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A COOPERATIVE POLE RESEARCH PROGRAM

CONSERVING ENERGY BY ENVIRONMENTALLY ACCEPTABLE PRACTICES
IN MAINTAINING AND PROCURING TRANSMISSION POLES

SEVENTH ANNUAL REPORT

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by

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ABSTRACT

This seventh annual report outlines our continued progress on each of six objectives.

Improved fumigants: We continue to evaluate previously established field tests, which indicate that chloropicrin continues to protect Douglas-fir poles after 17 years and piling after 12 years. Vorlex treated poles are being gradually recolonized by decay fungi, while the Vapam treated poles appear to have little resistance to decay fungi. The latter poles were retreated last summer and will be used to determine the effectiveness of fumigant retreatment. Solid methylisothiocyanate (MIT) continues to protect Douglas-fir poles, although the 20 percent MIT treatment has experienced slightly higher levels of colonization after 9 years. Additional tests to evaluate the effectiveness of gelatin encapsulated MIT or chloropicrin indicate that both chemicals continue to remain effective. In addition, there now appears to be little difference between the levels of control exhibited following addition of varying amounts of water to the poles along with gelatin encapsulated MIT. Closed tube bioassays indicate the chloropicrin remains at fungitoxic levels after 17 years, while no volatile fungitoxins appear to be present in Vapam or Vorlex treated wood.

The evaluation of untreated Douglas-fir posts treated with MIT, chloropicrin, or Vapam indicate that fumigants can not completely protect untreated wood in ground contact unless there is some other type of preservative treated barrier present. Although the MIT treatment provided the best protection, all of the posts experienced some surface decay and termite attack after 10 years. These results appear similar to those found with more recent tests of posts treated with various combinations of preservative

containing wraps and fumigants.

Evaluation of Mylone and tridipam, two solid chemicals that degrade to produce MIT, indicates that MIT production and fungal control are enhanced by the addition of basic pH buffers; however, only the pH 12 buffer resulted in rapid fungal control. These results indicate that the rate of fumigant release can be tailored to control specific decay problems.

We have also investigated the decomposition of Vapam in wood. As previously reported, there are over 14 potential decomposition products from this chemical. This past year we developed methods for assaying these chemicals, evaluated the long-term stability of each, and prepared test blocks for evaluating decomposition in wood. In addition, we have studied the migration of volatile compounds from Vapam and MIT treated blocks under controlled aeration. After 5,000 hours, detectable levels of MIT, carbon disulfide, and carbon oxysulfide are still present in air surrounding the Douglas-fir blocks. These tests indicate that low levels of volatile chemicals are continuously emitted from fumigant treated wood. While this poses little difficulty for utility poles, it may pose some hazard for wood in closed spaces. Evaluations will continue until the emission levels decline below detectable limits.

In addition to Vapam decomposition studies, we have also evaluated the decomposition, movement and fungitoxicity of MIT under a variety of environmental conditions. In general, wet wood held less MIT, but the degree of control produced was more rapid. These results suggest that dry wood will act as a reservoir of MIT, which will be released as moisture enters and swells the wood. This effect may provide an excellent long-term decay control strategy. The information from these studies will be used to develop more

specific recommendations for fumigant treatment.

Cedar Sapwood Decay Control: This past year we reestablished the field test of promising new pentachlorophenol replacements, incorporating 26 chemicals into these tests. These samples will be evaluated after 1 and 2 years to determine efficacy. In addition to the field test, we evaluated 13 new formulations or combinations of formulations in our laboratory screening tests. A number of chemicals including Isothiazolone, Amical 48 and a number of quaternary ammonium compounds appear promising and have been included in the field test.

Bolt Hole Decay Prevention: Test established 5 years ago to determine the effectiveness of sprays, liquids or pastes applied to field drilled bolts holes indicate that ammonium bifluoride, Boracol 40, and 10% penta provided greater protection than Polybor or Patox washers. In addition, no evidence of corrosion was associated with any of the treatments.

Fumigant treatments below the bolt holes continue to eliminate decay fungi, although samples removed from further down the pole indicate an incomplete distribution of MTT. These tests will be reevaluated this coming year.

Detecting Early Decay and Estimating Residual Strength: We continue to evaluate the use of fluorescent coupled lectins and infra-red spectroscopy for detecting fungi in wood and early decay under controlled laboratory conditions.

We have also continued evaluation of longitudinal compression (LCS) as a measure of ultimate wood strength using a series of 27 Lodgepole pine posts. While the dense knot clusters interfered with the analysis, LCS, in combination with other parameters, was a reasonably good predictor of bending strength. These tests will continue with more uniform material.

In addition to tests of LCS, we have evaluated the ability of small scale tests to determine the strength of various wood pole connectors. Our results were in close agreement with those obtained using full scale tests and illustrate the value of using small scale tests to develop strength information.

