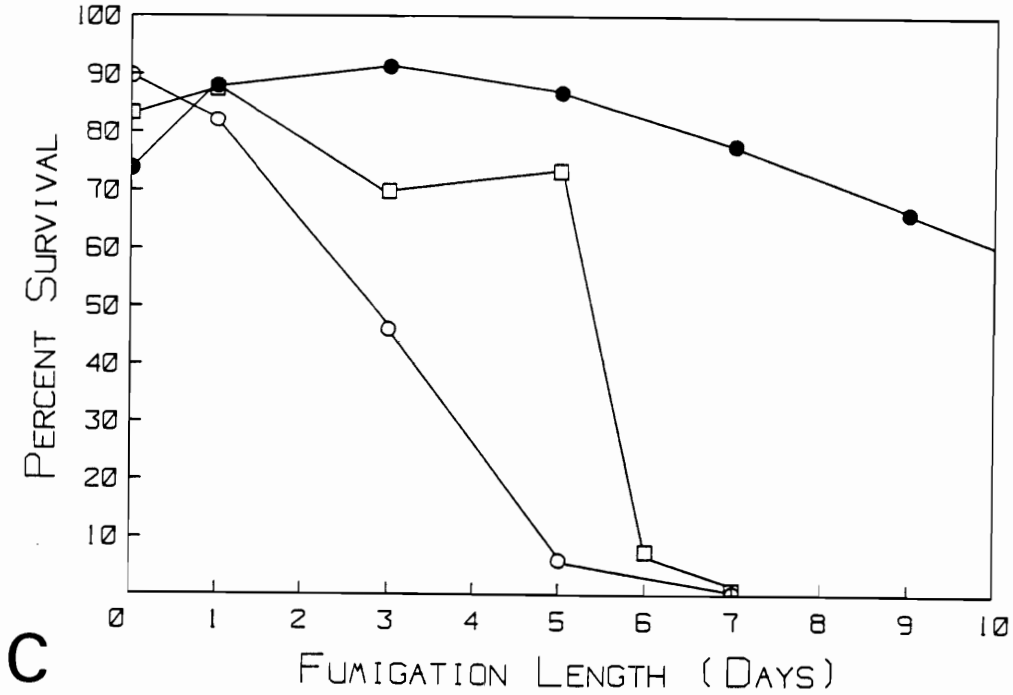


Figure III.2. Dosage-response relationships describing the influence of wood moisture content on the fungitoxicity of methylisothiocyanate (MIT) to Poria carbonica in Douglas-fir heartwood blocks. A) Infested wood blocks at 3 different moisture contents were exposed at 0.70 ug MIT/cc air, with one set of blocks at 18% MC exposed at 100% relative humidity (RH). B) Infested wood blocks at 4 different moisture contents (MC) were exposed at 0.25 ug MIT/cc air. (cont.)



