FACTORS INFLUENCING THE MOVEMENT OF CHLOROPICRIN VAPOR IN WOOD TO CONTROL DECAY

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(Received 15 January 1974)

ABSTRACT

Some of the factors affecting the movement of chloropicrin vapor in wood to control decay were studied in a series of four experiments. Chloropicrin moved much faster in permeable Douglas-fir heartwood than in wood of low permeability, partly because of more extensive liquid movement in the permeable woods. The lethal dosage of chloropicrin to the wood decay fungus *Poria monticola* was from 20 to 100 mg-h/liter for the conditions evaluated. Chloropicrin movement in a decaying Douglas-fir pole section was variable and was facilitated by the decayed area. Most areas in the pole received a high dosage of vapor, more than sufficient to kill decay fungi. Vapor could still be detected at most of the sampling sites six months after treatment. The release of chloropicrin vapor in wood could be controlled by dissolving paradichlorobenzene in the chemical to lower its vapor pressure and by confining chloropicrin in polymer slow-release capsules. These approaches increased the duration of the vapor in wood.

Additional keywords: Chloropicrin, *Poria monticola*, *Pseudotsuga menziesii*, *Thuja plicata*, diffusion, air permeability, fungal toxicity, sterilants, *in situ* treatments.

INTRODUCTION

An immediate need exists for an effective *in situ* treatment to control internal decay in preservative-treated transmission poles. This problem is particularly serious in nondurable, thin-sapwood species when severe checking in service penetrates the treated zone, allowing decay to develop in unprotected heartwood (Graham and Mothershead 1967; Tamblyn and Dale 1963). Conventional preservative solutions, injected into poles without pressure, will not permeate all of the decaying wood and, therefore, will not stop this decay. Field experiments by an Oregon utility (Hand et al. 1970) and the Oregon State University, Forest Research Laboratory (Graham 1973) show that high-vapor-pressure fungicides placed in holes drilled in transmission poles stop internal decay and afford some protection against reinfection.

It is evident that for this treatment to warrant commercial use, the vapor must diffuse in toxic concentrations to reach all decaying wood and must remain in wood long enough for the retreatment cycle to be economical. Some of the factors that may affect the control of decay with these sterilants are wood permeability, grain direction, temperature, wood moisture content, sterilant vapor pressure at the treating zone, amount of interaction—e.g. sorption between the sterilant and wood, and fungal toxicity of the chemical. The presence of decay pockets and seasoning checks in wood will

also influence the rate of vapor movement and loss from wood.

The purpose of this study was to investigate some of these factors through studies on the movement of chloropicrin (trichloronitromethane) in small wood specimens of different permeabilities and in a decaying Douglas-fir pole section with large seasoning checks. The toxic dosage of chloropicrin vapor for the decay fungus *Poria monticola* Murr. was investigated so that the effectiveness of the vapor dosages received at various positions in the pole section could be evaluated. *P. monticola* was used because of its importance in decaying poles (Eslyn 1970) and its relatively rapid growth rate. In addition, methods of extending the duration of effectiveness of the chemical by retarding the release of vapor in wood were evaluated.

MATERIALS AND METHODS

Permeability specimens

Two 5- × 5- × 46-cm (2- × 2- × 18-inch) end-matched specimens were prepared from each of two unseasoned heartwood planks, one of coastal Douglas-fir and the other of intermountain Douglas-fir. One specimen of each type of Douglas-fir was equilibrated to 12% MC, while the other was kept green (>30% MC) by a polyethylene wrap and storage in a cold room (2 C). Four additional specimens of similar specific gravity, but widely varying permeabilities, were prepared from wood that had been stored for several years in a constant temperature and relative humidity room (11% MC) and had been rated as to preservative treatability based on creosote penetration patterns in matched blocks (Miller 1961).

The longitudinal steady-state air-permeability coefficient was determined for each specimen from measurements on 1-inch-long wafers using equipment similar to that described by Resch and Ecklund (1964) except that a vacuum was applied instead of pressure.