Initiation of Decay in Air-Seasoning Douglas-fir: We continue to evaluate the data developed in the air-seasoning studies. This past year we began to develop information on the effects of various colony sizes on wood strength. This data will help us assign strength values to the colony size data we have developed from the air-seasoning study. At present, only Peniophora spp. has been tested, but P. carbonica, P. placenta, and Haematostereum sanguinolentum will also be included.

Evaluation of the temperatures required to eliminate fungi from Douglas-fir poles also continue. We have completed 9 test charges which indicate that the penta treatments involving a Boulton-seasoning cycle result in a more than adequate heating of the wood, while steam treatments associated with ammoniacal copper arsenate are more variable. We feel that longer heating periods are required for poles greater than 12 inches in diameter, but that the current 6 hour steam period will result in heating of the center to 67 C for over 1 hour in smaller poles.

Microfungi in Douglas-fir Poles: We continue to evaluate the effects of microfungi on properties of fumigant treated Douglas-fir poles. These tests indicate that prior colonization of fumigant treated wood by Scytalidium or Trichoderma species resulted in lower weight losses by P. placenta and P. carbonica.

Evaluation of a Cellon treated Douglas-fir laminated beam indicated that

severe penta depletion was associated with virtually all of the surface decay present. This beam had only been in service for 12 years in an extremely dry climate and it is unclear why the decay was so rapid.

ACKNOWLEDGEMENTS

Each year we call on a variety of utilities, wood treaters, and pole inspectors for materials, advice, or financial support. We would be lost without the efforts of the many individuals from these companies whose efforts truly make this research a cooperative program.

COOPERATORS

Electric Utilities

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- *Central Lincoln PUD
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*Asterisk denotes funding. All supplied poles, hardware or other assistance.

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OBJECTIVE I

DEVELOP SAFE AND ENVIRONMENTALLY ACCEPTABLE FUMIGANT TREATMENTS
TO CONTROL INTERNAL DECAY OF DOUGLAS-FIR POLES

A. PREVIOUS ON-GOING AND RELATED RESEARCH

Douglas-fir poles treated in 1969 with chloropicrin, Vapam, or Vorlex

Forty decaying Douglas-fir poles (18-24 m long) on the Santiam-Toledo line near Corvallis were treated in 1969 with 1 liter of chloropicrin, Vapam, or Vorlex (Table I-1) or were left untreated (controls). These poles have been sampled on an annual basis by culturing and closed tube bioassays ('84 Ann. Rept., pg 1-2).

Seventeen years after treatment, the results indicate that many of the poles have now been reinvaded by decay fungi (Figure I-1, Table I-2). Until this year, both chloropicrin and Vorlex continued to limit colonization; however, decay fungi have now begun to invade these poles and the levels of colonization differ little from the Vapam treatment. It is important to note

TABLE I-1
VOLATILE CHEMICALS TESTED FOR THEIR ABILITY TO CONTROL
DECAY FUNGI IN WOOD

| COMMON DESIGNATION | SOURCE AND TRADE NAME | ACTIVE INGREDIENT |
|-----------------------|--------------------------------------|--|
| Allyl alcohol | Eastman Kodak Co. Ek-518 | allyl alcohol |
| Chloropicrin | Dow Chemical Co. | Trichloronitromethane |
| MIT | NOR-AM Chemical Co. Degussa Corp. | methylisothiocyanate |
| Vapam | Stauffer Chemical Co. | 32% sodium N-methyl dithiocarbamate |
| Vorlex | NOR-AM Chemical Co. | 20% methylisothiocyanate 80% chlorinated C ₃ hydrocarbons |

that only 8, 6, and 5 percent of the cores removed from the Vorlex, chloropicrin, and Vapam treated poles, respectively, contained decay fungi. Seventeen percent of the cores removed from the untreated control pole contained decay fungi, but this pole was hollow and contained a large percentage of advanced decay. It is extremely difficult to culture decay fungi from very decayed wood.

In spite of the increased colonization by decay fungi, both chloropicrin and Vorlex continue to inhibit the growth of Poria placenta in the closed tube bioassay (Table I-3) except near the groundline zone. Since conditions near the groundline make this zone more likely to be reinvaded by decay fungi, it would appear the retreatment of the test poles is advisable.

