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Title: THE MOVEMENT OF CHLOROPICRIN VAPOR IN WOOD TO CONTROL DECAY

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Factors affecting the control of decay in wood with chloropicrin vapor were studied in a series of four experiments. Non-steady-state diffusion coefficients for the desorption of chloropicrin vapor from Douglas-fir heartwood wafers increased with increasing temperature and wood permeability. Longitudinal diffusion coefficients were about ten times larger than the transverse values.

The lethal dosage of chloropicrin for Poria monticola Murr. growing on birch wood was about 30 $\frac{\text{mg-hr}}{\text{l}}$ at 21°C. The fungus was more resistant to the vapor at 2°C and less resistant at 32°C than at 21°C.

An eight-foot long section of a decaying Douglas-fir pole section was treated through four holes with one pint of chloropicrin and the movement of chloropicrin vapor monitered for six months. The

treatment was effective in that the pole was sterilized and chloropicrin vapor remained in the pole more than six months even though the average temperature of the pole was high (21 ^{o}C). The distribution of chemical was uneven and inefficient as some areas received much higher than necessary dosages and other areas did not receive measurable dosages of vapor.

The release of vapor at the treating hole could be controlled by using chloropicrin confined in polymer capsules and solutions of paradichlorobenzene in chloropicrin. The duration of treatment could be effectively extended by these means, suggesting that an efficient and long lasting treatment might be realized by choice of a suitable treating hole pattern and by use of slow release methods.

The Movement of Chloropicrin Vapor in Wood to Control Decay

by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

THE MOVEMENT OF CHLOROPICRIN VAPOR IN WOOD TO CONTROL DECAY

INTRODUCTION

The standard method of treating wood members to protect them from biological deterioration is to inject fungitoxic liquids into their capillary structure under hydrostatic pressure. The ease with which fluids can be forced through this capillary network is essentially controlled by openings in the pits that connect adjacent wood cells. In softwoods, liquid movement depends on the degree of aspiration and encrustation of the bordered pit membrane and the resulting pore size distribution. Because of the relatively high viscosities of the preservatives used and surface tension effects, high pressures must be applied to force the chemical through the pit pores. The heartwood of many western softwood species is impermeable to liquids even when high pressures are applied.

A fungicidal vapor will penetrate wood more easily than liquid preservatives because of its low viscosity and the absence of liquid-vapor interfaces that must be overcome during impregnation. Since molecules of high vapor pressure chemicals will diffuse considerable distances under the vapor concentration gradient, hydrostatic pressure may not be necessary.

The remedial treatment of decaying wood products is one

promising application for vapor phase treatments. Internal decay in preservative-treated wood products, especially large members with thin sapwood is a problem. Liquid preservatives placed in poles in service cannot control this deterioration because of their limited movement through wood at atmospheric pressure. Field experiments recently conducted by the Oregon State University Forest Research Laboratory in cooperation with local electric utilities show that fumigants stopped internal decay in transmission poles and afforded some protection against reinfestation. Three chemicals that show promise for this type of treatment are the soil fumigants chloropicrin (trichloronitromethane), Vapam (sodium N-Methyl dithiocarbamate) and Vorlex (methyl isothiocyanate dissolved in chlorinated C3 hydrocarbons).

The treating procedure employed in these field experiments differs from that of conventional fumigation treatments in that the liquid chemical is placed in holes drilled in the wood member. Its vapor diffuses through the wood and, eventually, out of the structure. To be effective, the vapor must diffuse in toxic concentrations to reach the advancing hyphae of the decay fungi where sound wood is being attacked. To warrant commercial use, the vapor must remain in the wood long enough for the retreatment cycle to be economical.

The ultimate criterion for evaluating vapor phase treatments

must be the success with which wood treated in this way performs in service. Meanwhile, an understanding of the factors which influence the effectiveness of vapor phase remedial treatments will establish a scientific basis for this new wood preservation process and help to prevent its improper use. Two of these factors are the rate of vapor diffusion in wood and its fungitoxicity.

The rate of vapor diffusion through wood determines both the time required to stop decay at various locations in the structure and the duration of residual effectiveness. Some of the factors that may affect diffusion rate are: wood permeability, moisture content, grain direction and ambient temperature. The presence of decay pockets and seasoning checks also should influence the rate of diffusion and of loss of chemical from wood in service. Since this treatment relies on vapor to kill the decay organisms at large distances from the treating site where the concentration of pesticide present in the wood may be very low, knowledge of the minimal dosage of the vapor required to kill the fungi is important.

To investigate factors influencing the movement of chloropicrin through wood to stop decay, the following experiments were carried out:

1/ The effects of wood permeability, moisture content, grain direction and temperature on the non-steady-state diffusion coefficient were determined for the desorption of chloropicrin from small Douglas-fir wafers.

2/ The lethal dosage ($\frac{mg\text{-}hr}{l}$) of chloropicrin for the decay fungus Poria monticola Murr. was studied for the fungus growing on wood.

3/ The movement of chloropicrin in a decaying and checked Douglas-fir pole section was monitored for several months to obtain information on its distribution and duration.

4/ Methods of improving the efficiency of this treating method and of extending the duration of protection by retarding the release of fungitoxic vapor in wood were evaluated.

BACKGROUND

Vapor Phase Preservative-Treatment of Wood

Several investigators emphasize the potential of vapor phase treatments for the plasticization (37), dimensional stabilization (2, 3) and preservation (1, 37) of wood. They point out that wood can be impregnated more easily with chemicals in their vapor phase than in their liquid phase for the following reasons:

1/ The viscosity of a vapor is much lower than that of the corresponding liquid permitting much easier flow of the chemical through wood's capillary structure.

2/ There are no liquid-vapor interfaces to overcome, permitting easier passage of the chemical through the wood structure, particularly through the pit membrane pores.

3/ The intrinsic mobility of vapor molecules is much higher than that of liquid molecules permitting significant mass transfer by diffusion processes.

They also discuss the disadvantages of such a treatment:

1/ Large retentions of chemical, if required, are difficult if not impossible to obtain in a reasonable time.

2/ Absence of a physical mechanism (e.g., capillary force) to hold the chemical in wood may mean that effectiveness of the treatment will be shortlived unless means of fixing the chemical in wood or retarding the vapor loss from wood can be found.

Until recently, the application of vapor phase treatments to the protection of wood from decay organisms was limited mainly to disinfestation of wood by fumigation (27, 32, 22). Wood covered with a vapor barrier was exposed to a fumigant. Very high vapor pressure chemicals (e.g., methyl bromide) which do not interact significantly with wood, were chosen so the vapor would penetrate the wood rapidly (28, 22). Upon removal of the vapor barrier the chemical dissipated rapidly providing no long-lasting protection.

This concept was improved upon by placing soil fumigants in holes in wood (33, 21, 15, 16, 17, 18, 19, 20). Not only were the decay organisms killed, but residual protection against reinfestation was provided for several years.

In tests on decaying Douglas-fir transmission poles, Hand et al. (21) found that one pint of Vapam was sufficient to treat a pole effectively; one-half pint was ineffective. The chemical provided residual protection for about four years. Graham et al. (15, 16, 17, 19) found in field tests of decaying transmission poles that Vorlex and chloropicrin eliminated the fungal population in Douglas-fir poles within two years; Vapam was slightly less effective. A temporary wrap did not improve the effectiveness of Vapam. They also found, in screening tests using small wood blocks, that chloropicrin was more toxic to Poria carbonica Overh. than Vorlex and that both were

more effective than Vapam. Vapam was very mobile at 22°C but virtually immobile at 2°C. Graham (20) estimates a pole retreatment cycle of not less than five years.

Experiments on sound pole sections under laboratory conditions (18, 19) indicated that chloropicrin moved faster and more uniformly than Vapam both above and below the treating zone. Two to four months were required for movement four feet below the treatment zone by both chemicals but there was an important gravity effect in that vapor moved approximately twice as fast below as above the treatment zone.

Factors Affecting Diffusion of Vapor in Wood

Diffusion involves the spontaneous movement of one material through another from a zone of high concentration to one of low concentration. Diffusion of a vapor through wood may occur in two ways: by vapor diffusion through the void structure of wood and by bound or sorbed diffusion through the cell walls in series with free vapor diffusion through the cell lumens (43).

Vapor diffusion through wood's capillary structure involves relatively free movement through the large cell lumens with little interaction between the vapor molecules and the lumen surface. This movement is in series with hindered diffusion through the pit chambers and minute pit membrane pores resulting from the greater

interaction (i.e., sorption) between the vapor molecules and wood (43). The driving force for this type of diffusion is the vapor pressure gradient across the wood. Bound diffusion involves solution of the vapor molecules in the cell wall, diffusion of the molecules through random molecule jumps from site to site within the cell wall and finally desorption of the molecule from the cell wall (44). The driving force in this case is the concentration gradient of dissolved vapor across the cell wall.

Presumably, bound diffusion will be important if the chemical dissolves readily in wood (31). In addition, chemicals soluble in water may diffuse into cell walls if the wood is at a high enough moisture content (43). For example, glycerol does not enter extruded viscose fibers with an equilibrium moisture content corresponding to relative water vapor pressure less than 0.4, but will diffuse into wetter fibers (23). Any factors that affect either free vapor or bound liquid diffusion will influence the time required for a fungitoxic vapor to reach different positions in wood and for the vapor to dissipate.

An increase in temperature should result in an increase in the rate of vapor diffusion. The diffusion coefficients of water through wood during drying increase exponentially with temperature (42, 43, 6). This temperature dependence is attributed to the increase in vapor pressure with temperature and the resulting

steeper concentration gradient in the wood (43). In addition, there is some evidence that the diffusion coefficient (D) is temperature dependent. Elers (10) found a slight increase in D with temperature for the steady-state diffusion of ethylene in wood even though the same concentration gradient was maintained for all temperatures. Tarkow and Stamm (45) also noted a slight temperature effect for the diffusion of carbon dioxide through wood. This may reflect the effect of temperature on the physical adsorption of vapor molecules by the wood. At higher temperatures, less adsorption occurs and more vapor molecules are free to diffuse through the wood (28).

The permeability of wood, a measure of the ease with which a fluid will move through wood under hydrostatic pressure, may be related to rate of diffusion of vapor molecules through the capillary network of wood (41, 47). Pressure permeability is described by Poiseuille's law, which states that the volumetric flow rate varies with the fourth power of the capillary radii. Thus, the flow rate is controlled by the pits between cells and is dependent on the pit membrane pore size distribution; fluid flow through the smaller pores will be negligible.

Diffusion flow also occurs through the pits but the rate of movement now depends more on the total effective cross section of the pit membrane pores than on the pore sizes (41). If the pore

radii are small in comparison with the mean free path of the vapor molecules, however, the movement of vapor will be hindered and the pore size distribution may become important (41, 5). Although pressure permeation and diffusion occur by different processes, they are both controlled to a large extent by the same anatomical features of wood and may be related to each other.

Yokota (47) determined the diffusion coefficients for helium through several wood species and reported that woods of reputed low permeability also had low diffusion coefficients. Choong and Skaar (8) found the drying diffusion coefficients for redwood sapwood to be higher than those for heartwood, which may reflect permeability differences. However, Choong and Fogg (7) found no significant differences between the moisture diffusion coefficients of sapwood and heartwood specimens of six different tree species even though the air permeabilities of the woods tested varied considerably.

The diffusion rate will be much higher longitudinally than transversely because a vapor diffusing along the grain has fewer pits to pass through or, if cell wall diffusion is significant, fewer cell walls to diffuse through in moving a given distance. Yokota (47) found the ratio of longitudinal to transverse rates for the diffusion of helium through several Japanese wood species to be about 100. Elers (10) also found longitudinal diffusion to be about 100 times transverse diffusion for the movement of ethylene through

eastern hemlock heartwood. However, Tarkow and Stamm (45) found longitudinal carbon dioxide diffusion to be almost 1,000 times as great as transverse diffusion. The ratio for the diffusion of water through wood may vary from less than five to close to 75 depending on the wood density, the temperature and the air circulation around the wood (40, 7, 8). Most investigators find radial diffusion to be slightly faster than tangential diffusion although the differences are seldom statistically significant (4, 42, 10, 7).

Moisture content of wood may affect the diffusion of vapor through wood in two ways. The permeability of wood generally increases with decreasing moisture content below the fiber saturation point, presumably because the shrinkage occurring in the microfibrils of the pit membranes results in larger pores (41). At moisture contents close to the fiber saturation point, water condenses in the pit membrane pores, reducing the effective area for diffusion. Thus, the diffusion coefficients for non-swelling gases such as carbon dioxide (45) and helium (47) were lower at higher wood moisture contents. However, if the vapor is soluble in water, or swells wood and diffuses through the cell wall, the diffusion rate may increase with higher moisture contents. The transverse moisture diffusion coefficient increases exponentially with moisture content in wood (44).