Holes 1.3 cm (0.5 inch) in diameter and 3.8 cm (1.5 inch) deep were drilled into the center of one face of each specimen at midlength and at 10 and 20 cm (4 and 8 inches) above and below midlength. The holes were sealed with serum caps bonded to the wood with a silicone-rubber sealing compound, providing vapor sampling zones about 2.5 cm (1 inch) long. The specimens were sealed completely with paraffin wax to minimize moisture content changes. Four ml of liquid chloropicrin containing 0.5% Sudan IV dye were injected with a hypodermic syringe at midlength in each specimen. The specimens were stored upright in a conditioning room at 22 C and 11% MC. The concentration of vapor reaching each sampling zone was measured periodically by gas chromatography using a Varian Aerograph Model 200 gas chromatograph with a flame ionization detector, strip chart recorder, and 1.2-m (4-foot)-long teflon column (packed with Chromosorb Q solid support containing 7% Carbowax 20M liquid support).

It was not possible to use an internal standard in the analysis, as a substance mixed with the chloropicrin liquid initially may not diffuse through wood in the same relative concentrations. Instead ethanol was incorporated with each chloropicrin vapor sample as a "pseudo-internal standard." A 0.9-ml gas sample was taken from a sampling site with a 1.0-ml gas-tight syringe; then a 0.1-ml sample of saturated ethanol vapor was drawn into the syringe from a container of ethanol sealed with a serum cap. Temperature was held constant to ensure that the amount of ethanol drawn into the syringe would be constant. The ratio of chloropicrin peak area to ethanol peak area for each injection permitted corrections to be made for the detector response variability. When the test was terminated, the specimens were split so the distribution of dye, an indication of the minimum movement of chloropicrin liquid, could be measured.

Toxicity of chloropicrin to Poria monticola

Since the fungal toxicity of chloropicrin will be a function of the vapor concentra-

TABLE 1. *Characteristics of Douglas-fir pole section*

Diameter		35·6 cm (14 inch)
Specific gravity (ovendry weight/green volume basis)		0·45
"Sink-float" permeability rating for sound heartwood (Graham 1964)		Permeable
Average moisture content at start of test		
	2·5 cm (1 inch) deep	22%
	7·6 cm (3 inch) deep	40%
Average moisture content at end of test		
	2·5 cm (1 inch) deep	18%
	7·6 cm (3 inch) deep	32%
Average depth of preservative		3·8 cm (1·5 inch)
Checking	One major check extending deeper than the preservative-treated wood running the length of the pole.	
Decay	One decay pocket associated with the major check.	

tion and time of exposure to the chemical, the fungi-toxic dosage (concentration × time = ct) as defined by Harris (1963) was studied. Birch dowels 0.6 cm (0.25 inch) in diameter and 1.0 cm (0.4 inch) long were saturated with a malt nutrient solution and then infected with the fungus. Birch dowels were used because they were readily available and, having low natural durability, were rapidly infected by the fungus. Presumably, the resistance of the fungus to chloropicrin vapor is not affected significantly by wood species. Two matched 0.1-cm (0.04-inch)-thick wafers were split from the center of each infected dowel, providing identical test and control wafers.

Relative vapor concentrations ranging from 2.6 to 315 mg/l were obtained by preparing several solutions of chloropicrin in 10-weight machine oil, a saturated solution of butylated hydroxytoluene (BHT) and chloropicrin, and by using the vapor above pure chloropicrin at different temperatures. The vapor concentrations above the solutions were determined by gas chromatography. For each vapor concentration, wafers were suspended above the chloropicrin solutions in individual glass jars and then removed at predetermined time intervals, giving a range in concentration-time exposures at each concentration. Identical procedures were used for the test wafers and matched control wafers except that the controls were not exposed to chloropicrin vapor. The wafers were then placed in a sterile laminar-flow air bench for 12 h to permit absorbed chloropicrin to dissipate. They were then surface-sterilized by light flaming and placed in petri plates on Bacto nutrient agar. The plates were incubated at 26 C and examined after one and two weeks for any visible growth of fungus from the wafers. The shortest exposure time required to prevent growth of the fungus at each concentration was used to calculate the ct factor.

Treated pole section

The bottom 2.4-m (8 feet)-long section of a decaying pressure-treated (penta in oil) Douglas-fir pole that had been removed from service was used for this study. Table 1 lists some of the pole characteristics.