As mentioned in previous reports, the closed tube bioassay continues to

TABLE I-2

EFFECTIVENESS OF FUMIGANTS IN
DOUGLAS-FIR POLES TREATED WITH 1 LITER OF FUMIGANT AS DETERMINED
BY CULTURING INCREMENT CORES REMOVED FROM THE TREATED POLES

| YEAR | POLES CONTAINING DECAY FUNGI | | | | |
|------|------------------------------|----------------|----------------|----------------|----------------|
| | CONTROLS UNTREATED | VAPAM | | VORLEX | CP |
| | | WRAPPED | UNWRAPPED | WRAPPED | WRAPPED |
| 1968 | 8 | 8 | 8 | 8 | 8 |
| 1969 | | POLES TREATED | | | |
| 1970 | 8 | 4 | 4 | 0 | 1 |
| 1971 | 8 | 1 | 1 | 0 | 0 |
| 1972 | 8 | 0 | 1 | 0 | 0 |
| 1973 | 8 | 0 | 0 | 0 | 0 |
| 1974 | 7 | 4 ⁷ | 4 ⁷ | 0 ⁷ | 1 ⁶ |
| 1975 | 7 | 1 | 0 | 1 | 0 |
| 1976 | 5 | 2 | 3 | 0 | 0 |
| 1977 | 5 | 2 | 1 | 0 | 0 |
| 1978 | 5 | 3 | 2 | 0 | 0 |
| 1979 | 5 | 3 | 2 | 2 | 1 |
| 1980 | 5 | 1 | 3 | 1 | 0 |
| 1981 | 3 | 2 | 2 ⁶ | 1 | 0 |
| 1982 | 2 | 2 | 2 | 1 | 0 |
| 1983 | 2 | 2 | 2 | 1 | 0 |
| 1984 | 2 ² | 4 ⁶ | 1 ² | 1 ⁵ | 1 ⁵ |
| 1985 | 1 ¹ | 3 | 2 | 2 | 1 |
| 1986 | 1 | 3 | 1 | 3 | 3 ⁴ |

^aAll poles contained decay fungi before the fumigants were applied. The superscripts denote the number of poles remaining in test; the missing poles were inadvertently removed from service.

provide a simple, reliable method for assessing fumigant protection. This year; however, the closed tube bioassays from the Vorlex and chloropicrin treated poles indicate that the wood still retains considerable fungitoxicity. This results differs from previous assays (Table I-4) and suggests that results should be observed over several year period to make the most effective use of this test. Based upon our results, we continue to recommend a 10 year retreatment cycle for Vapam or Vorlex, and a 15 year cycle with chloropicrin. While it is likely that each of these chemicals will provide additional periods of protection, the relatively low cost of retreatment makes it advisable to retreat on these cycles. This should limit the risk of fumigant failure in poles with special treatment considerations such as voids or deep checks.

Because of the relatively constant level of decay fungi present in the Vapam treated poles after 16 years, 5 of the 8 test poles in this group that contained decay fungi were retreated with Vapam this past summer. The existing treatment holes were drilled out and 1 liter of Vapam was distributed between the 7 holes. Each hole was then plugged with a tight fitting dowel. In some cases, decay pockets near the original treatment holes had extended in the hole. In these instances, new treatment holes were drilled above the affected zone. The poles will be monitored for the presence of decay fungi and fungitoxic fumigant vapors this summer.

Douglas-fir poles treated in 1977 with allyl alcohol, methylisothiocyanate, or Vorlex

In 1977, solid methylisothiocyanate (MIT) and allyl alcohol were compared with Vorlex for their ability to control decay in poles. The treatment conditions were previously described ('86 Ann. Rept., pg 7), and the poles

TABLE I-4

DECLINE IN RESIDUAL FUMIGANT VAPORS IN DOUGLAS-FIR TRANSMISSION POLES
AT SELECTED POINTS AFTER APPLICATION OF CHLOROPICRIN,
VAPAM, OR VORLEX AS MEASURED BY THE CLOSED-TUBE BIOASSAY^a

| GROWTH OF THE ASSAY FUNGUS (AS % OF CONTROL) IN THE PRESENCE OF WOOD FROM POLES AT VARIOUS TIMES (YEARS) AFTER FUMIGANT TREATMENT ^b | | | | | | | | | | | | | | | | | | | |
|--|--------------------------|-----|-----|----|-------|-----|----|----|----|--------|----|----|----|----|--------------|----|----|----|----|
| METERS ABOVE GROUND | Control (no fumigant) | | | | Vapam | | | | | Vorlex | | | | | Chloropicrin | | | | |
| | 10 | 13 | 16 | 17 | 5 | 7 | 15 | 16 | 17 | 10 | 13 | 15 | 16 | 17 | 10 | 13 | 15 | 16 | 17 |
| 2.4 | 91 | 96 | 72 | 34 | 53 | 100 | 80 | 55 | 47 | 48 | 68 | 69 | 84 | 15 | 4 | 36 | 11 | 21 | 8 |
| 1.8 | 96 | 100 | 104 | 63 | 60 | 78 | 73 | 75 | 52 | 35 | 68 | 61 | 89 | 21 | 0 | 28 | 5 | 23 | 10 |
| 1.2 | 96 | 80 | 136 | 47 | 60 | 78 | 72 | 51 | 38 | 39 | 64 | 74 | 71 | 8 | 4 | 40 | 38 | 26 | 22 |
| 0 | 100 | 100 | 98 | 69 | 60 | 100 | 52 | 38 | 36 | 52 | 72 | 81 | 71 | 0 | 17 | 60 | 51 | 51 | 36 |

^a Each pole was treated with 1 liter of the selected chemical applied to three holes 1 m above the groundline and four holes at the groundline.