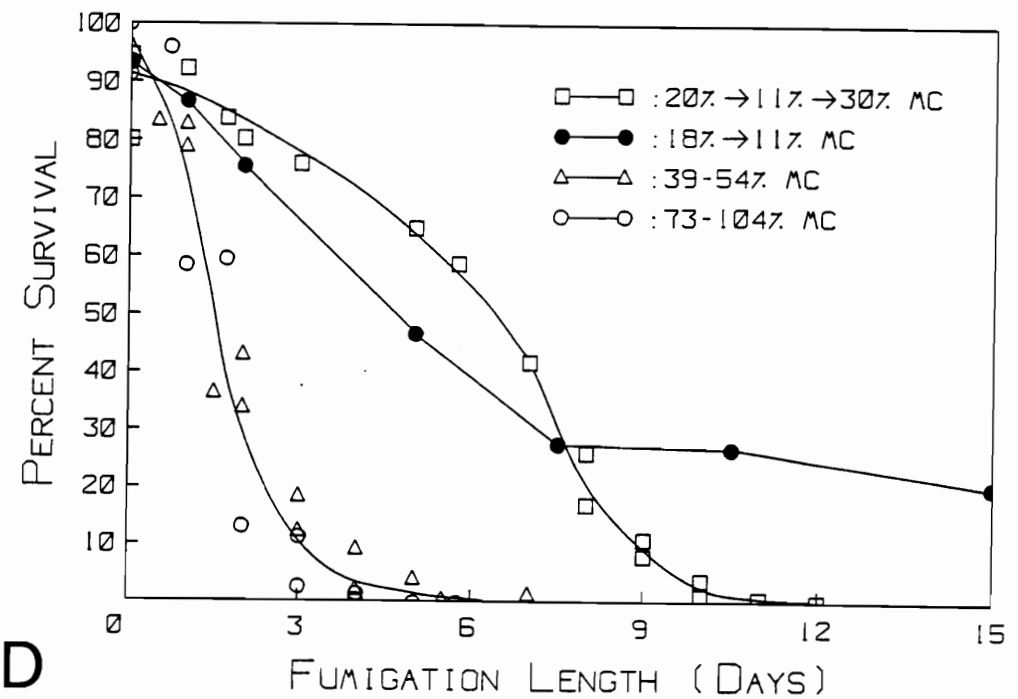


Figure III.2 (cont.). C) Infested wood blocks were exposed at 0.25 ug MIT/cc air at either 38-43% MC ○—○, 8-10% MC ●—●, or 8-10% MC with the relative humidity increased to 100% after 5 days □—□. D) Infested wood blocks were exposed at 0.10 ug MIT/cc air. Wood blocks below the fiber-saturation point dried from 18% and 20% to 11% MC at day 7, and were then exposed in one set to 100% RH to increase to 30% MC. Each point represents the average fungal survival in 5 blocks expressed as the percent of the maximum population density measured in each block.

Table III.1. Average methylisothiocyanate (MIT) vapor concentrations and times required to kill 98 percent of the P. carbonica propagules in Douglas-fir heartwood blocks at different wood moisture contents.

MIT Concentration ug/cc air	Days Exposure Killing 98% of Fungus[a]			
	8-10% MC	14-16% MC	28-43% MC	44-67% MC
0.70	--	5.5	1.5	2.3
0.25	27.3	20.4	6.2[a]	4.4[a]

[a] Numbers represent means of 5 replicate blocks. Means followed by a letter are not significantly different (a=0.05) at that MIT vapor concentration using the Student-Newman-Keuls test.

consistently influence the length of exposure required for 98% kill, with mean exposure times both increasing and decreasing with moisture content at the different MIT vapor concentrations. In wood fumigated at 0.10 ug MIT/cc air (Fig. III.2D), results varied between replicate experiments at 42-52% MC and 91-104% MC, but did not differ statistically with wood moisture content (a=0.05). Previous studies (Zahora and Corden, 1984a) also failed to find a significant difference in MIT fungitoxicity at 40% and 75% MC for MIT vapor concentrations above 2.5 ug MIT/cc air. This is not unexpected, since moisture content changes above the FSP should not substantially influence fungal growth, as long as oxygen is not limiting. For subsequent analysis, P. carbonica survival results were combined for MIT fumigations in blocks above the FSP.

Regression lines relating fungal survival [probit scale] to fumigation length [log scale] were used to estimate the length of fumigant exposure required to kill 98 percent of the P. carbonica propagules in blocks above the FSP. When MIT concentrations were decreased from 0.70 to 0.25 ug MIT/cc air, the estimated length of fumigant exposure increased from 1.8 to 5.2 days. Further reduction of MIT concentrations to 0.10, and 0.05 ug MIT/cc air did not statistically increase the length of fumigant exposure (Table III.2), which were estimated at 4.4, and 5.1 days, respectively. Fumigant concentrations between 0.25 and 0.05 were apparently equally effective in controlling P. carbonica in wood above the FSP.

These results were used to calculate the product of MIT concentration (ug/cc air) and exposure times (days) required to kill 98% (CT_{98} values) of the P. carbonica propagules in the blocks for

Table III.2. Statistical comparison of regression curves for fumigation length (log scale) and P. carbonica survival (probit scale) at different methylisothiocyanate (MIT) vapor concentrations for in Douglas-fir heartwood blocks above the fiber-saturation point.

Regression Comparison (ug MIT/cc air)	F^* value	Critical F value[a]
0.70, 0.25, 0.10, and 0.05	11.4	F(.99;6,34)=3.47
0.25, 0.10, and 0.05	0.46	F(.95;4,27)=2.73
0.70 and 0.25	21.3	F(.99;2,12)=6.93

[a] Reduced models include all data points from the regression plots being compared. Alternative conclusions are: if $F^* < F(1-a;r-1, n-r-1)$, then the lines are similar in both slope and intercept, or; if $F^* > F$, then at least one line in the comparison must differ with respect to either slope and/or intercept.

comparison with results estimated from an earlier study (Zahora and Corden, 1985b) that tested MIT concentrations above 2 ug/ml air (Table III.3). CT_{98} values in wood at 14-20% MC were comparable with earlier results, and remained constant at about 5 ug MIT/cc air/day throughout the range of MIT vapor concentrations tested. However, in wood above the FSP, CT_{98} values declined with decreasing fumigant vapor concentrations (or increasing fumigation length). Below 0.25 ug MIT/cc air, fungitoxicity of MIT was independent of MIT concentration and dependent only on length of exposure as discussed above. This suggests that very low MIT concentrations, which may not be toxic to inactive decay fungi in dry wood, become fungitoxic in wet wood. The increased susceptibility of P. carbonica to MIT in wet wood may be important in determining long-term wood protection, since fungal growth and active decay will only occur in wood above the fiber saturation point.