Fungitoxicity of Chloropicrin

Since chloropicrin probably moves through wood at relatively low concentrations in vapor phase treatments, the chemical must be very toxic to the decay organisms if the treatment is to be effective. For example, the concentration of chloropicrin in air saturated with the fumigant at 20°C is only about 170 mg/l (46); the concentration of vapor in wood at locations remote from the original treatment zone will be lower than this saturation value. The minimum lethal concentration and exposure time required to kill the decay organism must be known to evaluate the effectiveness of a vapor treatment.

Unfortunately, there is very little published information on the toxicity of chloropicrin to wood decay organisms. Graham et al. (15) found that .03 ml (i.e., 49.6 mg) of chloropicrin placed in a hole at mid-length of side-coated one- by one- by four-inch long Douglas-fir heartwood blocks infected at both ends with Poria carbonica Overh. was sufficient to destroy the fungus; as little as 1.24 mg of chloropicrin resulted in some killing. Partridge (32) exposed oak sections infected with the oak wilt fungus (Ceratocystis fagacearum (Bretz) Hunt) in a fumigation chamber containing one ml of chloropicrin (presumably liquid) per liter of space. Since this corresponds to 1,650 mg/l or more than enough liquid to

saturate the chamber with vapor, the concentration can be assumed to be about 170 mg/1. After three days of exposure, no fungus could be isolated from the wood.

Chloropicrin has been used extensively to control soil microorganisms so there is more information available on its toxicity to soil fungi. Godfrey (12) found that one and one-quarter cc of chloropicrin in a four gallon jar of soil (i.e., 136 mg/1) destroyed Fusarium, Armellaria and several other soil fungi species. Newton et al. (30) reported that one cc in 195 1 of space (8.5 mg/l) was sufficient to destroy the vegetative stages of several soil fungi, but concentrations of one cc in 54.5 1 or higher (18.3 mg/l) were required to kill the sclerotial stages. The times of exposure of the fungus to the chloropicrin were not given in most of these papers.

Since the amount of chloropicrin required to kill a fungus depends on the concentration of chemical and the duration of exposure, a useful way of expressing the lethal dosage is as a concentration - time ("ct") factor (28, 22). This is usually expressed as the concentration of fumigant vapor present in milligrams per liter multiplied by the exposure time (hours) required to kill the organism. This "ct" factor should be relatively constant for high concentrations of vapor. However, at low concentrations the "ct" value will increase with decreasing concentration (12) until at some low concentration of chemical, the organism will be able to survive indefinitely and the "ct" value will be arbitrarily large.

METHODS AND MATERIALS

I Non-Steady-State Diffusion of Chloropicrin from Wood

Non-steady-state diffusion is defined by Fick's second law of diffusion. For unidirectional diffusion, this takes the form:

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} \quad \text{----------} \quad (1)$$

where $\frac{dC}{dt}$ is the change of concentration of the diffusing species in the medium with time, D is the diffusion coefficient and $\frac{d^2C}{dx^2}$ is the second derivative of concentration with respect to distance. This equation can be solved if D is not concentration dependent and certain specified boundary conditions apply. Assuming that the slab has a uniform concentration of C_o of chemical before the experiment (t=o), and that the concentration of chemical at the surface during the process of experiment is in equilibrium with the surroundings:

$$C = C_o \text{ for } o \leq x \leq L \text{ at } t = o$$

$$C = o \text{ for } x = o, L \text{ at } t > o$$

Equation (1) has the solution:

$$C(x, t) = \frac{4C_o}{\pi} \sum_{n=o}^{\infty} \frac{1}{2n+1} \sin \frac{(2n+1)\pi x}{L} \exp - \left(\frac{(2n+1)\pi}{L}\right)^2 Dt \quad --(2)$$

where C (x, t) is the concentration of vapor in the slab as a function of depth in the slab (x) and time (t) (26). In practice, it is easier

to measure the total amount of substance that has been given off than to measure the local concentrations. Thus, the following relationship, which expresses the average concentration in the slab at time t, $\bar{C}(t)$, is used:

$$\bar{C}(t) = 1/L \int_{o}^{L} C\,dx = 8C_o \sum_{n=o}^{\infty} \frac{1}{(2n+1)^2} \exp - \left(\frac{(2n+1)\pi}{L}\right)^2 Dt \quad (3)$$

This equation converges rapidly as t becomes large and can be approximated by the first term:

$$\frac{\bar{C}(t)}{C_o} = 8/\pi^2 \exp - \frac{\pi^2 Dt}{L^2} \quad \text{----------} \quad (4)$$

By taking logarithms of both sides:

$$\ln \frac{\bar{C}(t)}{C_o} = \ln 8/\pi^2 - \frac{\pi^2 Dt}{L^2} \quad \text{----------} \quad (5)$$

The diffusion coefficient D can be determined from the slope of the plot of

$$\ln \frac{\bar{C}(t)}{C_o} \text{ vs } t \text{ for large values of } t.$$

To apply equation (5) and determine D, the boundary conditions were met by equilibrating wood wafers over saturated chloropicrin[1/] vapor for some time then monitoring (by weighing) the loss of

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1/ Larvacide 100, certified 99% chloropicrin. Morton Chemical Co., Chicago.

chloropicrin from the specimens exposed to a near zero concentration of vapor. The wafers were sealed on all except two opposing faces to limit vapor movement to one direction in the wood. The saturated vapor condition was used because the amounts of chloropicrin adsorbed by wood exposed to lower vapor pressures were too small to measure the weight change accurately with the balance used which has a tolerance of $\pm$.001 gm. Capillary condensation may occur during this equilibration process but should be limited to the smallest capillaries so that the desorption process should still be diffusion controlled.

(i) Test Specimens - Selection and Characterization

Douglas-fir heartwood specimens were cut from three green freshly sawn planks and from five cm square pieces that had been stored for several years in a constant temperature and relative humidity room in which wood attained a moisture content of 12 percent. The green planks were selected from mills in the coastal and intermountain regions of Oregon to provide wide differences in permeability. The stored material had been rated as to preservative treatability based on creosote penetration patterns in matched blocks (29).

Sections of the green wood were allowed to equilibrate to nominal moisture contents (MC's) of 20%, 12% and 6% in constant

temperature and relative humidity rooms. To minimize drying defects in wood dried to lower moisture contents, the pieces were exposed first to the less severe drying conditions of the higher equilibrium moisture content rooms.

The permeabilities of the specimens equilibrated to 12% MC were evaluated by the "sink-float" test (13) and by steady-state air permeability measurements.

The "Sink-float" Test

Specimens 1.25 cm in diameter and 1.25 cm long were removed with a plug cutter from each piece of Douglas-fir heartwood and oven-dried. The specimens were submerged in distilled water in a dessicator and aspirated at a vacuum corresponding to 27 in. of Hg for six minutes and then the dessicator was vented to the atmosphere. Specimens that sank were rated permeable (P). The specimens were aspirated for an additional 20 minutes. Specimens that sank after venting were rated intermediate (I) in permeability while those that floated were rated refractory (R).

Steady-State Air Permeability Measurements

Longitudinal, radial and tangential specimens were sawn from each piece of wood. The longitudinal specimens were three cm thick in the direction of air flow whereas the radial and

tangential specimens were 0.5 cm thick. Specimens were side- and edge-sealed with paraffin to permit air flow only in the desired direction.

All measurements were made with the air permeability apparatus shown schematically in Figure 1. A nearly constant pressure drop (ΔP) measured by the manometer, was maintained across the specimen during a test by means of the large volume vacuum reservoir. Air flow through the specimen under this pressure difference was measured by the flowmeter. The "specific permeability" coefficient (kg) in darcies was obtained using the integrated form of Darcy's law as adapted for gas flow (9, 39):

$$kg = \frac{1.013 \times 10^{8}}{1.3 \times 10^{3}} \quad \frac{QL\,\eta\,(Pa-\Delta P)}{A\Delta P\,(\bar{P})} \qquad \text{--------} \quad (6)$$

where Q is the air flow rate in ml per second measured at the pressure Pa-ΔP, Pa is atmospheric pressure in mm of Hg, L is the thickness of the test specimen in cm, η is the viscosity of air at 20°C.

$$(1.81 \times 10^{-4} \quad \frac{\text{dyne-sec}}{\text{cm}^2})$$

A is the area of the test specimen in cm^2 through which air is being drawn, $\bar{P}$ is the average pressure across the specimen in mm of Hg, and ΔP is the pressure difference across the test block in mm of Hg. The constant 1.013×10^{8} converts kg from cm^2 units to darcies (39) and 1.3×10^{3} converts pressure measured in mm Hg

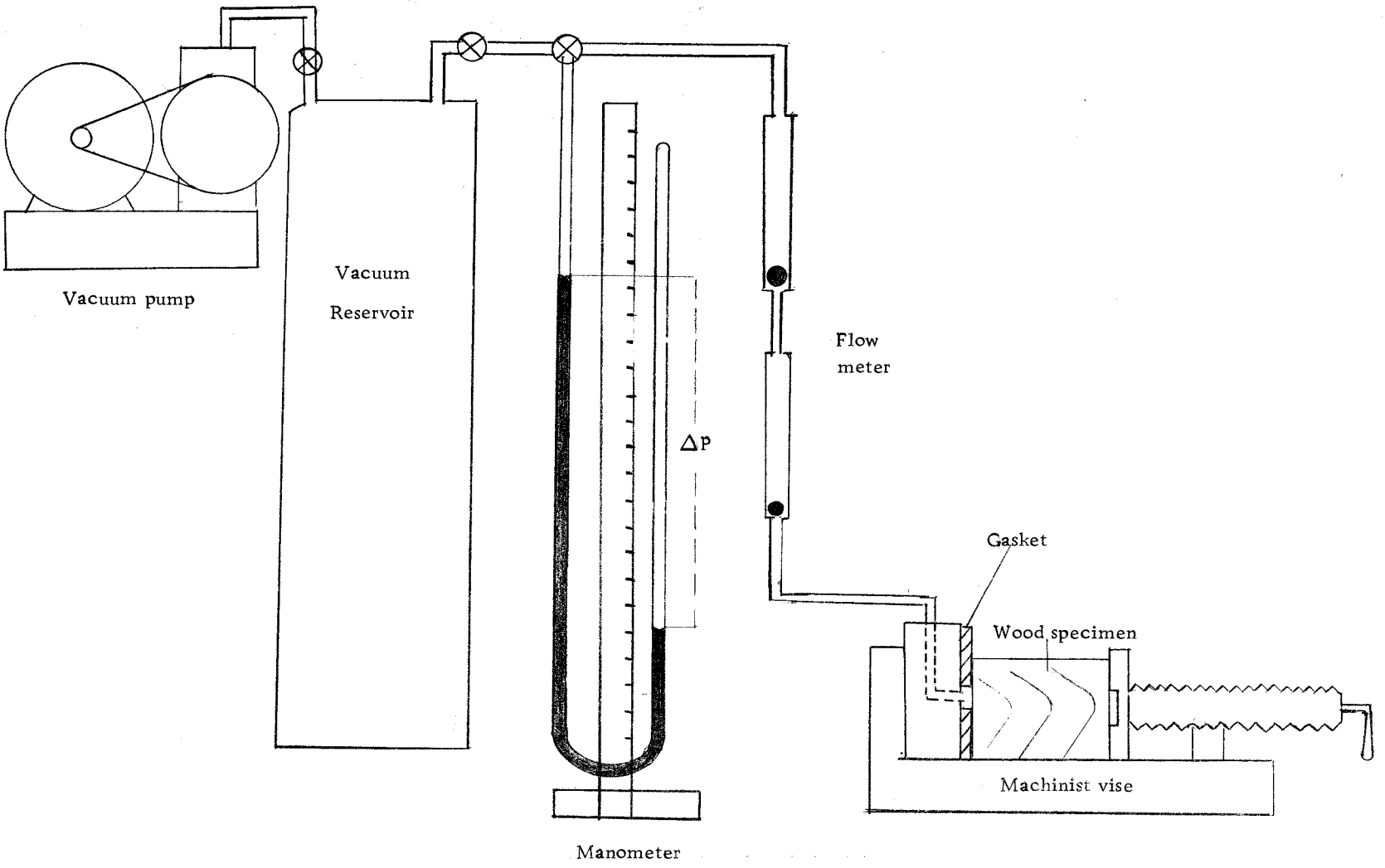


Figure 1. Schematic presentation of steady-state air permeability apparatus for wood.

to dynes/cm^2.

(ii) Test Specimens - Preparation and Conditioning

Diffusion wafers, 5.1 cm square and 1.0 cm thick, were cut from the freshly sawn wood to provide a set of longitudinal, radial and tangential wafers at each moisture content (MC). Three sets of wafers were prepared from the 12% MC wood to be tested at ambient temperatures of 11°, 21° and 32°C.

Similarly, longitudinal, radial and tangential wafers were cut from the treatability-rated wood for testing at 12% MC and 21°C. Matched wafers were prepared in all cases as controls to correct for weight changes during desorption due to slight moisture content fluctuations.

Light weight aluminum foil was bonded to the sides and edges of the wafers with a phenol-resorcinol adhesive [2/] to limit vapor diffusion to one direction. Although this coating, of several coatings tested, was the most resistant to the corrosive effects of chloropicrin, the aluminum foil was corroded after long exposure times. Adsorption of chloropicrin by the coatings tested is shown in Appendix I.