^b For the closed-tube bioassay, a core was removed at each height from eight poles. A 2.5-cm long segment of the core was sealed in a test tube below the agar slant which had been inoculated with Poria placenta. Suppressed growth of P. placenta compared to growth of the fungus where no wood was present (control) indicates the presence of fungitoxic vapors. The lower the percentage, the higher the concentration of fumigant vapors in the wood.

TABLE I-3

RESIDUAL FUMIGANT VAPORS IN PRESSURE-TREATED
DOUGLAS-FIR POLES 17 YEARS AFTER FUMIGANT APPLICATION
AS MEASURED USING THE CLOSED TUBE BIOASSAY

| METERS ABOVE GROUND | SEGMENT LOCATION FROM SURFACE (cm) | GROWTH OF THE ASSAY FUNGUS AS A % OF THE CONTROL ^a | | | |
|---------------------------|---|--|-------|--------|--------------|
| | | NO FUMIGANT ^b | VAPAM | VORLEX | CHLOROPICRIN |
| 2.4 | 0-2.5 | 34 | 19 | 16 | 16 |
| | 12.5-15 | c | 75 | 13 | 0 |
| 1.8 | 0-2.5 | 47 | 44 | 16 | 0 |
| | 12.5-15 | 78 | 59 | 25 | 19 |
| 1.2 | 0-2.5 | 47 | 38 | 0 | 6 |
| | 12.5-15 | 47 | 38 | 16 | 38 |
| 0 | 0-2.5 | 63 | 28 | 0 | 28 |
| | 12.5-15 | 75 | 41 | 0 | 44 |
| CONTROL (NO WOOD) | | 32 mm ^d | | | |

^a For the closed-tube bioassay, a core was removed at each height from eight poles. A 2.5-cm long segment of the core was sealed in a test tube below the agar slant which had been inoculated with Poria placenta. Suppressed growth of P. placenta compared to growth of the fungus where no wood was present (control) indicates the presence of fungitoxic vapors. The lower the percentage, the higher the concentration of fumigant vapors in the wood.

^b Values represent one pole.

^c A slash "-" symbol indicates no wood available to test (i.e., advanced decay).

^d Average growth of the test fungus in 16 tubes.

have been sampled on an annual basis for the presence of decay fungi by culturing and fungitoxic vapors using the closed tube bioassay.

The results indicate that there has been little change in the number of poles containing decay fungi in any of the treatments (Table I-5). The results still indicate that 100 percent MIT is performing slightly better than the 20 percent MIT treatment. The allyl alcohol poles, which continue to be infested with high levels of decay fungi will be retreated this summer. Delay in the field tests last summer prevented this task from occurring at that time. In addition, the control poles from this test will also be treated.

While the number of poles infested with decay fungi remains relatively high, the number of cores infested still remains quite low (Figure I-2). This suggests that the fumigant can not prevent recolonization by decay fungi in isolated portions of the pole, but does limit the continued colonization of the wood by these fungi.

Evaluation of residual fungitoxic vapors in the same poles using the closed tube bioassay indicate that the 100 percent MIT treatment continue to provide high levels of fungal inhibition, while the 20 percent MIT treatment provides little fungitoxicity (Table I-6). Similarly, the Vorlex treatment provided only sporadic inhibition, suggesting that poles in the treatment should begin to be reinvaded by decay fungi. The decreased performance of Vorlex in this test compared to the Santiam to Toledo line and marine piling tests is suprising and suggests that other factors, such as the presence of voids or deep checks in these poles at the time of treatment, may be affecting performance.

Figure I-1. Population of decay fungi isolated from internally decaying pressure-treated Douglas-fir poles treated with Vapam, Vorlex or chloropicrin. Values represent the average of 12 cores removed annually from selected heights above and below groundline.