In addition to its effect on fungitoxicity, wood moisture content also influenced the extractable MIT sorbed by the wood blocks, with higher MIT concentrations in wood below the FSP than in wood above the FSP. The specific concentrations detected in individual fumigation experiments were similar to those found in the MIT adsorption study (Table III.4 and III.5). The results from the adsorption study were considered more accurate than those obtained in the toxicity study, and will be described in detail in the adsorption section below.

MIT Fungitoxicity with Changing Wood Moisture Content

The reduced fungitoxicity of MIT in dry wood may have resulted

from the P. carbonica being less susceptible to MIT in a desiccated (inactive) form, which may include the formation of resistant spores during the drying of blocks before fumigation. To further investigate the influence of wood moisture content on MIT fungitoxicity, dry (below the FSP) P. carbonica infested blocks were fumigated at high RH, which caused block moisture contents to increase during fumigation.

When wood blocks initially at 18% MC were fumigated at 0.70 ug MIT/cc air and 100% RH, MIT fungitoxicity was greater than in blocks that were maintained dry during fumigation, but lower than in blocks initially above the FSP (Figure III.2A). After fumigation for 5 days, the final block moisture contents were very close to the FSP of Douglas-fir (28-30% MC). Although exposure of dry blocks to 100% RH in the absence of fumigant (Figure III.1) reduced fungal recovery, it never completely killed the fungus. The shortened time required for complete fungal kill in dry blocks fumigated at high RH conditions suggests that fungal propagules formed in dry wood loose their resistance when wood moisture content is increased and physiological activity of the fungus can resume.

The influence of increasing wood moisture content during fumigation on MIT fungitoxicity was even more pronounced when blocks were initially fumigated under dry conditions (Figure III.2C). In this fumigation, 2 groups of blocks at 10% MC were fumigated at 0.25 ug MIT/cc air for 5 days before the RH of chambers was increased to 100%. As in nonfumigated controls (Figure III.1), the survival of P. carbonica decreased sharply after 1 day at 100% RH, but instead of slowly increasing, the fungi were essentially killed (survival less

Table III.3. Estimated methylisothiocyanate (MIT) concentration X exposure times necessary to kill 98% (CT_{98} values) of the Poria carbonica propagules in Douglas-fir heartwood blocks fumigated under dry or wet conditions.

Wood Moisture Content Range (%)	CT_{98} values[a] in wood fumigated at MIT concentrations of: (ug MIT/cc air)				
	8.0	3.0	0.70	0.25	0.10
14-20%	6.1	5.1	3.7	5.4	--
above FSP (>30%)	3.9	3.1	1.3	1.3	0.44

[a] CT_{98} values (ug MIT/cc air/day) were estimated from Zahora (1983) for MIT concentrations of 3.0 and above, and from regression analyses of data in Fig. III.2 for the rest.

than 0.5%) by the by the second day. This decrease in survival occurred at a faster rate than in blocks initially fumigated at 38-43% MC. Wood blocks adjusted quickly to the new RH conditions, with blocks increasing to about 28% MC, and sorbed MIT concentrations decreasing from about 700 to 150 ug MIT/g oven dry wood after only one day at 100% RH. This change in wood moisture content during fumigation resulted in a substantial release of sorbed MIT from the dry wood. This release would temporarily increase MIT vapor concentrations in the blocks by about 4 fold, resulting in a more rapid kill.

Similar results were also observed in wood fumigated at 0.10 ug MIT/cc air (Figure III.2D). The initial decrease in survival in these blocks during dry fumigation may be the result of drying. When the RH was increased to 100%, the rate of fungal kill increased to about that observed in wood initially fumigated at wood moisture contents above the FSP. Sorbed MIT concentrations also rapidly decreased from about 170 to 40 ug MIT/g oven dry wood after 1 day at 100% RH. Even though substantial MIT was apparently released in these blocks, it did not increase the rate of kill beyond that observed in wood initially above the FSP, probably because the MIT vapor concentrations were not increased beyond the range where rate of kill was independent of vapor concentration (see Table III.2).

The rapid kill of P. carbonica in blocks when the RH was increased to 100% probably resulted from an increased susceptibility of fungal propagules, along with a temporary increase in MIT vapor concentrations within the blocks as sorbed MIT was volatilized and released. The greatly increased susceptibility of P. carbonica to

MIT in wet wood may help explain why Vapam, which degrades to produce MIT, but is mostly water, has performed well as a wood fumigant.