Four 2.2-cm (0.875-inch)-diameter treating holes were drilled at right angles into the center of the pole 1.5 m (5 feet) from the bottom. These holes were enlarged to 2.5 cm (1 inch) in diameter to a depth of 10.2 cm (4 inches) to provide a seat for large rubber serum caps used to seal the

TABLE 2. *Rate of chloropicrin movement through wood of different permeabilities*

Specimen	Moisture content %	Longitudinal Steady-state air permeability (Darcy's)	Time required for the vapor to move 10 and 20 cm above and below the treating zone (hours)				Extent of liquid movement (cm)	
			10 cm		20 cm			
			Above	Below	Above	Below	Above	Below
Intermountain Douglas-fir	25	0·00024	>550*	30	>550	320	2	12
Intermountain Douglas-fir	12	·00082	220	200	>550	>550	5	5
Coast Douglas-fir	27	·0035	190	95	>550	>550	5	6
3·5**	10	·0054	50	21	>550	>550	5	7·5
Coast Douglas-fir	12	·0084	190	60	>550	>550	7	7
2·5**	10	·011	10	6	75	165	7·5	10
5·5**	11	·034	1·5	0·2	24	13	8	11
6·0**	11	·088	2	0·4	14	24	8	8

* Test terminated after 550 hours; no measurable chloropicrin present.

** Permeability rating (Miller 1961).

holes. Similarly vapor sampling sites 3.8 cm (1.5 inches) long and 1.3 cm (0.5 inch) in diameter were prepared at various depths in the pole at 30.5-cm (1 foot) intervals along the pole. The pole was placed upright in a conditioning room (22 C and 11% MC) near the gas chromatograph.

One pint (475 ml) of chloropicrin, stained red with 0.5 g of Sudan IV dye, was injected through the treating holes with a large syringe. Vapor samples were taken from the sampling sites with a gas-tight syringe at various times over a six-month period. The concentration of chloropicrin at the different sites was determined by gas chromatography and plotted as a function of time to evaluate the movement and distribution of chloropicrin in the pole. The areas of these concentration-time curves were measured with a polar planimeter to determine the dosage of vapor that reached each site.

When the experiment was terminated, the pole section was cut up to ascertain the location of internal checks and decay pockets and the distribution of the Sudan IV dye.

Methods of retarding the release of vapor in wood

Two means of retarding the rate of chemical loss from wood to extend the life of the treatment were investigated. Chloropicrin was confined in polymer containers that retarded the loss of chemical, but still permitted diffusion of the vapor through the container walls; also paradichlorobenzene was dissolved in chloropicrin to lower its vapor pressure.

Two-dram, four-dram, and six-dram (7.4, 14.8, and 22.2 cm^3) polyethylene vials ("polyvials"—Van Waters & Rogers Co., catalog no. 66017) and 15.2-cm (6-inch)-long by 1.6-cm (0.625 inch)-diameter sections of Tygon tubing sealed at both ends were used as slow-release containers; one was half-filled and the other a quarter-filled to determine the effect of internal area contacted by the free liquid on permeation rates. The polyvials were exposed in conditioning rooms at successive temperatures of 22, 2, 32, and 22 C for various times; the Tygon containers were tested only at 22 C.

The loss rates per unit area and unit vial-wall thickness at each temperature and the

TABLE 3. *Lethal dosages* of chloropicrin for* Poria monticola *growing on wood*

Chloropicrin solution	Temperature (°C)	Concentration chloropicrin vapor** (mg/ℓ)	Time to kill fungus (hr.)	Lethal dosage (mgxhr/ℓ)
Pure chloropicrin	32	315	<0·033	<10
	21	180	0·15	27
Chloropicrin in oil	21 - A	112	0·36	40
Chloropicrin saturated with BHT	21	99	0·36	36
Chloropicrin in oil	21 - B	83	0·43	36
Pure chloropicrin	2	67	1·5	100
Chloropicrin in oil	21 - C	5·8	<4·5	<26
Chloropicrin in oil	21 - D	2·6	9·0	23

* Concentration - time ("ct") values.

** Concentrations for pure chloropicrin vapor determined from vapor pressures at each temperature, assuming ideal gas law applies. Other concentrations determined by gas chromatography.

"permeation constants" (Rogers 1964) were determined for the loss of chloropicrin from the polyvials.