2/ Cascophen LT-68-0 timber lamination adhesive. Bordon Chemical Co.

Tests at temperatures of 11°C and 32°C and at specimen moisture contents of 6% and 20% were conducted in an Aminco climate chamber with an air circulation rate of 4.2 m^3 per minute (150 ft^3 per min). Because of the long time required for each test, those at 21°C and 12% MC were made in a standard room at approximately these conditions where air was blown over these test specimens with a large fan to simulate the air circulation conditions of the Aminco cabinet.

For each test, specimens with their matched controls were conditioned until they had reached a constant weight.

(iii) Non-Steady-State Desorption Measurements

When the specimens were equilibrated, they were weighed on top loading Mettler P-160 balances in the Aminco cabinet and standard room. Air movement in the Aminco cabinet made it necessary to shut off the power to take the weighings. Since weighings were made through ports equipped with polyethylene gloves without opening the cabinet, conditions did not change appreciably in the cabinet during weighing. Test specimens were sealed in a desiccator within the conditioning cabinet and standard room. The desiccator was lined with filter paper equilibrated to test conditions and saturated with chloropicrin. Control specimens were placed in a second desiccator without chloropicrin. The

specimens were allowed to adsorb chloropicrin for various times depending on the ambient temperature. Exposure times were about the maximum possible before chloropicrin began to corrode the aluminum foil.

The specimens were removed from the desiccators, weighed immediately to determine the total chloropicrin pickup, then weighed periodically to obtain the desorption curves. Changes in the test specimens' weights due to fluctuations in the conditioning atmosphere were corrected for by the weight changes in the matched controls. At the end of each test, the wood moisture content at each condition was determined by oven-drying pieces cut from the centers of the controls.

(iv) Supplementary Test

When specimens equilibrated to 20% MC were placed over chloropicrin, the coating was destroyed by the vapor in a very short time. When specimens were equilibrated to 12% MC, coated, then re-equilibrated to 20% MC and placed over chloropicrin, the coating was again destroyed very rapidly. Since this corrosion made it impossible to study the effect of moisture content on non-steady-state diffusion as planned, a method that did not require movement of vapor in only one direction was used. This was accomplished by injecting liquid chloropicrin into the center of wood specimens and

by analysing the concentration of chloropicrin vapor at different distances from the treatment zone using a gas chromatograph as will be described later. This approach also was used to evaluate the influence of wood permeability on the movement of chloropicrin vapor for comparison with the results of the diffusion study.

Two 5- by 5- by 120 cm long end-matched specimens were prepared from each of two green heartwood planks of coastal and intermountain Douglas-fir. One specimen of each type of Douglas-fir was equilibrated to 12% MC while the other was kept green by a polyethylene wrap and storage in a cold room. Four additional specimens of similar specific gravity but widely varying permeabilities were prepared from the treatability-rated wood.

Holes 1.25 cm in diameter and 3.5 cm deep, were drilled into the center of one face of each specimen 10 and 20 cm above and below mid-length. 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 long. The specimens were sealed completely with paraffin wax to minimize moisture content changes. Four ml of liquid chloropicrin containing 0.5 percent Sudan IV dye were injected with a syringe and hypodermic needle at midlength in each specimen. The specimens were stored in a conditioning room at 22°C and 11% EMC. The concentration of vapor reaching each sampling zone was measured periodically

by gas chromatography.

All measurements of chloropicrin gas were made using a Varian Aerograph model 200 gas chromatograph equipped with a flame ionization detector and a strip chart recorder to record the detector's response. A column capable of resolving ethanol and chloropicrin peaks was prepared by packing a 1.25 meter teflon tube with Chromosorb Q solid support containing 7% Carbowax 20M liquid support.

In quantitative analysis using the gas chromatograph there are several potential sources for variability in detector response. These include faulty or inconsistent injection technique and variation in temperature, gas flow or voltage. The conventional method of correcting for this variation is to include in all test samples an "internal standard", a fixed proportion of a known compound, which elutes from the column at a different time than the substance measured. If injections are of equal size, the internal standard will give an identical response (peak area) for all injections providing there is no variation in detector response. The variations in the internal standard peak areas are used to correct the response peaks of the substance studied.

This approach would not work for my study as any substance mixed with the chloropicrin liquid initially can not be expected to diffuse through wood as a vapor maintaining the same relative

concentration with respect to the chloropicrin vapor. Instead, I incorporated ethanol as a "pseudo internal standard" with each chloropicrin vapor sample. 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. The amount of ethanol drawn into the syringe should be constant if the temperature remains constant. The ratio of chloropicrin peak area to ethanol peak area for each injection (Rt) permitted corrections to be made for the detector response variability. The actual concentration of chloropicrin for each injection was determined by comparing the Rt values with the ratio of chloropicrin peak area to ethanol peak area for saturated chloropicrin vapor (Rs). Since the concentration of saturated chloropicrin vapor at room temperature is about 170 mg/l, the concentration for a given injection is given by

$$\frac{(Rt)}{(Rs)} \times 170 \text{ mg/l.}$$

II Fungitoxicity of Chloropicrin

The lethal concentration - time, "ct", dosage for the wood decay fungus Poria monticola Murr. was determined by exposing infected wooden wafers to different concentrations of chloropicrin vapor for various times. This organism was studied because of its

importance as a wood pole decayer (11) and its rapid growth rate. The test wafers were prepared from birch dowels 0.64 cm in diameter and one cm long, which had been saturated with a malt nutrient solution then inoculated with the fungus. When the fungus had completely infested the dowels, two matched one mm thick wafers were split from the center of each dowel.

Relative vapor concentrations of chloropicrin 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) in chloropicrin, and by using the vapor above pure chloropicrin at different temperatures. The vapor concentrations above these solutions were determined by gas chromatography.

The flow diagram for the steps in the fungitoxicity test are shown in Figure 2. Identical procedures were used for the test wafers and matched control wafers except that the controls were not exposed to chloropicrin vapor. This procedure ensured that the fungus was originally viable, that none of the procedural steps was responsible for killing the fungus and, for the chloropicrin-oil solutions, that the oil vapor was not toxic to the fungus.

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

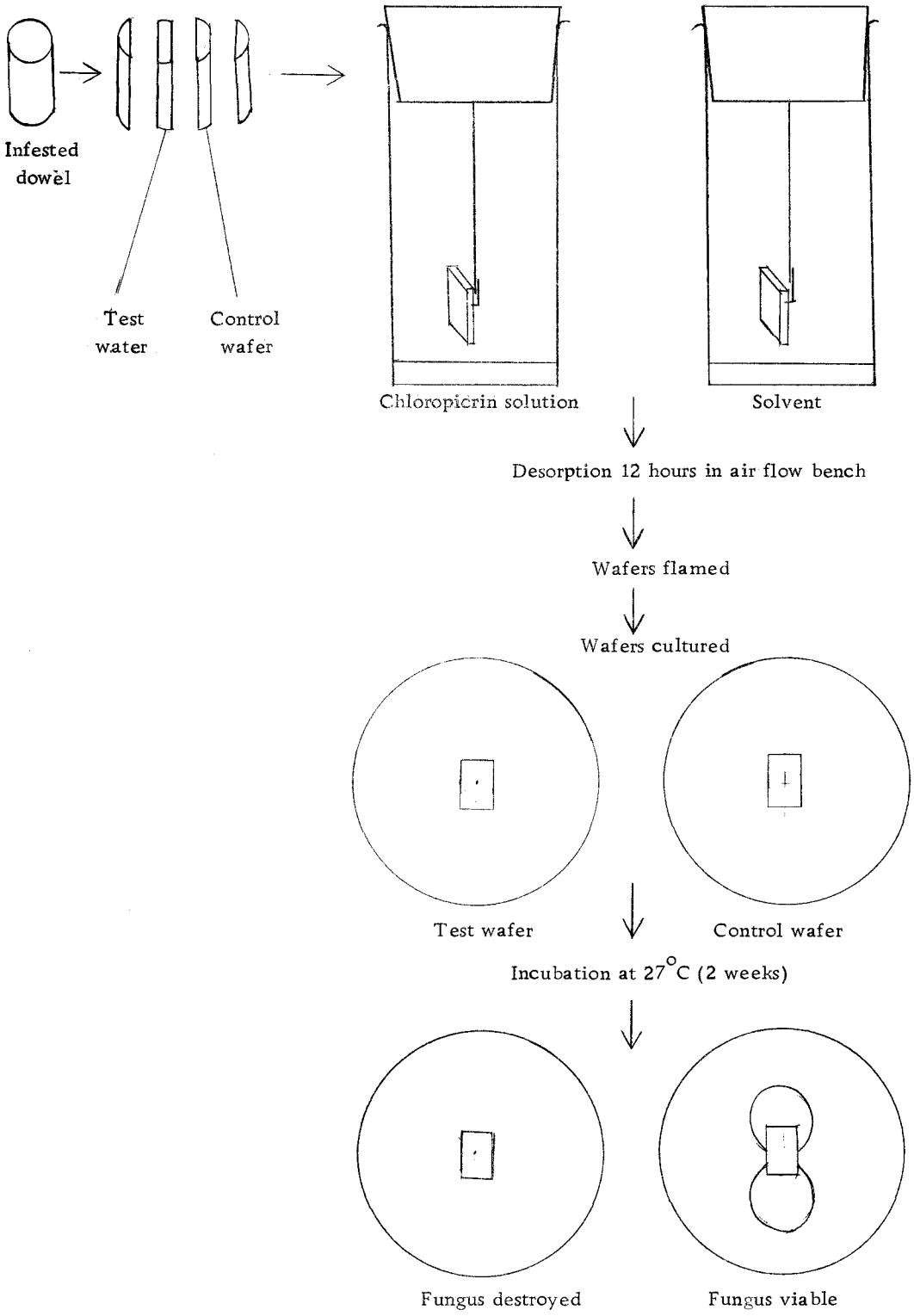


Figure 2. Flow diagram for chloropicrin fungitoxicity test.

exposures at each concentration. They were placed in an air flow bench for 12 hours to permit adsorbed chloropicrin to dissipate, then they were lightly flamed to destroy surface contaminates and placed in petri dishes on Bacto nutrient agar to which was added three drops of 25% lactic acid per ten ml of agar to retard bacterial growth. The plates were incubated at 27°C and examined after one and two weeks for viable fungi. The shortest exposure time required to kill the fungus at each concentration was used to calculate the "ct" factor.

III Movement of Chloropicrin Vapor in a Typical Douglas-fir Pole Section

The bottom 2.4 m long section of a decaying pressure-treated Douglas-fir pole that had been removed from service was used for this study. Some characteristics of the pole were as follows:

Diameter		35.6 cm
Specific gravity (OD/Green basis)		0.45
"Sink-float" permeability rating for sound heartwood		Permeable
Average moisture content at start of test	2.5 cm deep	22%
	7.5 cm deep	40%
Average moisture content at end of test	2.5 cm deep	18%
	7.5 cm deep	32%
Depth of preservative		3.8 cm

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. Bioassays showed a viable decay fungus growing in this area.

Four 2.2 cm diameter treating holes were drilled at right angles into the center of the pole 1.52 m from the bottom. These holes were enlarged to 2.5 cm in diameter to a depth of 10 cm to provide a seat for large rubber serum caps used to seal the holes. Vapor sampling sites 3.8 cm long and 1.25 cm in diameter were prepared at various depths in the pole at 30.5 cm intervals along the pole, by drilling a 1.25 cm diameter hole to the desired depth then expanding the hole to 1.6 cm forming a seat for a serum cap 3.8 cm from the bottom of each hole. Serum caps were bonded in place with a silicone rubber sealant. The pole was placed upright in a conditioning room (22°C and 11% EMC) near the gas chromatograph.

One pint (475 ml) of chloropicrin, stained red with 0.5 gm of Sudan IV dye, was injected through the serum caps at the 1.52 m level of the pole 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 liquid chloropicrin as indicated by the dye. Thirty-two small wood plugs from points in the pole that received low dosages of chloropicrin were bioassayed to detect the presence of viable fungi.

IV Methods of Retarding the Release of Fumigant Vapor in Wood

One means of retarding the rate of chemical release is to confine the liquid in polymer containers that permit a limited diffusion of the chemical through the walls. If one considers the wall of the container to be a plane membrane, a permeation constant can be determined for a given fumigant and polymer. The flow rate of vapor per unit area of the membrane (J) under steady-state conditions is given by Fick's first law:

$$J = -D \frac{dC}{dx} \qquad \text{----------} \qquad (7)$$

where D is the diffusion coefficient and $\frac{dC}{dx}$ is the concentration gradient across the membrane. If D is independent of concentration and if the concentration gradient in the membrane is linear, i.e.,

$C(x) = kP$ where P is the vapor pressure inside the container, then:

$$\frac{dC}{dx} = \frac{kP}{L} \quad \text{---------- (8)}$$

where L is the membrane thickness. Thus:

$$J = -\frac{Dk\,P}{L} . \quad \text{---------- (9)}$$

Since C and k are usually not known, this is often expressed as:

$$J = \frac{pP}{L} \quad \text{---------- (10)}$$

where J is expressed as cm^3 of gas at standard temperature and pressure passing per second through one cm^2 surface area of the membrane for L = one mm and P = one cm of mercury; p is designated the "permeation constant" (26).