MIT Adsorption in Douglas-fir Heartwood

At a constant vapor concentration of 0.25 ug MIT/ml air, MIT adsorption by Douglas-fir heartwood blocks was strongly influenced by wood moisture content, but was apparently not greatly influenced by wood decay (Tables III.4 and III.5). The MIT adsorption concentrations calculated from the two adsorption experiments did not correspond as expected, with lower MIT concentrations in Table III.5 than would be expected based on Table III.4. This could relate to these fumigation studies being conducted at ambient temperature, which may have varied between experiments. Similar variability in adsorption concentrations during replicate fumigations was also observed in the previously described fungitoxicity studies, which also were not maintained under strict temperature control. Although this prevents the combination of these two tables to form a unified picture of MIT adsorption over the full range of moisture contents, these results permit some generalizations about MIT adsorption in Douglas-fir heartwood.

MIT adsorption in decayed and non-decayed blocks that were fumigated together under the same conditions differed substantially, with decayed blocks having higher adsorption concentrations in blocks above 10% MC, but lower adsorption in blocks below 10% MC. Although these differences were often substantial, wood decay also reduced the final block moisture contents, which may be the true reason for the observed differences. The influence of wood moisture content on MIT

Table III.4. Influence of wood moisture content (MC) and decay by P. carbonica on methylisothiocyanate (MIT) sorption in Douglas-fir heartwood blocks in first experiment.[a]

Wood MC (%)[b]	% Weight Loss Due to Decay[c]	MIT Sorption (ug/g OD wood)	Partition Coeff.[d]
9.6 (0.2)	0	687 (26)	2750
8.0 (0.3)	11	601 (63)	2400
15.5 (0.3)	0	246 (9)	980
13.9 (0.8)	10	293 (9)	1170
32.4 (0.5)	0	111 (11)	440
29.2 (1.0)	11	133 (10)	530
64.4 (5.9)	0	123 (5)	490
67.8 (9.3)	11	158 (8)	630

[a] Groups of 6 sound and 6 P. carbonica decayed blocks were fumigated together in a continuous flow fumigation apparatus for 7 days at 0.25 ug MIT/ml air. Values represent means and standard deviations (in parenthesis) of each group of six blocks.

[b] Blocks were initially adjusted to either 10%, 20%, 40%, or 70% MC.

Figures represent the final moisture contents of blocks.

[c] Individual decayed block weight losses ranged from 7% to 14%.

[d] Partition coefficients represent the total MIT content in wood (per g) divided by the MIT vapor concentration (per cc).

Table III.5. Influence of wood moisture content (MC) and decay by P. carbonica on methylisothiocyanate (MIT) sorption in Douglas-fir heartwood blocks in second experiment.[a]

Wood MC (%)[b]	% Weight Loss Due to Decay[c]	MIT Sorption (ug/g OD wood)	Partition Coeff.[d]
1.7 (0.2)	0	238 (24)	950
0.9 (0.2)	23	226 (12)	900
8.0 (0.3)	0	312 (8)	1250
6.4 (0.2)	19	215 (35)	860
22.0 (1.7)	0	97 (6)	390
19.0 (1.5)	21	136 (7)	540

[a] Same as in Table III.4.

[b] Blocks were equilibrated and exposed at 0%, 55%, or 93% RH over salt solutions. Figures represent the final moisture contents of blocks.

[c] Individual decayed block weight losses ranged from 9% to 27%.

[d] Same as in Table III.4.

adsorption was large enough to mask any differences in adsorption that could be attributed to wood decay, suggesting that decay influences were not great compared to moisture content influences.

MIT adsorption concentrations were highest in wood at about 10% MC, and decrease both below and above this moisture content. This relationship is very similar to that found in Chapter II (Fig. II.3), but is even more pronounced in this study, where constant MIT vapor concentrations were maintained throughout the exposure period. Adsorption concentrations decreased substantially as the wood moisture content increased from about 10% up to the fiber-saturation point. These results compare favorably with partition coefficients of 700 (18-22% MC wood) and 500 (36-43% MC wood) that were calculated using the data of Zahora and Corden (1985b) from experiments conducted at 1-3 ug MIT/cc air for 32 hr.

The mycelium of P. carbonica also showed a similar relationship, with dry mycelium sorbing much higher MIT concentrations than mycelium fumigated at higher moisture contents. Mycelium fumigated for 1 week (0.25 ug MIT/cc air) at 55% RH (11% MC) sorbed 61 ug MIT/g oven-dry fungus, whereas mycelium fumigated at 93% and 100% RH (36% and 54% MC, respectively) both sorbed less than 4 ug MIT/g oven-dry fungus.