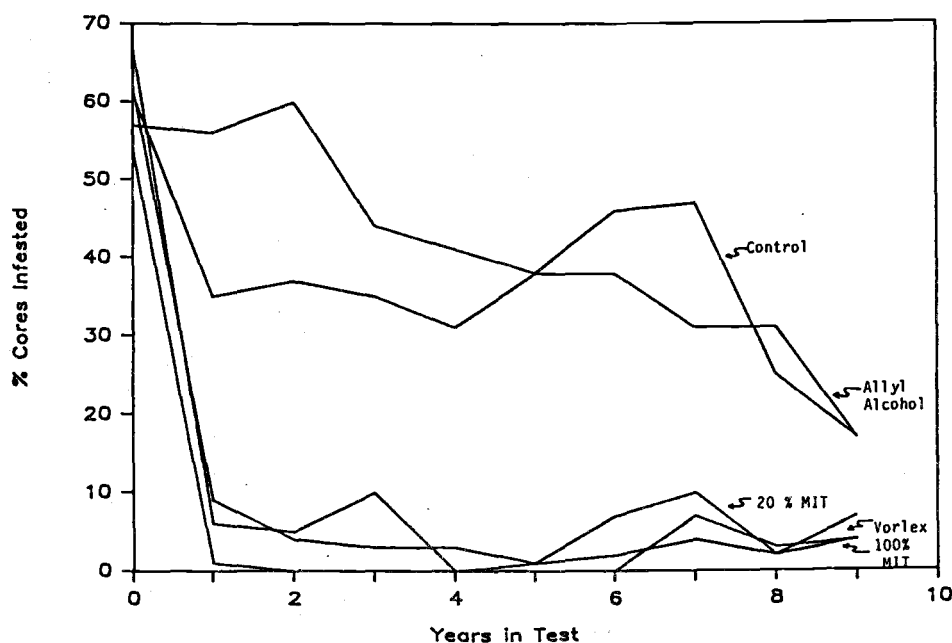
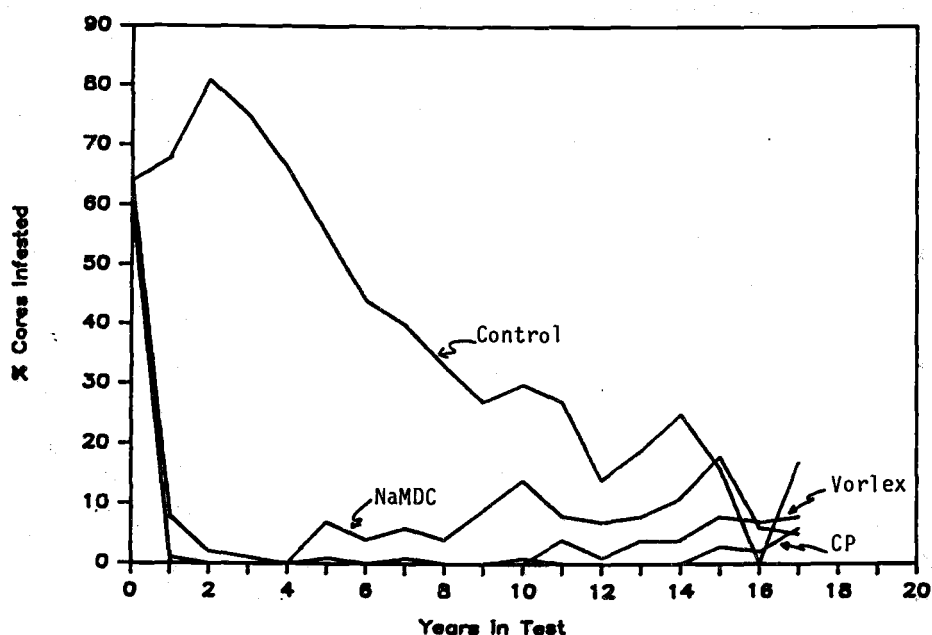


Figure I-2. Changes in the population of decay fungi isolated from internally decaying pressure-treated Douglas-fir poles treated with fumigants. Each value is based on 15 cores removed at -0.3 to 2.4 m from the groundline from the poles listed in Table 5.

TABLE 1-5

EFFECTIVENESS OF FUMIGANTS
IN DOUGLAS-FIR POLES
TREATED IN 1977 AS MEASURED BY CULTURING
INCREMENT CORES REMOVED FROM THE TREATED POLES FOR
THE PRESENCE OF DECAY FUNGI^a

| YEAR | UNTREATED | NUMBER OF POLES CONTAINING DECAY FUNGI | | | |
|------|----------------|--|----------------|----------------------|----------------|
| | | ALLYL | VORLEX | METHYLISOTHIOCYANATE | |
| | | ALCOHOL | | 20% ^b | 100% |
| 1977 | 9 | 9 | 7 | 9 | 8 |
| 1978 | 9 | 9 | 3 | 6 | 2 |
| 1979 | 9 | 9 | 4 | 4 | 0 |
| 1980 | 9 | 9 | 3 | 3 | 0 |
| 1981 | 5 ^s | 6 ^s | 0 ^s | 1 ^s | 0 ^s |
| 1982 | 5 | 6 | 0 | 1 | 1 |
| 1983 | 5 | 6 | 0 | 3 | 2 |
| 1984 | 5 | 5 | 2 | 4 | 2 |
| 1985 | 4 | 5 | 1 | 2 | 1 |
| 1986 | 4 | 5 | 2 | 2 | 1 |

a Poles were treated with fumigants in 1977, and annually thereafter three cores were removed at five heights from the groundline and cultured for fungi. Superscripts denote poles remaining in test since 1981. Others were inadvertently treated with Vapam by a commercial applicator.

b Diluted in diesel oil.