The rate at which a chemical permeates a membrane is temperature dependent in two ways. The vapor pressure of the chemical is higher at higher temperatures resulting in a steeper concentration gradient across the wall, and the diffusion coefficient is temperature dependent and will be higher for higher temperatures. Calculation of the permeation constant takes the former effect into account since it is expressed as permeation for one cm Hg pressure difference. The latter effect can be used to determine the temperature coefficient of the permeation constant (i.e., the heat of activation Q for the process, as defined by:

$$p = p_o \exp(-Q/RT) \text{ or } \log p = -2.303\,(Q/RT) + \text{Constant.} \quad (11)$$

Q is determined from the slope of the plot of Log p vs 1/T). Thus, by determining the permeation constant for a given system and the temperature dependence of the permeation constant, it should be possible to design containers for a given situation, that will generate fumigant at a predictable rate.

The loss of a fumigant from wood can also be retarded by dissolving some substance in the fumigant to lower its vapor pressure. For an ideal solution, the vapor pressure of the volatile component is given by Raoult's law:

$$P = PoX \quad (12)$$

where P is the vapor pressure of the component over the solution, Po is the vapor pressure of pure fumigant and X is the mole fraction of fumigant in the solution.

If a significant amount of a chemical can be dissolved in the fumigant prior to treatment, the effectiveness of the treatment might be extended, especially so if the dissolved chemical has some fungitoxic properties of its own.

(i) Polymer Slow Release Capsules

(a) Polyethylene Vials. Two dram, four dram and six dram (7.4, 14.8 and 22.2 cm^3) translucent polyethylene vials (polyvials) for neutron activation analysis (Van Waters and Rogers Catalogue

66017) were used as slow release containers for chloropicrin. Vorlex and Vapam were also studied for comparison.

Wall thickness and surface area of each vial were measured. Two vials of each size were used for each fumigant; one was half-filled and the other quarter-filled to determine the effect of internal area contacted by the free liquid on permeation rates. The vials were heat-sealed and weighed periodically to determine the loss of fumigant within $\pm$ .001 gm. The vials were exposed in conditioning rooms at successive temperatures of 22^{o}, 2^{o}, 32^{o} and 22^{o}C for various lengths of time depending on the vapor evolution rate. The experiment was terminated after 48 days when some vials were empty.

From the slopes of the weight loss vs time curves for each vial, fumigant and temperature, the total loss rates and loss rates per unit area and unit vial wall thickness were determined in mg/hr. The permeation constant was calculated only for chloropicrin as the vapor pressure of the Vorlex formulation was not known and no Vapam was lost from the vials. The temperature dependence of the permeation constant for chloropicrin was also determined by plotting log p vs 1/ T for the different vials. After the test, each vial originally containing chloropicrin was cut into three pieces and the density of the plastic determined by water immersion.

(b) Tygon Tubing Containers. Containers 18 cm long and 1.6 cm in diameter were prepared by collapsing Tygon tubing to force out all the air then sealing the ends with corks coated with silicone rubber sealant. When the sealant had cured, liquid fumigant was injected into the tube with a syringe and the needle hole sealed with a hot soldering iron. The loss rates of the fumigants at 22°C were determined by weighing the tubes periodically.

(ii) Fumigant Solution

A saturated solution of paradichlorobenzene in chloropicrin was prepared and the chloropicrin vapor pressure reduction determined by gas chromatography.

(iii) Comparison of Slow-release Methods in Wood

Three 10- by 10- by 120 cm long western redcedar timbers were prepared with vapor sampling sites at 15 cm intervals along their lengths. They were treated at mid-length with 12 ml of chloropicrin as follows :

Timber 1: Chloropicrin containing 0.1 gm Sudan IV dye.

Timber 2: Chloropicrin containing 20.8 gm of paradichlorobenzene.

Timber 3: Chloropicrin sealed in a four-dram polyvial.

For Timber 3, I calculated the wall thickness required to ensure vapor release from four-dram polyvials for about four months at an average temperature of 22°C (6.4 mg/hr). The desired wall thickness (.071 cm) was obtained by forcing the vial over a cylindrical wooden

shaft centered in a lathe and turning off excess plastic.

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

RESULTS AND DISCUSSION

Non-Steady-State Diffusion Study

Effect of Temperature

In most cases, the diffusion coefficient (D) at 12% MC was higher at higher temperatures (Table 1). This increase usually was much greater between 21° and 32°C than between 11° and 21°C. The difference in surface emissivity of specimens tested in the Aminco cabinet and the standard room may have been an important factor affecting the test results; i.e., the surface resistance to the desorption of chloropicrin from wafers tested in the standard room at 21°C may have slowed down their total diffusion rates.

The temperature effect undoubtedly results from the increasing vapor pressure of chloropicrin with increasing temperature and, possibly, from the effects of temperature on sorption. The vapor pressures of chloropicrin at the three test temperatures are as follows (46):

11°C	11.5	mm Hg
21°C	20	mm Hg
32°C	35	mm Hg

This effect will be an important factor in treating wood products in service as daily and seasonal temperature variations will influence

Table 1. Non-Steady-State Diffusion Coefficients for the Desorption of Chloropicrin from Douglas-Fir Wafers at Different Temperatures, Moisture Contents and Grain Directions.

Moisture content %	Direction of flow 1/	Diffusion coefficient (D) $(\frac{cm^2}{sec} \times 10^6)$ at temperature shown 2/		
		11°C	21°C	32°C
		Coast Douglas-fir 1		
	L		2.76	
6	R	-	0.10	-
	T		0.24	
	L	1.47	2.67	2.99
12	R	0.15	0.19	0.37
	T	0.16	0.16	0.37
		Coast Douglas-fir 2		
	L		1.55	
6	R	-	0.19	-
	T		0.16	
	L	1.49	2.30	5.29
12	R	0.15	0.18	0.32
	T	0.19	0.18	0.46
		Intermountain Douglas-fir		
	L		1.97	
6	R	-	0.17	-
	T		0.16	
	L	1.39	2.02	4.22
12	R	0.13	0.19	0.54
	T	0.12	0.20	0.50

1/ L - Longitudinal, R - Radial, T - Tangential

2/ Specimens at 12% MC and 21°C were tested in standard room with low rate of air flow compared to the Aminco cabinet where the remaining specimens were tested.

the diffusion rate and consequently the effectiveness of the treatment.

Effect of Moisture Content

A valid evaluation of the moisture content effect at 21°C could not be made because air circulation was greater at 6% than at 12%. As previously explained, corrosion of the coating made it impossible to conduct the experiment with wafers at 20% MC.

Effect of Flow Direction

Longitudinal diffusion coefficients were about ten times greater than the transverse values. Radial and tangential diffusion coefficients were similar in most instances.

Effect of Wood Permeability

The D values appear to be related to wood permeability for longitudinal flow (Table 2). Specimens rated permeable (P) by the "sink-float" test generally had higher diffusion coefficients than those rated refractory (R). There was a positive correlation between steady-state air permeability and D, significant at the 5% level of confidence. However, there was no significant relationship between wood permeabilities and D values for radial and tangential flow.

Table 2. Relationship Between Wood Permeability and the Non-Steady-State Diffusion Coefficient for the Desorption of Chloropicrin from Douglas-Fir Heartwood Wafers at 21°C.

Flow direction	Specimen[1/]	Sink-float permeability rating [2/]	Steady-state air permeability (Darcies x 10^3)	Non-steady state diffusion coefficient (D) (Cm^2/sec x 10^6)	Correlation coefficients (r) for X vs Y [3/]
			X	Y	
Longitudinal	IF	R	1	2.02	
	2.5	R	12	1.86	
	3.5	R	8	1.35	
	CF-1	I	16	2.67	
	5.0	P	16	2.91	+.76
	5.5	P	37	3.24	s
	6.0	P	32	2.72	
	CF-2	P	16	2.30	
Radial	IF		.06	.19	
	2.5		.33	.18	
	3.5		.12	.14	
	CF-1		.19	.19	
	5.0		.25	.16	
	5.5		.07	.28	-.51
	6.0		.50	.14	ns
	CF-2		.37	.18	
Tangential	IF		.05	.20	
	2.5		.57	.30	
	3.5		.22	.12	+.08
	CF-1		.56	.16	ns
	5.0		.33	.39	
	5.5		.13	.21	
	6.0		.67	.18	
	CF-2		.41	.18	

1/ IF - Intermountain Douglas-fir. CF - Coastal Douglas-fir. Numbers refer to longitudinal preservative penetration ratings from 2.5 (refractory) to 6.0 (permeable).

2/ R - Refractory, I - Intermediate, P - Permeable.

3/ s - significant at the 5% level of confidence,
ns - not statistically significant.

Supplementary Test

There was a very definite effect of wood permeability on the rate of vapor movement along the grain for the eight supplementary test specimens (Table 3). The time required for detectable amounts of vapor to reach 10 and 20 cm above and below the original treatment level is much greater for the woods of low air permeability. The green specimens had lower air permeability values than the matched 12% MC ones and, for coast Douglas-fir, vapor movement was correspondingly slower in the green specimen. Chloropicrin moved as a liquid through resin canals in the green intermountain fir specimen resulting in vapor measurements below the treatment zone much quicker than expected from its permeability value.

The effect of wood permeability on the rate of chloropicrin vapor movement appears to be more important than indicated by the non-steady-state diffusion test results (Table 2). One explanation for this is that in the supplementary specimens, chloropicrin moved as a liquid considerable distances above and below the treating level by capillary action. The extent of liquid movement in each specimen as given by the dye distribution in the wood is shown in Table 3. Liquid moved further and in larger amounts in the more permeable wood. Since capillary movement is rapid compared to diffusion flow, chloropicrin moved much more rapidly in the permeable specimens.

Table 3. The Rate of Chloropricin Movement Through Wood of Different Permeabilities.

Specimen	Moisture content %	Longitudinal steady-state air permeabilities (Darcies)	Time required for the vapor to move 10 and 20 centimeters above and below the treating zone (hours)				Extent of liquid movement (cm)	
			10 centimeters		20 centimeters			
			Above	Below	Above	Below	Above	Below
Intermountain fir	25	.00024	> 550[1/]	30	> 550	320	2	12
Intermountain fir	12	.00082	220	200	> 550	> 550	5	5
Coast fir	27	.0035	190	95	> 550	> 550	5	6
3.5	10	.0054	50	21	> 550	> 550	5	7.5
Coast 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

1/ Test was terminated after 550 hours. No measurable chloropicrin present at this time.

Chloropicrin movement in the supplementary test specimens simulates that occurring in actual wood structures better than desorption of vapor from wafers does. Thus the permeability properties of wood will influence the treatment considerably.

Fungitoxicity of Chloropicrin to Poria Monticola Murr.

At 21°C the lethal "ct" dosages were in the range of 20 to 40 $\frac{\text{mg-hr}}{\text{l}}$ for the chloropicrin concentrations studied (Table 4). The high dosage (100 $\frac{\text{mg-hr}}{\text{l}}$) required for the fungus exposed to chloropicrin at 2°C suggest that the fungus is more resistant to the fumigant under conditions of slow growth. At 32°C, the fumigant was more toxic than at 21°C.

The lethal "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, due probably to toxicity of the oil vapor. The oil vapor did not have an observable effect on the growth of the fungus for short exposure times but did for longer exposures. For example, although a control wafer exposed to oil vapor for 15 hours developed fungal growth after two weeks incubation, the growth was obviously suppressed compared to that of wafers not exposed to oil. Although there is some question concerning the variation of the "ct" value with concentration of chloropicrin vapor, the results are

Table 4. Lethal Dosages[1/] of Chloropicrin for Poria Monticola Murr. Growing on Wood.

Chloropicrin solution	Concentration of chloropicrin vapor 2/ (mg/l)	Time to kill fungus (hr.)	Lethal dosage ($\frac{mg\text{-}hr}{l}$)
Pure chloropicrin at 32°C	315	< .033	< 10
Pure chloropicrin at 21°C	180	.15	27
Chloropicrin in oil at 21°C - A	112	.36	40
Chloropicrin saturated with BHT at 21°C	99	.36	36
Chloropicrin in oil at 21°C - B	83	.43	36
Pure chloropicrin at 2°C	67	1.5	100
Chloropicrin in oil at 21°C - C	5.8	< 4.5	< 26
Chloropicrin in oil at 21°C - D	2.6	9.0	23

1/ Concentration - time ("ct") values.

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

encouraging in that chloropicrin appears to maintain its effectiveness at low concentrations.

These fungitoxicity values must be used with caution as the lethal dosage of a given chemical will vary from one organism to another and will depend on the temperature at which the fungus is growing. Some stages of fungus growth present in the wood such as resting spores may require a higher dosage than growing mycelium.