CONCLUSIONS

The decay fungus P. carbonica was much more susceptible to the fumigant methylisothiocyanate (MIT) in wet wood (above the fiber-saturation point [FSP]) than in dry wood (below the FSP). Increased susceptibility was apparently dependent on the water content of the fungus, as fungi in dry wood rapidly became more susceptible during fumigation if RH was increased. This may relate to the fungus being more susceptible to MIT when actively growing, which suggests that temperature may also be important in determining fumigant effectiveness. CT_{98} values remained constant at about 5 ug MIT/cc air/day in wood at 14-20% MC, but constantly decreased with MIT concentration in wood above the FSP. This suggests that the relationship between fumigant dose and fungitoxicity is very different in dry and wet wood.

Increasing the moisture content of wood in equilibrium at a low MIT vapor concentration will cause a rapid release of bound MIT from wood, as MIT sorption equilibrates to the new moisture content. This effect was not greatly influenced by decay from the brown rot fungus P. carbonica, suggesting that bound MIT will be released whenever dry wood becomes moist and susceptible to decay. Although P. carbonica is less sensitive to MIT in dry wood than in wet wood, binding of high MIT concentrations in dry wood may improve overall fumigant effectiveness. The MIT bound in dry wood may serve as a fumigant reservoir which is rapidly volatilized when wood becomes wet and susceptible to active fungal decay. This release may help explain the excellent long term performance of MIT in wood.

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GENERAL CONCLUSIONS

The results from the MIT sorption, diffusion, decomposition, and fungitoxicity studies in Douglas-fir wood described above, along with previous research (Zahora and Corden 1985b), provide insight into MIT-wood-fungus interactions. These interactions determine the effectiveness of fumigant treatments involving MIT as the active fungitoxicant. Although this information could be incorporated within a basic numerical model describing the movement and effectiveness of specific MIT treatments in wood poles, additional information on rates of sorption equilibrium, nonsteady-state diffusion, and fumigant fungitoxicity will be needed. This information is needed to verify both the validity of necessary assumptions, and the accuracy of the final model. However, with current knowledge, the relative influence of treatment and environmental parameters on the rate, effectiveness, and persistence of fumigants can be estimated. The following discussion describes how the information currently available on MIT movement and interactions in wood could be combined into a model, emphasizing how the various components should interact and what information is still needed to develop an accurate, working model.

The most useful product of any model predicting the effectiveness of fumigant treatment of wood poles will be the description of physical movement of the fumigant through the wood. In any real application of fumigants to wood, nonsteady-state conditions prevail for movement over time and space. Ideally, it would be desirable to create a mathematical model which directly

predicts the observed nonsteady-state diffusion of MIT in wood. A pre-requisite of such a model would be the acquisition of diffusion coefficients. The calculation of such values from nonsteady-state observations (initial stages of adsorption and desorption) in wood specimens would necessarily allow for the combined influence of MIT diffusion and sorption that prevailed under the conditions of the test. Unfortunately, diffusion in wood is dependent on both bound and vapor components, each of which may be dependent on MIT concentration, wood moisture content, and whether wood was adsorbing or desorbing fumigant for each diffusion direction. This represents a large number of conditions influencing fumigant diffusion, which would be very difficult to include in a fundamental mathematical description of MIT movement that could be used to derive diffusion coefficients, or actually model fumigant movement in poles.

An alternative for modeling MIT movement in wood could be to develop an approach based on numerical methods of mathematical analysis, wherein nonsteady-state diffusion could be modeled using a combination of steady-state diffusion coefficients and equilibrium sorption data. In this type of model, a wood pole would be broken into a series of discrete regions, each with its own diffusion and sorption properties based on wood type (sapwood, heartwood, preservative treatment) and moisture content. These characteristics would then determine the specific diffusion coefficients in each diffusion direction, and the equilibrium sorption ratio between vapor phase and bound MIT in that region. Equilibrium sorption and steady-state diffusion conditions would be assumed in each region and MIT movement into or out of adjoining regions would be based on the

regions relative MIT vapor concentrations. The model would be continually updated over a series of small time increments to estimate longer-term movement under nonsteady-state conditions. The validity and accuracy of the model would depend in part on the size of the discrete regions, and the length of time increments used. Time increments must be as small as possible for greatest accuracy in representing nonsteady-state diffusion conditions, although there may be some trade-off between the duration of time increments and the size of the discrete regions. This type of approach has been successfully developed and used by Humphrey and Bolton (In press) to model heat and moisture transfer in wood. Only the underlying principles of a similar model for fumigant movement in poles will be outlined here; information is not currently available to verify the accuracy of a working model that has incorporated specific numerical information. In addition, the formulation of the algorithm is a lengthy procedure which is beyond the scope of this study.