TABLE 1-6

RESIDUAL FUMIGANT VAPORS IN
DOUGLAS-FIR POLES 9 YEARS AFTER APPLICATION AS MEASURED
USING THE CLOSED TUBE BIOASSAY^a

| METERS ABOVE GROUND | SEGMENT LOCATION FROM SURFACE (cm) | GROWTH OF ASSAY FUNGUS AS % OF CONTROL | | | | |
|---------------------------|---|--|---------|----------------------|------------------|------|
| | | NO | ALLYL | METHYLISOTHIOCYANATE | | |
| | | FUMIGANT | ALCOHOL | VORLEX | 20% ^b | 100% |
| 2.4 | 0-2.5 | 68 | 62 | 47 | 79 | 3 |
| | 12.5-15 | 59 | 53 | 41 | 85 | 35 |
| 1.8 | 0-2.5 | 68 | 59 | 50 | 35 | 24 |
| | 12.5-15 | 59 | 71 | 32 | 88 | 32 |
| 1.2 | 0-2.5 | 50 | 59 | 15 | 100+ | 28 |
| | 12.5-5-15 | 44 | 65 | 85 | 85 | 18 |
| 0.6 | 0-2.5 | 35 | 38 | 3 | 38 | 6 |
| | 12.5-15 | 48 | 35 | 68 | 74 | 35 |
| CONTROL (NO WOOD) | | 34 mm ^d | | | | |

a For the closed-tube bioassay a core was removed at each height from four to six poles (Table 5). A 2.5-cm long core segment was sealed in a test tube below an agar slant inoculated with Poria placenta. Suppressed growth of P. placenta compared to growth of the fungus where no wood was present (control) indicates the presence of fungitoxic vapors. Lower percentages indicate increased inhibition.

b In diesel oil.

c A slash mark (-), indicates that no solid wood was available for the assay due to the presence of advanced decay.

d Average growth in 8 tubes.

Evaluation of fumigants for pile top decay control: Bulkhead piles and untreated marina piling located in Florence, Oregon

Twelve years after treatment with Vapam, Vorlex, or chloropicrin, the creosoted bulkhead piling located at Florence, Oregon continue to remain relatively free of decay fungi (Table I-7). This past year, there was a slight increase in the percentage of cores from the chloropicrin and Vorlex treatments which contained decay fungi, while the Vapam treatment remained unchanged. The results indicate that retreatment is probably not yet necessary, although a conservative 10 year treatment cycle is still recommended for Vapam or Vorlex treatments. The results of the bulkhead piling tests closely follow those in Douglas-fir poles.

Eleven years after treatment with Vapam, Vorlex, or chloropicrin, the untreated marina piling also located at Florence continue to have low levels of colonization; however, the Vapam and Vorlex treatments have gradually

TABLE I-7. Fungal population in Douglas-fir bulkhead piling treated with fumigants in 1974 as determined by culturing increment cores removed from selected locations on each pile^a.

| CHEMICAL | CORES CONTAINING DECAY FUNGI (%) | | | | | | | | | | | | |
|---------------|----------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| | '74 | '75 | '76 | '77 | '78 | '79 | '80 | '81 | '82 | '83 | '84 | '85 | '86 |
| VAPAM | 73 | 2 | 0 | 0 | 2 | 8 | 12 | 8 | 12 | 7 | 6 | 5 | 8 |
| VORLEX | 72 | 2 | 0 | 0 | 2 | 4 | 0 | 1 | 0 | 5 | 1 | 0 | 7 |
| CHLORO-PICRIN | 59 | 4 | 0 | 0 | 0 | 3 | 0 | 1 | 0 | 0 | 0 | 0 | 2 |

a. Five cores were removed from each pile, one each at 0.3, 0.6, 0.9, 1.2, and 1.8 m below the pile top.

been recolonized and retreatment of these piles is advisable (Table I-8). Nearly all of the Vapam treated piles have been recolonized, although the degree of colonization is far lower than when the piles were originally treated. Similarly, half of the Vorlex treated piles have been recolonized, but the degree of colonization is only about one quarter that found in 1975, when the piles were first treated. Only 1 chloropicrin treated pile has been recolonized and the degree of colonization is quite low. These results differ from those found with piles or poles that have been pressure-treated with oil-borne preservatives and suggest that the oil may slow the rate of fumigant loss from the wood, or act as a barrier that limits the types or numbers of organisms that can recolonize the wood. As a result of these differences, use of fumigants to protect untreated wood not in ground contact should involve shorter retreatment cycles to insure complete protection. While this may increase maintenance costs slightly, fumigants can still provide a simple means for protecting untreated wood in service.