Pole Study

The important features of the pole section including the locations of the major checks, treating sites, vapor sampling sites, the decay pocket and distribution of liquid chloropicrin are shown in Figure 3. Figures 4 and 5 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 integrating the concentration-time curves for all sites are included in Figure 3. They are expressed here as $\frac{\text{gm-hr}}{\text{l}}$ or $\frac{\text{mg-hr} \times 10^{-3}}{\text{l}}$ to conserve space.

The fumigant moved through the pole as a wave characterized by a lag time 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. The

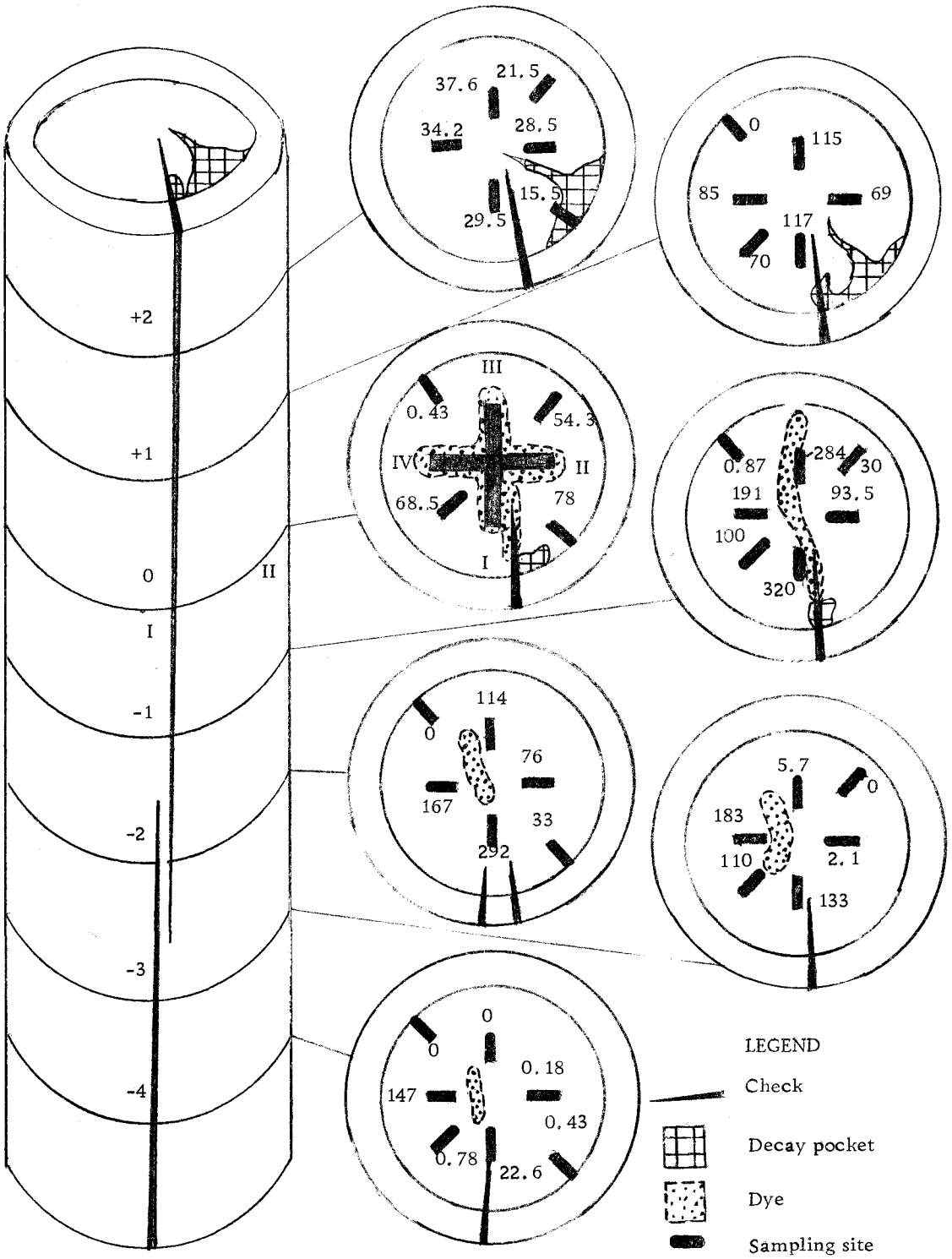


Figure 3. Schematic diagram of pole section. Numbers at sampling sites represent dosages received $(\frac{g\text{-}hr}{l})$.

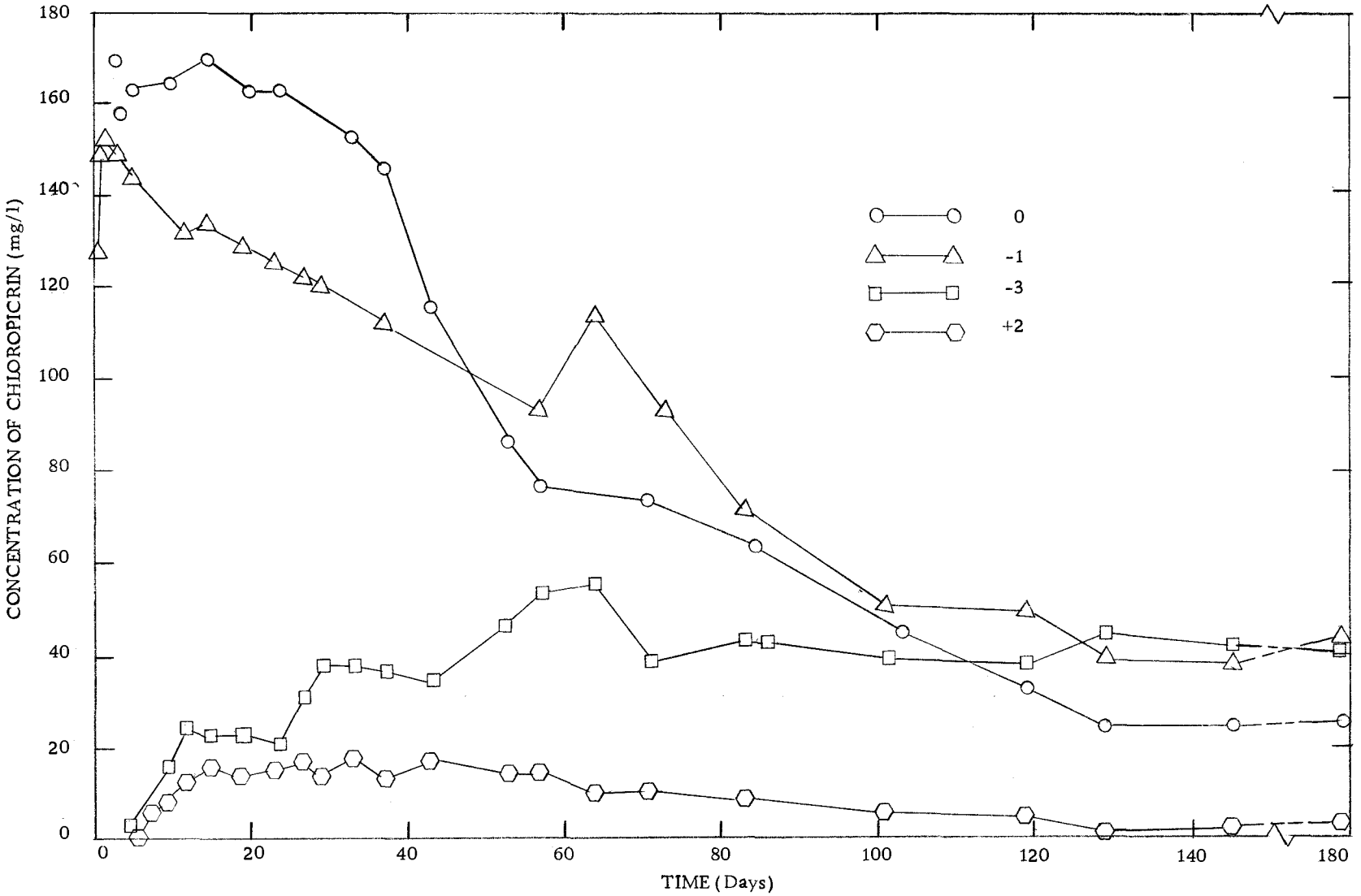


Figure 4. Concentrations of chloropicrin vapor in the Douglas-fir pole section above and below treating hole I.

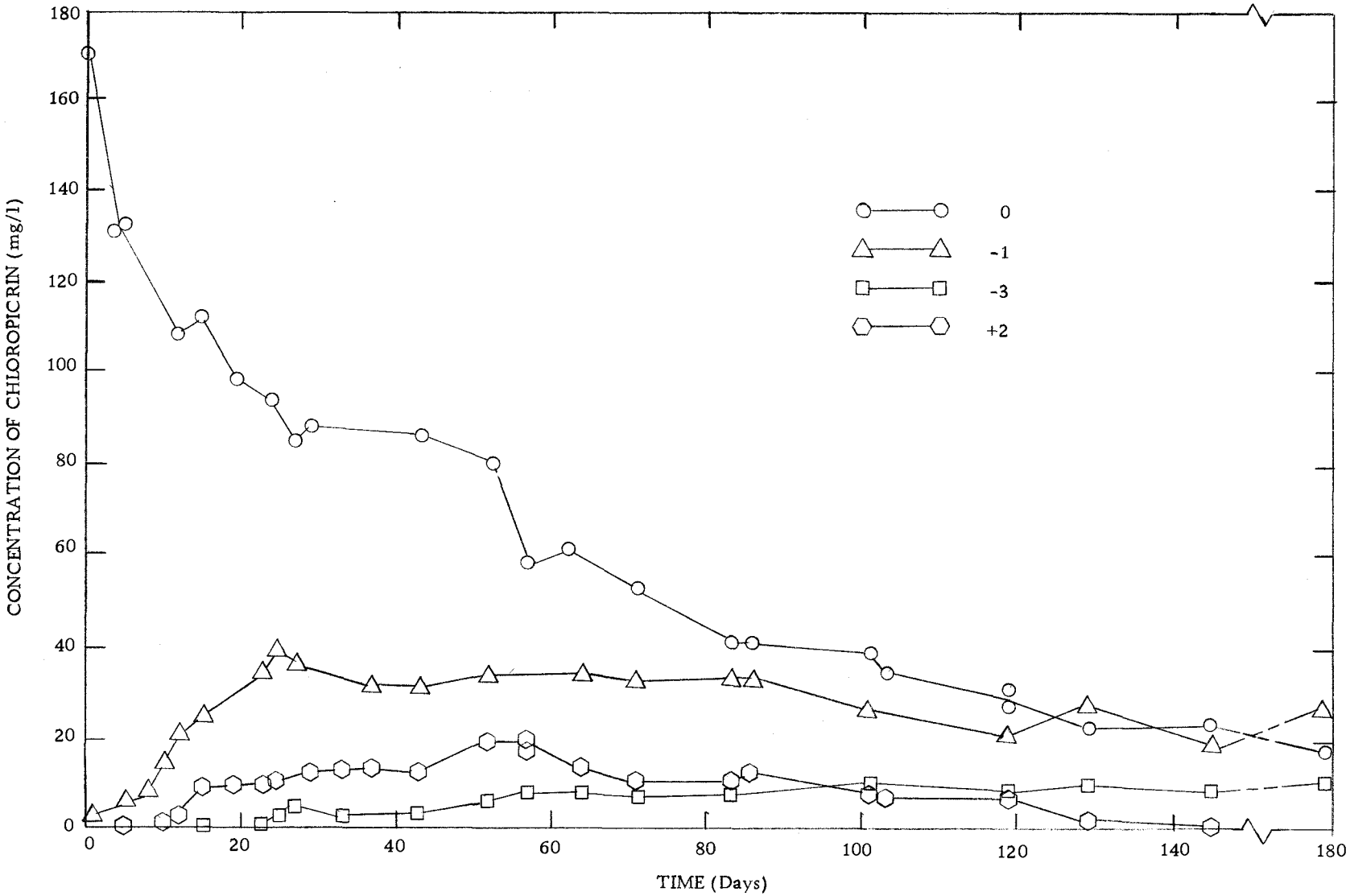


Figure 5. Concentrations of chloropicrin vapor in the Douglas-fir pole section above and below treating hole II.

internal structure of wood restricted vapor movement enough to provide a slow even release and a relatively long lasting supply of fumigant.

There was a significant gravity effect on fumigant movement with more rapid movement and generally higher dosages of vapor below the treating zone than above it. This effect is understandable, since the density of chloropicrin vapor is about 5.7 times that of air and capillary movement of free liquid occurred mainly below the treating zone.