MIT Movement

For Douglas-fir, whose specific gravity is about 0.45 (oven-dry weight and wet volume basis), each region in a numerical model would be composed of 70% void space, and 30% solid wood material (1.5g/cc). Gross MIT flow into adjacent regions would depend on the steady-state diffusion coefficient in that direction, the MIT vapor concentration difference and common surface area between regions, and the time interval. The transfer of MIT between regions would change the total MIT content of the regions, which would be partitioned between the wood and vapor phases. This balance would depend on the

equilibrium partition coefficient (bound/vapor) for MIT sorption within each region. More elaborate versions of the model would also account for the likely time dependence of MIT vapor uptake within the solid wood material of each discrete region.

MIT partition coefficients are dependent on wood moisture content, and whether the wood is adsorbing or desorbing fumigant (Figures II.2, II.3, and Tables III.4, III.5). Large equilibrium adsorption/desorption ratios have been observed at low moisture contents, suggesting that separate MIT partition coefficients would be needed for wood that was adsorbing and desorbing fumigant. At moisture contents that are found in wood poles in service, [usually above 10% MC (Graham 1973b)], the differences between adsorption and desorption partition coefficients were much smaller, and may be ignored without significantly influencing the function of the model.

The relative movement of MIT through a typical pole in service can be estimated using the current knowledge of MIT steady-state diffusion coefficients (Tables II.5, II.6) and equilibrium partition coefficients. As an example, the expected relative movement of MIT through a low moisture content pole (about 12% MC) containing a high moisture content decay pocket (about 70% MC) is illustrated in both longitudinal (Fig. IV.1A) and cross-sectional (Fig. IV.1B) views. Figure IV.1A illustrates the very rapid longitudinal as compared to lateral diffusion rate. A pocket of high moisture content wood decreases longitudinal, but increases lateral diffusion coefficients for MIT movement (Table II.5). Lateral MIT movement will be further accentuated in the high moisture content decay pocket by the lower MIT partition (vapor/bound) coefficient (Tables III.4 and III.5),

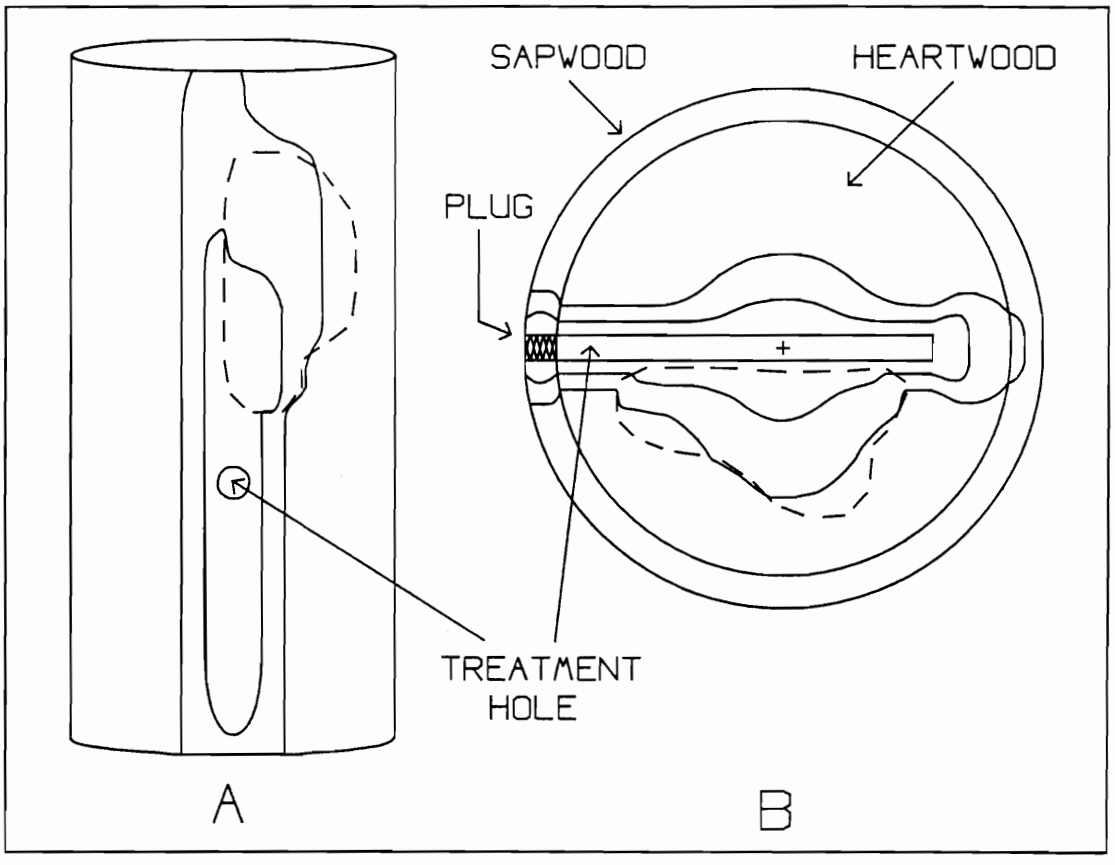

Figure IV.1. Expected relative rates of MIT movement in longitudinal (A) and transverse (B) views through a pole based on steady-state diffusion coefficients (Table II.5) and adsorption partition coefficients (Tables III.4, III.5). Regions enclosed by dashed lines represent high moisture content pockets, while solid lines represent relative MIT concentration contours.