Table I-8. Presence of decay fungi in untreated Douglas-fir marina piles treated with fumigants in 1975 as determined by culturing increment cores removed from selected locations on each pile^a.

| CHEMICAL | NUMBER OF PILES OR % OF CORES CONTAINING DECAY FUNGI | | | | | | | | | | | |
|--------------|--|----|----|----|----|----|----|----|----|----|----|----|
| | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 |
| <u>PILES</u> | | | | | | | | | | | | |
| Vapam | 6 | 2 | 1 | 3 | 4 | 4 | 3 | 2 | 3 | 1 | 3 | 5 |
| Vorlex | 6 | 4 | 5 | 4 | 3 | 6 | 1 | 2 | 2 | 2 | 1 | 3 |
| Chloropicrin | 6 | 3 | 0 | 3 | 2 | 3 | 1 | 0 | 4 | 0 | 0 | 1 |
| <u>CORES</u> | | | | | | | | | | | | |
| Vapam | 32 | 4 | 7 | 6 | 13 | 15 | 8 | 7 | 12 | 2 | 6 | 15 |
| Vorlex | 37 | 6 | 3 | 5 | 11 | 12 | 1 | 3 | 6 | 5 | 2 | 8 |
| Chloropicrin | 55 | 3 | 0 | 6 | 3 | 5 | 1 | 0 | 6 | 0 | 0 | 2 |

a. Seven cores were removed from each pile, one each at 0.3, 0.6, 1.2, 1.8, 2.4, and 3.6 m below the pile top.

Fumigant protection of untreated Douglas-fir posts

Preliminary tests indicate that fumigants, in combination with preservative containing wraps can limit fungal colonization of freshly cut Douglas-fir posts. The use of fumigants without the need to pressure treat with preservatives could simplify treatment, eliminate the need for costly equipment, and reduce the dependency on currently used preservatives. To evaluate the prospects of fumigant treatment of untreated wood, 20 untreated Douglas fir post sections (2.5 m long by 25.5 to 30.5 cm in diameter) obtained from a cooperating mill were full length kerfed to a depth of 7.5 cm at three locations 120 degrees apart. The posts were set in the ground to a depth of 0.6 m. The posts were sampled prior to fumigant treatment for the presence of fungi by removing increment cores from 3 equidistant locations around each post -0.3, 0, 0.3, 0.9, 1.2, and 1.5 m from the groundline. These cores were cultured for the presence of Basidiomycetes. In addition, the presence of non-Basidiomycetes was noted. The cores were observed for 30 days after plating, then discarded.

Once the poles had been sampled, two 1.9 cm diameter by 30.5 cm long holes were drilled at a 45 degree angle into the wood 0.6 m above the groundline in each of the 3 kerfed zones. The posts were randomly divided into 4 groups of five, and each of the posts in 3 groups were treated by adding 0.5 l of either Vapam, chloropicrin, or MIT to each post. The holes were then plugged with 1.4 cm diameter by 5 cm long dowels.

The poles were exposed at Corvallis, Oregon and were sampled on an annual basis for the first 4 years after treatment by removing increment cores from the locations near those sampled prior to treatment for culturing and identification of Basidiomycetes. In addition to culturing, the poles were

examined for the presence of high moisture levels using a resistance type moisture meter and for surface decay using the Pilodyn at locations on 2 sides of the pole 15 cm above and below the post groundline. Moisture content was measured at 1, 3, 5 and 6.5 cm from the post surface.

Four and ten years after treatment, all of the posts were removed from the ground and carefully examined for evidence of soft rot and insect attack. Additional increment cores were removed at this time for use in a closed tube bioassay to estimate residual fumigant protection.

The results indicate that fumigant treatment slowed but did not prevent Basidiomycete colonization. Visual examination revealed that all of the posts had evidence of surface decay after 4 years and all contained both surface decay and termite attack after 10 years of exposure. In general, posts treated with MIT were in better condition than untreated control posts, while the performance of the Vapam and chloropicrin treated posts fell between the two former treatments.