The effectiveness of retarding the release of vapor at the treatment zone by using a slow-release container and by using a saturated solution of paradichlorobenzene (PDB) in chloropicrin was evaluated. Three 10- × 10- × 122-cm (4- × 4- × 48-inch) western red cedar timbers were prepared with vapor sampling sites at 15-cm (6-inch) intervals along their lengths. They were treated at midlength with 12 ml of chloropicrin as follows:

Timber 1. Chloropicrin containing 0.1 g Sudan IV dye;

Timber 2. Chloropicrin containing 20.8 g of paradichlorobenzene, which reduced the vapor pressure of the chloropicrin to 0.60 of that of pure chloropicrin (as determined by gas chromatography);

Timber 3. Chloropicrin sealed in a 4-dram polyvial.

The concentration of chloropicrin at each site was determined periodically by gas chromatography.

RESULTS AND DISCUSSION

Permeability specimens

The rate of chloropicrin vapor movement up and down standing Douglas-fir heartwood specimens was generally greater in wood with high air permeability values (Table 2). Capillary movement of liquid chloropicrin, as indicated by the dye distribution, was usually greater in the more permeable wood, which contributed to the permeability effect on vapor movement. Liquid movement of the chemical through the resin canals in the green intermountain Douglas-fir specimen resulted in vapor detection below the treating zone much quicker than expected from its permeability value. Chloropicrin was detected below the treating zone earlier than above the treating zone, probably because of capillary movement of liquid below the treating zone and the high density of chloropicrin vapor (5.7 × air density).

Toxicity of chloropicrin to P. monticola

At 21 C the ct values were in the range of 20 to 40 mg × h/l or 0.02 to 0.04 g × h/l for the chloropicrin concentrations studied (Table 3). The high dosage (100 mg × h/l)

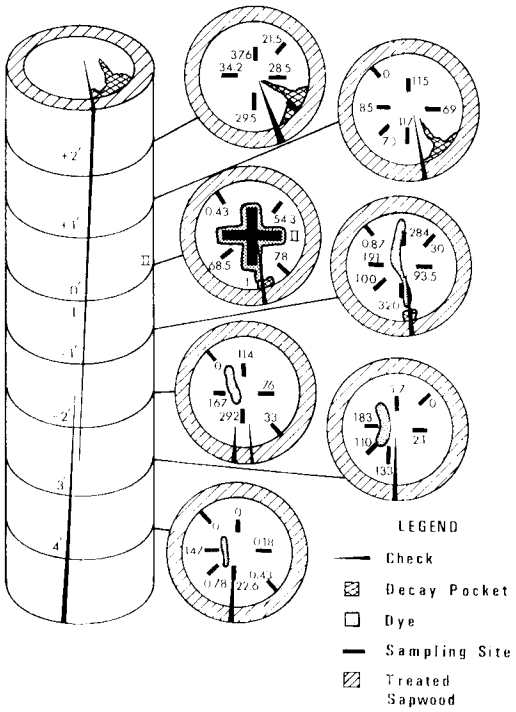

FIG. 1. Schematic diagram of pole section. Numbers at sampling sites represent dosages received (g × hr /l).

required for the fungus exposed to chloropicrin at 2 C may result from the slower respiration rate of the fungus at this temperature or from a temperature effect on the rate of vapor diffusion. At 32 C the ct value was lower than at 21 C.

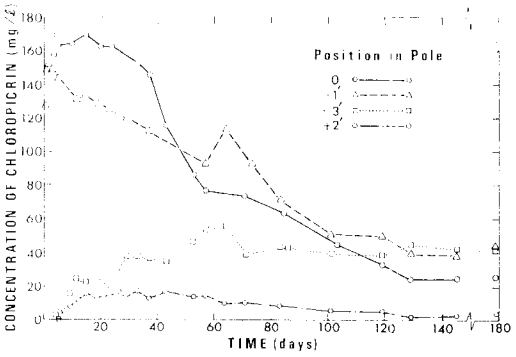

FIG. 2. Concentrations of chloropicrin vapor in the Douglas-fir pole section above and below treating hole I.