The amount of chloropicrin vapor reaching the sampling sites varied greatly around the pole at each sampling level due to the presence of the checks and decay pocket. The transverse distribution of vapor was limited except where facilitated by these features. Also sampling sites associated with the vertical movement of chloropicrin liquid received higher dosages of chloropicrin vapor than the others. A comparison of Figures 4 and 5 demonstrates this effect. The sampling sites of Figure 4, which were associated with a check, received higher concentrations of chloropicrin vapor than those of Figure 5 which were located in sound unchecked wood. In one area of the pole, chloropicrin moved as a liquid more than four feet below the treating zone (Figure 3). This movement occurred mainly in the latewood and was not associated with ring shakes or other internal checking, although the wood in this

region was brash and may have contained incipient decay.

The decay pocket appeared to extend only about four feet below the top of the pole. However, vapor movement below this area was much greater than that in the sound wood on the opposite side of the pole where no chloropicrin could be measured at the +1, -2 and -4 levels. This ability of the vapor to move more easily in decaying wood results in heavier dosages where the treatment is most necessary. No viable decay organisms were present in the pole showing that the treatment, although irregular, was effective. The treatment was not as efficient as desired since dosages received close to the treating zone and the paths of liquid chloropicrin movement were much higher than the lethal dosage determined in Part II.

Better treatments might be obtained by using different treating hole patterns to improve the distribution of chemical. When the study was terminated, there were still relatively high concentrations of chloropicrin in the pole. Thus the duration of effectiveness exceeded six months even under the conditions of high average temperature and high wood permeability in this study. Retarding the release of vapor at the treating zone should reduce the concentration of chemical diffusing in the wood and extend the duration of the treatment's effectiveness even more.

Diffusion coefficients were calculated numerically (finite

difference technique) for the movement of chloropicrin vapor above and below treating hole II using the concentrations measured at 83 and 119 days. The D values were 2.2×10^{-4} cm^2/sec above and 14.9×10^{-4} cm^2/sec below the treating zone. These values are much higher than for the non-steady-state diffusion demonstrating the effect of capillary movement on the diffusion rate.

Methods of Retarding the Release of Fumigant Vapor

(i) Polymer Slow Release Containers

(a) Polyethylene Vials. The rates of fumigant loss from the polyvials, expressed as milligrams per hour (mg/hr), and as mg/hr per cm^2 of surface area per mm of wall thickness for the fumigants chloropicrin and Vorlex and as permeation constants for chloropicrin are given in Tables 5 and 6. Figure 6 shows typical weight loss curves for the three chemicals at the temperatures studied. Vapam did not move through the vial walls in appreciable amounts at any of the test conditions. Vorlex was generated 20 to 50% faster (by weight) than chloropicrin. Since Vorlex is considerably less dense than chloropicrin (about 1.1 vs 1.65 gm/cm^3) this represents a fairly large difference in rate loss by volume. Two of the Vorlex vials (six-dram one-quarter full and two-dram one-quarter full) ran dry in the course of the experiment after about

Table 5. Rate of Chloropicrin Loss from Polyethylene Vials.

Temperature °C 1/	Loss from 1/2-full and 1/4-full vials of capacities shown					
	6 Dram		4 Dram		2 Dram	
	1/2	1/4	1/2	1/4	1/2	1/4
	Loss in mg/hr					
22	4.59	4.59	3.47	3.39	1.73	1.91
2	.76	.76	.49	.49	.29	.26
32	12.2	19.8	11.5	11.5	5.59	6.00
22	6.50	6.45	4.53	4.38	2.23	2.24
	Loss per cm^2 surface area per mm wall thickness in mg/hr.					
22	.124	.117	.098	.095	.064	.070
2	.020	.019	.014	.014	.011	.010
32	.329	.503	.325	.323	.206	.219
22	.176	.169	.128	.123	.082	.082
	Permeation values 2/ x 10^5					
22	.223	.210	.178	.172	.115	.125
2	.116	.109	.078	.078	.060	.053
32	.340	.526	.336	.336	.213	.227
22	.297	.297	.229	.222	.148	.148

1/ Vials were cycled through these temperatures in the sequence shown.

2/ 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.

Table 6. Rate of Vorlex Loss from Polyethylene Vials.

Temperature °C 1/	Loss from 1/2-full and 1/4-full vials of capacities shown					
	6 Dram		4 Dram		2 Dram	
	1/2	1/4	1/2	1/4 2/	1/2	1/4
	Loss in mg/hr					
20	5.64	5.51	4.81	-	2.70	2.64
2	.95	.93	.71	-	.40	.39
32	16.0	15.4	13.3	-	5.68	6.30
20	6.45	6.45	5.18	-	2.83	- 3/
	Loss per cm^2 surface area per mm wall thickness in mg/hr.					
20	.151	.147	.129	-	.100	.097
2	.025	.025	.019	-	.015	.014
32	.430	.413	.356	-	.210	.232
20	.173	.172	.139	-	.105	- 3/

1/ Vials were cycled through these temperatures in the sequence shown.
2/ Vial began leaking Vorlex immediately.
3/ Vial ran dry.

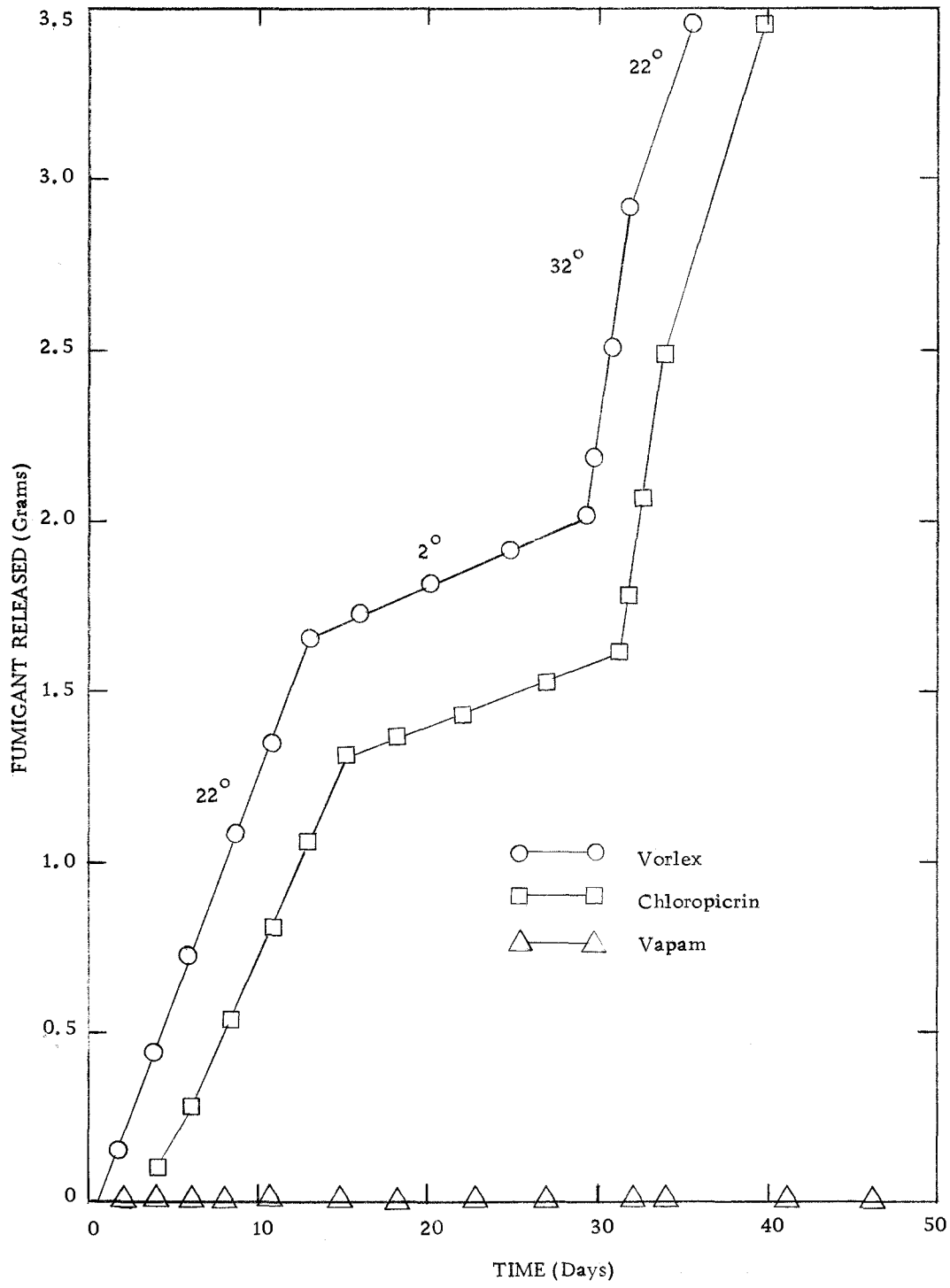


Figure 6. Loss of fumigants from six-dram polyvials.

50 and 40 days, respectively. In both cases the rate of Vorlex loss remained constant until there was no more free liquid in the vials indicating that all components of Vorlex are capable of diffusing through polyethylene at approximately the same rate.

The loss rate of both chloropicrin and Vorlex at 22°C was six to seven times higher than that at 2°C for all vial sizes; the loss rate at 32°C was two to four times higher than that at 22°. The permeation values (Table 5) for chloropicrin represent the loss rates corrected for different vapor pressure gradients across the vial walls at the different temperatures. Figure 7 shows the temperature dependence of the permeation values. Theoretically, the plot of Log p vs 1/T should be linear; however for these tests, the temperature coefficient appears to increase with temperature, probably because the chemicals render the polyethylene more permeable. This is supported by the fact that the rate loss at 22°C was higher after the vials had been cycled at the three temperatures than for the initial test at 22°C (Tables 5 and 6). The heats of activation determined between 22°C and 2°C ranged from 5.2 to 6.6 Kcal per mole.

The loss rates depended on the size of the vials. Although corrections of these values to account for different vial surface areas and wall thicknesses decreased this variation somewhat, the larger vials still had greater permeation values than the smaller

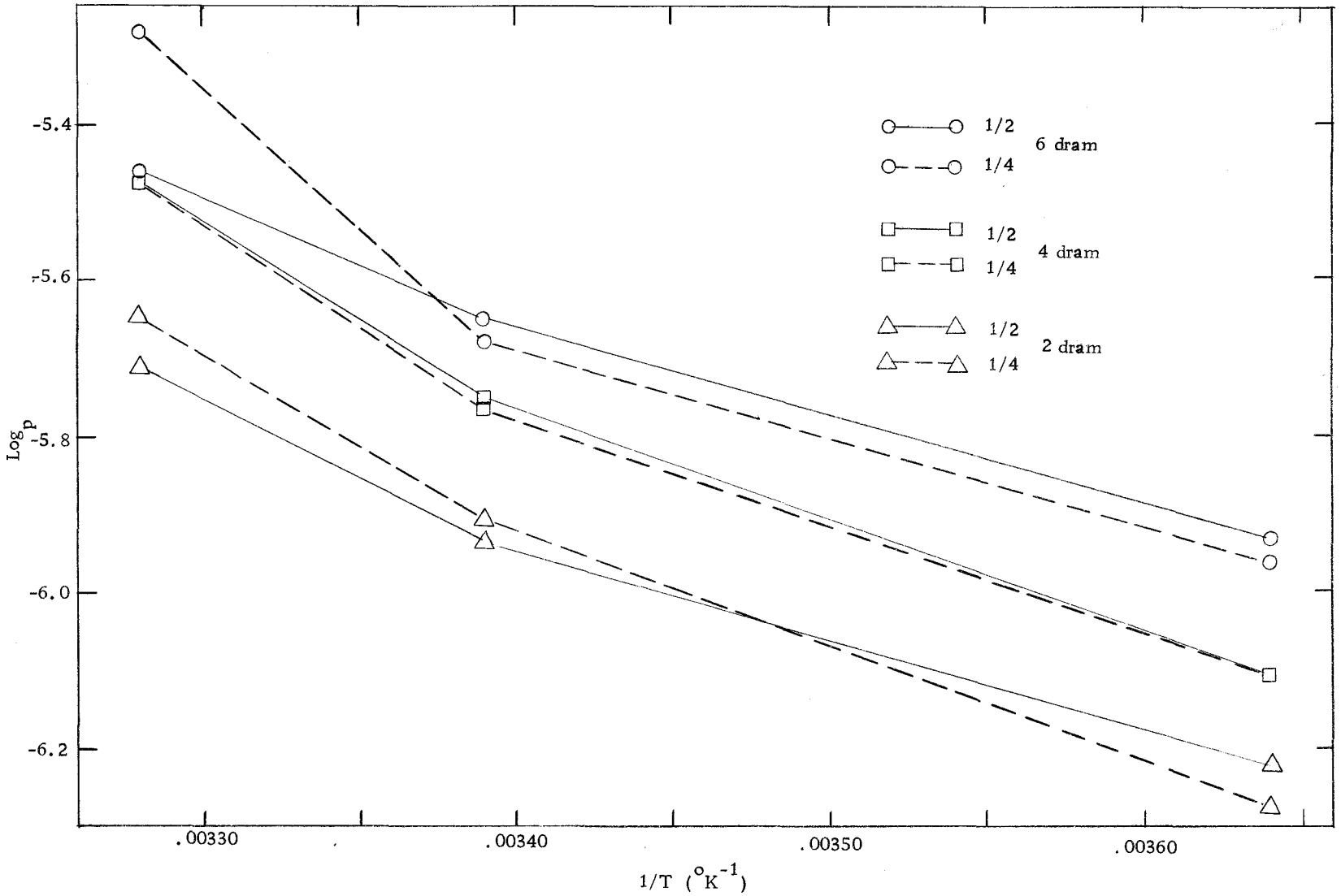


Figure 7. Temperature dependence of permeation values for the diffusion of chloropicrin through polyethylene vials.

ones. This may be partially accounted for if the concentration distribution of fumigant in the vial wall was not linear, i.e., the thicker walls did not retard the rate of loss as much as predicted. Another possible explanation is that the forming process for the different vial sizes resulted in different physical or chemical properties for the polyethylene. For example, the density of the polyethylene increased with decreasing wall thickness as follows:

Polyvial size	Average Density (gm/cm^3)
6 dram	.938
4 dram	.946
2 dram	.953

There is evidence that a microporous structure exists in certain amorphous polymers (e.g., polyethylene) (34). The presence of such voids, which decrease the plastic density, would result in increased permeation rates by permitting convective flow across the voids. The degree of crystallinity of the plastic also affects its density and permeability. 3/ Since the crystalline regions are thought to be impervious to the diffusing chemicals, the higher

---

3/ For example, Rogers et al. (35) presented the percent amorphous polymer and the solubility of methyl bromide in polyethylene of different densities given below:

Density of Polyethylene (gm/cm^3)	% amorphous polyethylene	Solubility (gm CH_3Br per gm polyethylene)
.954	23	.09
.938	29	.12
.922	38	.16

the crystallinity of a polymer, the lower will be the net area for diffusion and the longer will be the average path length of molecules crossing the membrane; consequently, the diffusion rates will be lower.