which suggests that less MIT will be sorbed and removed from active movement in the wet than in the dry wood. Figure IV.1A illustrates restricted longitudinal MIT movement in the wet pocket, which might be expected based on the reduction in steady-state diffusion coefficients. However, it is difficult to estimate the influence of wood moisture content on overall longitudinal MIT movement without development of a numerical model that incorporates the influence of decreased partition coefficients in the high moisture content decay pocket. A decreased partition coefficient should partially compensate for the decreased longitudinal diffusion coefficient in wet wood, with the relative importance of each component determining the overall influence of a wet pocket on longitudinal movement of MIT.

In cross-sectional view (Figure IV.1B), the rate of MIT movement in a pole would be expected to be greater radially than tangentially, with more rapid MIT movement in the high moisture content decay pocket. Combining the two views suggests that the central column of a pole should receive the highest concentrations of fumigant. The current treatment practice of drilling multiple treatment holes in a spiral pattern around the pole, each through the center of pole, will overlap these treatment columns. It is expected that this will excessively treat the very center of the pole in comparison to the outer heartwood between treatment holes, due to the relatively poor tangential diffusion, especially in dry wood. Overall treatment coverage should improve with increasing wood moisture, especially in the range of 15% to about the fiber-saturation point. This suggests that MIT fumigation of wood poles may provide better results in

climates or during seasons having high relative humidity, where the higher wood moisture contents would improve MIT diffusion.

The much higher steady-state diffusion coefficients for MIT in Douglas-fir sapwood as compared to heartwood (Tables II.5 and II.6) may also influence the effectiveness of fumigant treatments. Diffusion coefficients were 7-times higher in CCA treated and non-preservative treated sapwood than in heartwood, suggesting that MIT will be lost very rapidly through the sapwood shell of poles. This may create a hard-to-treat boundary between the heartwood and sapwood, which will have substantially lower MIT vapor concentrations due to rapid MIT diffusion into the sapwood. Treatment of poles with an oil-borne preservative treatment should restrict loss of MIT through the sapwood, but MIT will still diffuse faster through the oil-treated sapwood than through the heartwood. Modeling will be necessary to determine the influence of these different MIT diffusion coefficients on MIT concentrations in wood poles.

The dosage and formulation of the fumigant treatment producing MIT as its active fungitoxicant will also influence MIT movement through poles, although the influence on overall fumigant effectiveness is difficult to estimate without incorporating all MIT-wood-fungus interactions into a numerical model. Treatment with pure MIT should maintain a very high (probably saturated) MIT vapor concentration in the treatment hole until all of the solid MIT has volatilized to replace MIT moving into the wood. Changing fumigant dosage will influence the length of time before this occurs, which determine the range and concentration of MIT movement in the pole. Once the solid MIT is depleted and vapors moving into the wood can no

longer be replenished, MIT concentrations will begin to decrease as wood starts to desorb fumigant to replace vapors diffusing into regions with lower MIT concentrations.

Formulations that retard MIT release or production (Morrell and Corden 1986a) may decrease the maximum MIT vapor concentration in the treatment hole providing the concentration gradient driving diffusion into the pole. The relative decrease in MIT vapor concentration will depend on the relative rates of MIT diffusion into the pole and replenishment by the treatment formulation. These "slow release" treatments should increase the time that fumigant will be present in a pole, but will also probably decrease the fumigant concentrations obtained at any point in the pole. Formation of a numerical model will be necessary to determine how long effective MIT concentrations will remain in the pole, and the overall effectiveness of "slow release" MIT formulations in comparison to more standard treatments.

Decomposition

Decomposition of MIT (formation of non-MIT products) in wood poles during fumigation will influence overall fumigant effectiveness by reducing the concentration of MIT present in the wood, while producing non-MIT residues that may influence decay fungi in the poles. MIT decomposition to form residues not removed by aeration occurs slowly in Douglas-fir heartwood at rates that are estimated at about 0.9% and 1.6% of the bound MIT per week in wood at 12% and 60% MC, respectively (Chapter I). These residues can provide some decay protection by being either toxic to (DMTU and MMTU) or slowing the rate of wood decay by (Sulfur and nonextractable residues) the fungus

P. carbonica in Douglas-fir heartwood. The residue levels produced at any given point in a fumigated pole will depend on the wood moisture content and the total MIT dosage reaching that point in the pole. Use of a model incorporating specific MIT concentrations will be necessary to determine the concentrations of MIT residues deposited in poles using various treatment practices. The ability of these residues to provide residual protection against fungal reinvasion can then be estimated in the pole.