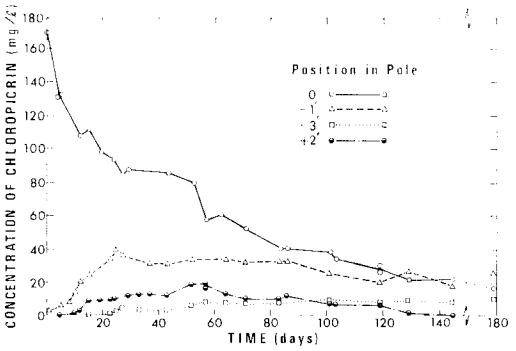

FIG. 3. Concentrations of chloropicrin vapor in the Douglas-fir pole section above and below treating hole II.

The toxic ct dosage did not appear to increase with decreasing concentration over the range of concentrations studied. In fact, the ct factors were lower than average for the two lowest chloropicrin concentrations, possibly because of toxicity of the oil vapor.

The fungal toxicity values must be used with caution, as the lethal dosage of a given chemical will vary with temperature and from one fungus to another. Some stages of fungal growth present in wood, such as chlamydospores, will require a higher dosage than growing mycelium. However, it appears that the dosages of vapor received at those locations in the pole section reached by measurable amounts of vapor are much higher than needed to control the decay of wood by *P. monticola.*

Treated pole section

The important features of the pole section, including the locations of major checks, treating sites, vapor sampling sites, the decay pocket, and the distribution of Sudan IV dye, are shown in Fig. 1. Figures 2 and 3 show the concentrations of chloropicrin vapor at various times for some of the sampling sites directly above and below treating holes I and II. The dosages of vapor received at the sampling sites, as determined by measuring the areas of concentration-time curves for all sampling sites, are included in Fig. 1. They are expressed here as g × h/liter.

TABLE 4. *Rate of chloropicrin loss from partially filled polyethylene vials*

Temperature* °C	6 Dram		4 Dram		2 Dram	
	1/2 full	1/4 full	1/2 full	1/4 full	1/2 full	1/4 full
	(Loss per cm^2 surface area per mm wall thickness in mg/h)					
22	0·124	0·117	0·098	0·095	0·064	0·070
2	0·020	0·019	0·014	0·014	0·011	0·010
32	0·329	0·503	0·325	0·323	0·206	0·219
22	0·176	0·169	0·128	0·123	0·082	0·082
	Permeation values** $x10^5$					
22	0·223	0·210	0·178	0·172	0·115	0·125
2	0·116	0·109	0·078	0·078	0·060	0·053
32	0·340	0·526	0·336	0·336	0·213	0·227
22	0·297	0·297	0·229	0·222	0·148	0·148

* Vials were cycled through these temperatures in the sequence shown.

** Cm^3 gas at standard temperature and pressure per second per cm^2 surface area per mm wall thickness per cm Hg vapor pressure difference.

The sterilant moved through the pole as a wave characterized by a time lag before chemical reached a given site, followed by a period of increasing concentration, a long period of relatively constant concentration, and a period of decreasing concentration. Chloropicrin movement was faster and vapor dosages were greater below the treating zone than above it.

The amount of chloropicrin vapor reaching the sampling sites varied greatly around the pole at each sampling level, because of the presence of the checks and the decay pocket. The transverse distribution of vapor was poor except where facilitated by the last features. Also, sampling sites associated with the vertical movement of chloropicrin liquid, as indicated by the dye, received higher dosages of chloropicrin vapor than the other sites. For example, sampling sites of Fig. 2 that were associated with a check received higher concentrations of chloropicrin vapor than those of Fig. 3 located in sound, unchecked wood.

When the study was terminated, there were still relatively high concentrations of chloropicrin in the pole. Thus, the duration of effectiveness exceeded 6 months, even under the conditions of high average temperature and high wood permeability in this study.

Methods of retarding the release of fumigant vapor in wood

Temperature had a marked effect on the rate of chloropicrin released from the polyvials (Table 4). The loss rates at 22 C were higher after the vials had been cycled at the three temperatures than for the initial test at 22 C, indicating that chloropicrin renders polyethylene more permeable with time. The larger polyvials released vapor faster than the smaller ones, even when the loss rates were corrected for wall thickness and surface area differences. Thus, it is not possible to characterize absolutely the movement of chloropicrin through polyethylene and one cannot accurately predict the rate of vapor release from any polyethylene container without first conducting some trial studies. However, the values determined here give an indication of the rates of permeation one can expect and should aid in the design of slow-release capsules.

There was no consistent relationship between the amount of chloropicrin in vials and permeation rates, which is understandable since the chemical potential of satu-