Although it is impossible to absolutely characterize the movement of the fumigants through polyethylene, this type of analysis may aid in the design of slow release capsules.

There was no consistent relationship between the amount of fumigant in the vials and the permeation rates, since the chemical potential of saturated vapor is the same as that of free liquid (5).

(b) Tygon Tubing Containers. Both chloropicrin and Vorlex vapor diffused through the Tygon containers very rapidly; Vapam did not move through the walls in measurable amounts (Figure 8). Since air was unable to move through the walls to replace the chemicals as they were lost, the resulting vacuum caused the tubes to collapse and retarded the rate of chemical loss. This resulted in a rapid initial rate of vapor release followed by a longer period of reduced vapor production. Since the permeation rate is initially very high for this system as compared to that in the polyethylene vials, it should be possible to generate fumigant vapor at any desired rate by selection of polymer system, container wall thickness and container surface area.

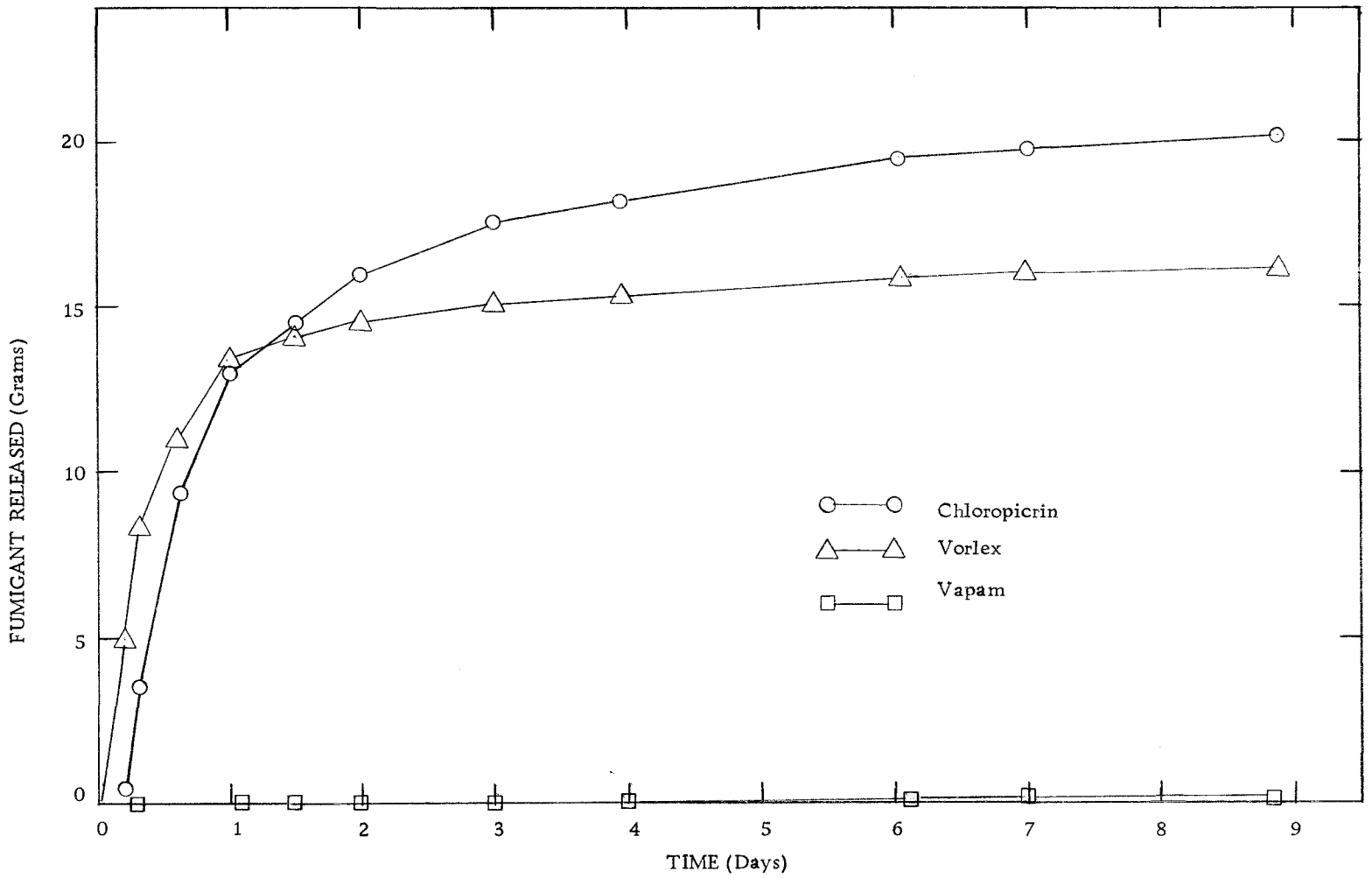


Figure 8. Loss rate of fumigants from sealed Tygon tubing containers.

(ii) Fumigant Solutions

At room temperature, the mole fraction of chloropicrin in a saturated solution of chloropicrin and paradichlorobenzene was found to be 0.52. By Raoult's ideal solution law (equation (12), this should lower the chloropicrin vapor pressure to 0.52 of its saturated value. The actual vapor pressure of chloropicrin above this solution, as determined by gas chromatography, was 0.60 of the saturated value. The rate of loss of chloropicrin from a structure should be retarded accordingly.

Paradichlorobenzene (mothballs) vapor is an effective insect repellent (27) and also has fungistatic properties (36). Since its vapor pressure is fairly low as compared with chloropicrin (about 0.4 mm Hg vs 20 mm Hg at room temperature), paradichlorobenzene vapor should remain in wood long after the chloropicrin has dissipated and should prolong the residual protection of wood against decay fungi and insects.

(iii) Comparison of Treatment Methods

The use of chloropicrin in a polyvial and a saturated solution of paradichlorobenzene in chloropicrin to retard the evolution of vapor increased the duration of chloropicrin in western redcedar timbers over that of chloropicrin injected as a free liquid (Table 7).

Table 7. Dosage of Chloropicrin Vapor Received at Various Distances Above and Below the Treated Zone of Western Redcedar Timbers. 1/

Treatment	Distance in centimeters from treating hole	Dosage received when test terminated ($\frac{mg\text{-}hr}{1}$)	Estimated final dosage ($\frac{mg\text{-}hr}{1}$)	Maximum concentration measured (mg/1)	Approximate duration of chloropicrin vapor in timbers (days)
	+45	0	0	0	0
	+30	2, 400	2, 400	10.8	35
Pure chloropicrin	+15	22, 200	22, 200	52	43
	0	96, 000	96, 000	180	42
	-15	44, 000	44, 000	100	43
	-30	9, 400	9, 400	25.2	35
	-45	650	650	5.2	28
Chloropicrin	+45	0	0	0	0
saturated with	+30	1, 700	1, 700	6.5	46
Paradichlorobenzene	+15	25, 000	25, 000	32.4	58
	0	71, 000	71, 000	100	56
	-15	37, 500	37, 500	39.5	58
	-30	9, 300	9, 300	12.8	56
	-45	1, 300	1, 300	3.2	41
	+45	97	200	0.45	100
	+30	285	595	6.8	120
Chloropicrin in four-	+15	18, 000	37, 000	21.6	125
dram polyvial	0	-	-	-	-
	-15	15, 000	31, 000	27.0	125
	-30	4, 200	8, 800	7.4	120
	-45	190	400	0.9	100

1/ 10-by-10-by-120-cm long.

The concentration of chloropicrin vapor at different times, 15 cm above the treating holes for timbers treated by these three methods, is shown in Figure 9.

When the test was terminated after 60 days, no more chloropicrin could be measured in the timbers treated with chloropicrin alone or with chloropicrin saturated with paradichlorobenzene (PDB). The polyvial still contained 9.88 gm of chloropicrin, enough to provide vapor for 65 more days based on its vapor evolution rate of 6.32 mg per hour. Final dosages and durations were estimated based on these values. Although the dosages received at the different levels were approximately the same for the three treating methods, the duration of treatment was extended about one-third by using chloropicrin saturated with PDB and was tripled by enclosing the chloropicrin in a polyvial. However, the maximum concentrations attained at the sampling sites were lower for the methods that retarded the release of chloropicrin vapor. Some concentration levels may be too low to be effective against decay organisms.

When the study was terminated, the treating hole of the timber treated with PDB in chloropicrin was coated with PDB crystals. There was a strong PDB odor 15 cm above and 20 cm below the treating hole. This should contribute considerably to the effectiveness of the treatment.

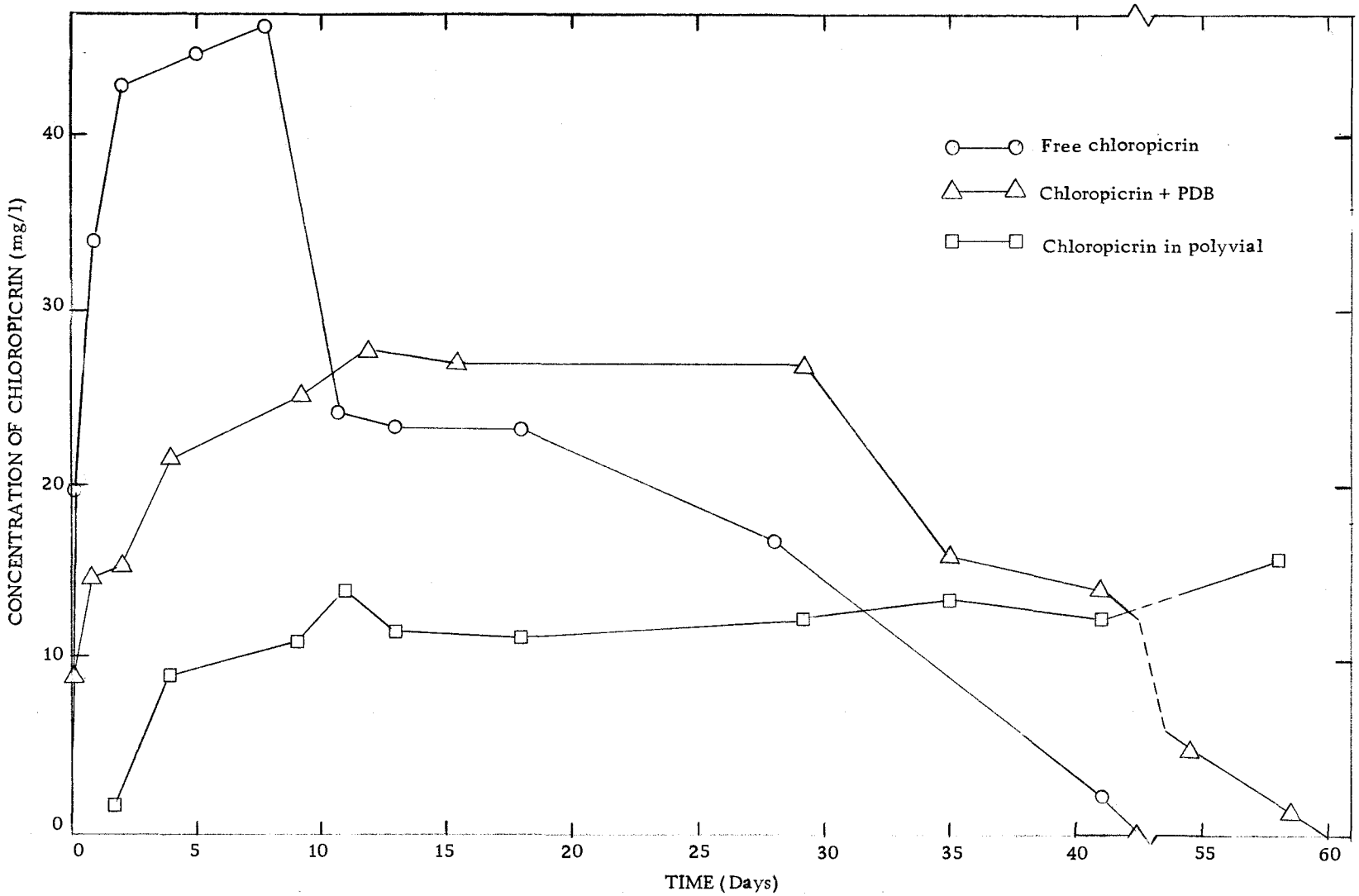


Figure 9. Chloropicrin vapor concentrations in western redcedar timbers 15 cm above the treating zone.