MIT decomposition will also slowly reduce MIT concentrations in the wood and may substantially influence overall MIT movement and effectiveness in wood. The rate of MIT loss through chemical reactions within poles may be higher than the rates estimated above, since these rates did not include any MIT loss through the production of volatile compounds that could diffuse out of the wood. Production of CS_2 and COS have been observed in wood (Chapter I; Morrell 1987), and their production may account for substantial reductions in MIT concentrations beyond those observed for formation of products not removed by aeration described in Chapter I. Loss of MIT through decomposition may be especially important in the effectiveness of slow release formulations that may increase the length of time that the fumigant is present in the wood.

Fungitoxicity

The MIT fungitoxicity studies (Chapter II; Zahora and Corden 1985b) provide information on the concentrations and exposure durations that are necessary to kill decay fungi already present in Douglas-fir wood. This information strongly suggests that the decay

fungus P. carbonica is much more susceptible to MIT vapor concentrations in wood at moisture contents above than below the FSP. In wood below the FSP, where decay fungi should be dormant and not actively decaying the wood, P. carbonica is susceptible to constant CT_{98} values of about 5 ug MIT/cc air/day over a wide rage of MIT vapor concentrations (Table III.3). This suggests that control of decay fungi in dry wood is dependent only on the total dose (product of concentration and time) of MIT, which is independent of the concentration of MIT vapor providing that dose. In wood above the FSP, where the fungus should be actively decaying the wood, the effective dose of MIT is apparently strongly dependent on the MIT vapor concentration providing the dose. The experiments desorbed in Section III did not determine the minimum MIT vapor concentration below which MIT would no longer kill P. carbonica in wood, no matter how long the fungus was exposed to MIT. This information is needed to determine the overall effectiveness of MIT fumigations, including how far MIT moves at fungitoxic levels through wood, and for how long effective concentrations will remain in wood after a fumigant treatment.

Effective use of any model describing fumigant movement in wood also requires information on MIT fungitoxicity and fungistaticity to decay fungus propagules that initiate reinvasion. Fungal spores or hyphae that are not growing on wood may be susceptible to different doses of MIT than fungi that are already established and decaying wood. Concentrations on MIT that do not kill the decay fungus may be fungistatic, thereby preventing fungal growth and wood damage. These fungistatic concentrations will be important in estimating when

retreatment is necessary to prevent damage to the strength of a pole.

Although MIT diffusion and sorption data can be used to model or estimate the expected MIT movement in wood poles (Fig. IV.1), it, alone, does not indicate the effectiveness of a treatment. Poria carbonica in high moisture content decay pockets should be most easily controlled, since MIT should diffuse rapidly into the pocket and the fungus within the pocket will be highly sensitive to the fumigant. The fungus will be harder to kill in drier areas of the pole, although decay should not be active in this wood. Thus environmental conditions prior to fumigation could potentially influence fumigant effectiveness. Edges of active decay pockets may be influenced by seasonal moisture conditions, with extended dry periods leaving viable fungus in dry wood surrounding the wet decay pocket. Fumigation with MIT may kill the fungus in the wet pocket, but not in the dry wood surrounding the pocket, even though the surviving fungus may be closer to the treatment hole. Fortunately, MIT concentrations that may not be toxic to P. carbonica in dry wood, can rapidly become effective when wood becomes moist and able to support decay activity [increased fungal susceptibility and release of sorbed MIT (Chapters I and III)]. Graham and Corden (1980) report little difference in fumigant effectiveness between spring and fall treatments. This suggests that fumigant treatments may persist long enough in poles to compensate for any seasonal fluctuations in pole moisture content.

The influence of wood moisture content on MIT sorption may be an important consideration in interpreting the results from standard sampling procedures such as the closed-tube bioassay (CTB), and

fungal culturing (Scheffer and Graham 1975; Graham and Helsing 1979) used to estimate the effectiveness of fumigant treatments. The closed-tube bioassay will respond to all MIT released from the wood increment core when placed in a tube containing an agar medium that produces a high RH. Although MIT vapor concentrations may be the same in increment cores, the CTB will detect the higher amount sorbed MIT in dry than in wet wood, even though the effectiveness of the MIT in the wet wood will be much higher. Similarly, culturing techniques may detect viable, but inactive fungi in dry wood, when sorbed MIT may be sufficient to kill the fungus if wood moisture conditions become conducive for fungal growth within the pole.

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