SUMMARY OF RESULTS

Non-Steady-State Diffusion Study

1/ The diffusion coefficients for the desorption of chloropicrin vapor from Douglas-fir heartwood wafers increased with increasing temperature. The process appeared to be controlled by surface emissivity rather than by rate of internal diffusion.

2/ Diffusion coefficients for longitudinal vapor movement were about ten times as large as those for transverse movement. There were no consistent differences between radial and tangential diffusion coefficients.

3/ Rate of chloropicrin movement along the grain in wood depended on the air and liquid permeability properties of wood.

Fungitoxicity Test

1/ The lethal dosage of chloropicrin for Poria monticola Murr. growing on birch wood at 21°C ranged from 20 to 40 $\frac{\text{mg-hr}}{\text{l}}$. The fungus was more resistant to chloropicrin at 2°C and less resistant at 32°C.

Pole Study

1/ Chloropicrin eradicated all wood decay organisms originally present in the pole section studied.

2/ Relatively high concentrations of chloropicrin remained in the pole when the study was terminated after six months.

3/ Application of liquid chemical through four holes equally spaced around the pole did not provide a uniform distribution of chloropicrin. Measurable concentrations of chloropicrin vapor did not reach some parts of the pole while higher than necessary levels of chloropicrin were received in other regions.

4/ Advanced decay favored the movement of chloropicrin and high dosages of vapor in adjacent wood.

5/ Chloropicrin moved faster and further below than above the treating zone.

Slow Release Mechanisms

1/ Polyethylene vials released chloropicrin and Vorlex vapors much slower than Tygon tubing containers. Vapam did not diffuse through either type of container.

2/ Temperature had a marked effect on the rate of vapor release with faster release at higher temperatures.

3/ Chloropicrin and Vorlex rendered polyethylene more permeable with time.

4/ Chloropicrin saturated with paradichlorobenzene extended the chloropicrin residual by about one-third and provided a source of PDB vapor for a long period after the chloropicrin had dissipated.

PRACTICAL CONSIDERATIONS

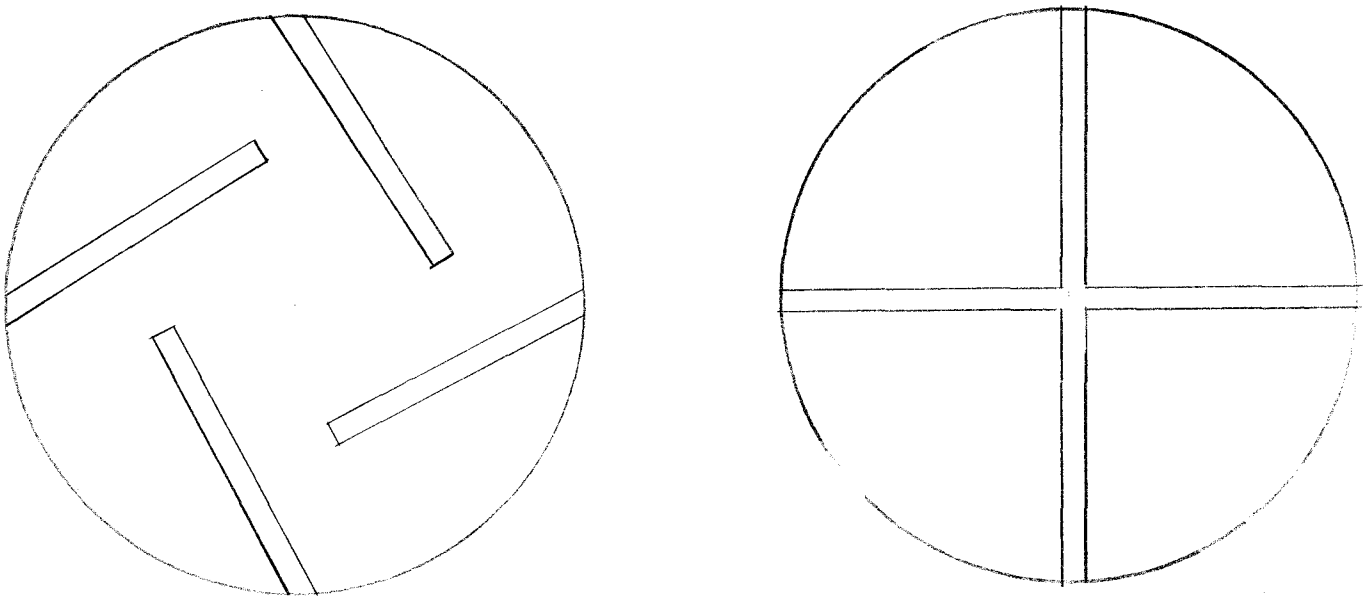
The goal of this study was to investigate some of the important considerations in the remedial treatment of wood with chloropicrin vapor to provide a basis for the design of satisfactory treating procedures. The results indicate that chloropicrin can stop decay in wood products with prospects for long-lasting protection if certain factors that influence movement of fumigants through wood are recognized.

High wood permeability will favor the distribution of lethal concentrations of vapor through wood but will reduce the duration of effectiveness. The presence of decay fungi in wood results in a higher inherent permeability of the wood and should facilitate vapor movement. However, the high moisture content of decaying wood will counteract this effect somewhat. The effectiveness of the treatment will depend considerably on climatic conditions. The higher the equilibrium moisture content of the wood, the lower will be its permeability and the rate of vapor movement. The higher the mean ambient temperature of the wood, the faster and further the vapor will move and the shorter will be its duration in the wood. Since fungi are less resistant to chloropicrin at high temperatures the treatment will be more effective under these conditions.

Injection of large amounts of liquid fumigant at one level in a

pole will result in a high vapor pressure gradient across the wood providing lethal concentrations of vapor at relatively long distances from the treating zone. However, this method of treating is inefficient in that large amounts of liquid must be used resulting in higher than necessary dosages close to the treating zone. The generally poor transverse movement of the fumigant will make it difficult to obtain a uniform distribution of chemical if the treating hole pattern used in this study is applied. These difficulties can be overcome by improved treating hole patterns and by the controlled release of fumigant. For example, the treating hole pattern shown in Figure 10 reduces the distance vapor must diffuse transversely to treat the cross section.

An even better initial distribution of chemical can be realized by applying the fumigant through several small holes distributed over the wood's surface. If pure liquid chloropicrin is used with such a treating hole pattern, a higher than necessary concentration of chemical will develop throughout the wood. Also, the smaller volumes of chloropicrin that must be used to keep the treating cost low will result in a short-lived treatment. This suggests the application of slow release capsules through treating holes distributed throughout the wood for the most economical and efficient treatment. Ideally, the treating hole pattern and rate of chemical release should be designed so that vapor is generated in the wood at the same rate



Suggested treating pattern

Treating pattern used in this study

Figure 10. Treating patterns for applying fumigant to a pole.

as it is lost from the wood surfaces while maintaining a concentration level sufficient to kill the decay organisms and to prevent reinfestation. Slow release capsules also eliminate the need to handle fumigants as a free liquid in the field permitting safer and easier treatments.

Since the amount of air circulation around the wood will affect the rate of vapor loss from the wood surface, the use of durable vapor-resistant wraps may be desirable to extend the treatment's residual protection.

In drier climates where the water table is low, decay can extend for a considerable distance below the ground line (14). For optimum results from the vapor phase treatment, all of the decayed areas must be reached by the vapor. To obtain lethal concentrations of fumigant at these depths without excavating the member, chloropicrin should be applied as a pure liquid. In such situations a combination treatment of pure liquid in addition to liquid confined in slow release capsules may provide the most effective treatment.

CONCLUSIONS

1/ Chloropicrin is a promising chemical for the remedial treatment of wood with high toxicity to decay fungi and long persistence in wood.

2/ Climatic conditions will influence the effectiveness of the treatment since the rate of chloropicrin vapor movement and the toxicity of chloropicrin vapor to decay organisms increase with increasing temperature.

3/ Treatment of wood with chloropicrin in polymer slow release capsules warrants more study because of its potential for improving the duration, efficiency, effectiveness and safety of the treatment.

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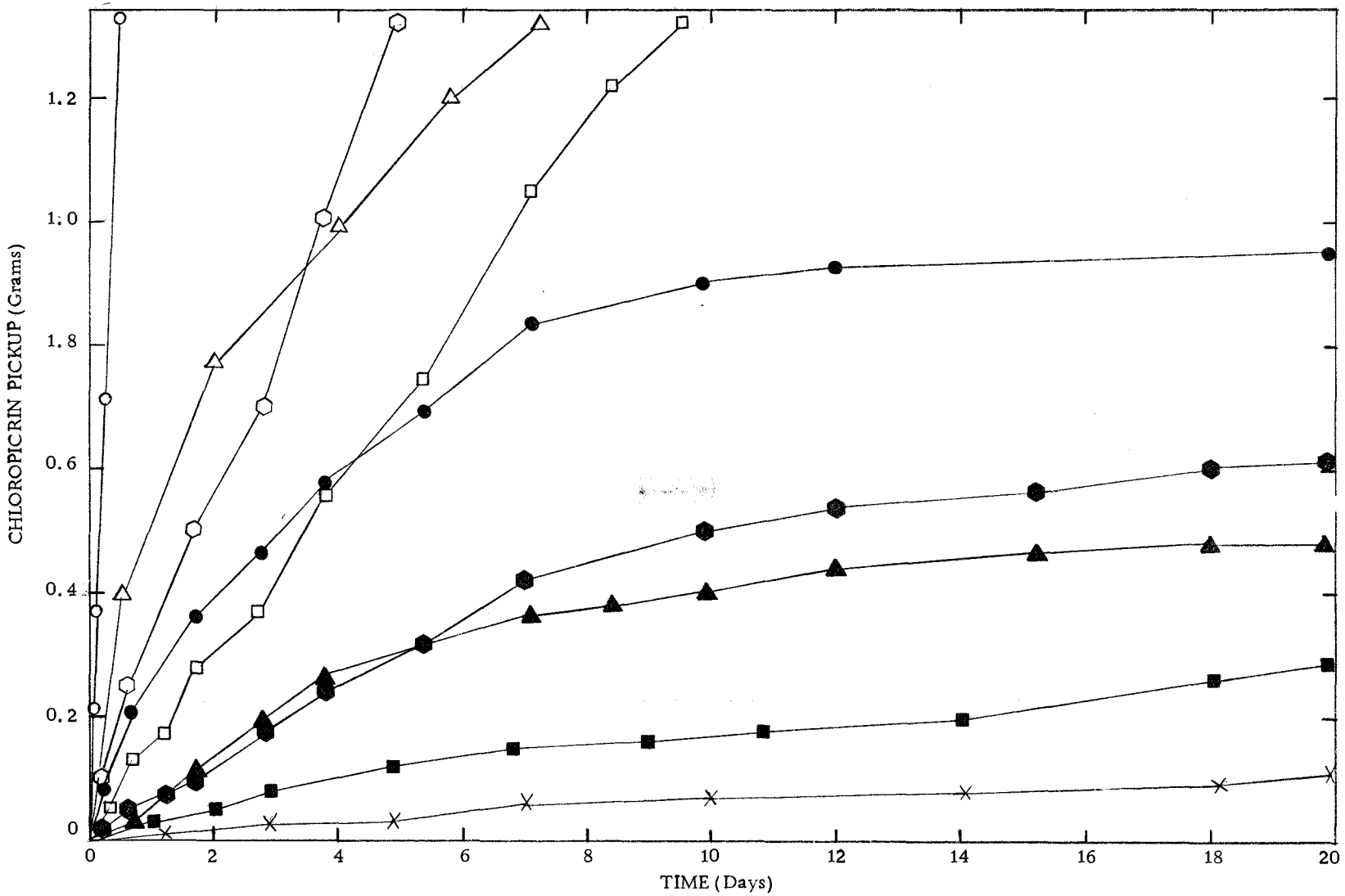
APPENDIX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