Culturing increment cores removed from the posts indicated that many of the posts contained Basidiomycetes (Figure I-3). This process revealed that fewer MIT treated posts were infested by these fungi, while 80 percent of the Vapam and all of the chloropicrin treated and control posts contained Basidiomycetes. Examination of individual cores revealed that all 3 chemicals limited Basidiomycete colonization and there was little difference between number of cores with fungi in each treatment (Figure I-4). Preliminary identification of Basidiomycetes isolated from these poles revealed that most of the poles were initially colonized by a fungus which produced extremely fine hyphae. This isolate was sent to the U.S. Forest Products Laboratory for identification. Through the first 4 years of isolations, the poles were

gradually colonized by this fungus. In previous examinations of Douglas-fir poles, P. carbonica and P. placenta, were the most commonly isolated Basidiomycetes. In this study, P. carbonica was only isolated from one untreated control post, even after 10 years of exposure, while P. placenta was isolated from all of the control posts, 2 Vapam treated posts, and one chloropicrin treated posts. This pattern suggests that the fumigant treatment has altered the posts in a manner that makes it difficult for these 2 fungi to colonize the wood; however, the presence of advanced decay in some cores indicates that other Basidiomycetes have replaced these fungi in the wood.

While fumigants appeared to have a strong effect on the Basidiomycete colonization, they had little effect on colonization by non-Basidiomycetes (Figure I-4). Many non-Basidiomycetes cause soft rot damage or exhibit tolerance to toxicants and these fungi could adversely affect the long term fumigant performance.

Examination of wood moisture content revealed that conditions for decay were present in all poles near the groundline two years after installation (Table I-9). Generally, the moisture content of the outer surface was not conducive to decay during the warm summer months, but the posts were in standing water during the moist Willamette valley winters. As expected, internal moisture contents were generally higher than those found near the surface, particularly at the groundline. These results indicate that conditions in all of posts were conducive to decay development.

The effect of excess winter moisture on surface condition can be clearly seen by the results of Pilodyn examination of the wood surface (Table I-10). None of the posts experienced any increases in pin penetration above the groundline, but pin penetration below the groundline increased sharply. This

effect was most pronounced in the control posts, which exhibited little resistance to pin penetration, but the effect was also noted in the NAMDC and chloropicrin treated posts. Pin penetration also increased in the MIT treated posts, but the levels were generally lower than in the other treatment groups. These results suggest that MIT is providing some protection to the post surface; however, it is not sufficient to completely inhibit attack.

Closed tube bioassays of cores removed from 15 cm above and below the groundline indicate that NAMDC treated wood retained little volatile fungitoxicity 4 years after treatment, while MIT and chloropicrin treated posts retained considerable fungitoxicity (Table I-11). The lack of fungitoxic vapors in the NAMDC treated wood is consistent with previous studies that indicate a short residual time for volatile fungitoxic components of this chemical; however, deposition of non-volatile fungitoxic compounds may enhance long term performance. Generally, fumigant levels, as measured by the closed tube bioassay, were lower near the wood surface, reflecting the harsher environment in this zone as well as the increased surface area from which the volatile gases can escape. In addition, previous studies suggest that one fumigant, chloropicrin, is bound in lower quantities to decayed wood and the presence of surface decay in the posts may have limited the amount of fumigant present in the outer wood zone.

After 10 years, the closed tube bioassay continues to indicate the presence of fungitoxic vapors in the above ground portion of the chloropicrin treated posts, although the surface levels remain fairly low. As expected, Vapam treated posts retained little residual fungitoxicity, while wood removed from MIT treated posts exhibited only mild fungitoxicity in the bioassay. The decline in fungitoxicity in the MIT treated posts was surprising since this

chemical was associated with the lowest levels of Basidiomycete colonization.

The results indicate that fumigants can provide long-term protection of the internal portion of untreated Douglas-fir posts, but do not adequately protect the surface against attack by insects and decay fungi. The wood surface is susceptible to leaching and provides a large surface areas for dissipation of volatile chemicals from the wood. Thus, the presence of surface decay in fumigant treated wood is not unexpected. More recent tests of fumigant treatments in combination with externally applied preservative containing wraps indicate that the presence of shallow surface preservatives can markedly improve surface protection.

Table I-9. Moisture content of Douglas-fir posts treated with MIT, chloropicrin, Vapam, or left untreated and exposed in ground contact.^a

| CHEMICAL | MOISTURE CONTENT (%) | | | | | | | | | | | |
|----------|----------------------|----|-----|----|------|----|-----|----|------|----|-----|----|
| | 1978 | | | | 1980 | | | | 1986 | | | |
| | 1.0 | | 6.5 | | 1.0 | | 6.5 | | 1.0 | | 6.5 | |
| | T | B | T | B | T | B | T | B | T | B | T | B |
| MIT | 9 | 23 | 16 | 26 | 11 | 28 | 23 | 30 | 12 | 13 | 20 | 27 |
| Vapam | 12 | 17 | 15 | 26 | 11 | 38 | 23 | 30 | 12 | 13 | 19 | 29 |
| CP | 12 | 16 | 15 | 29 | 11 | 40 | 28 | 32 | 12 | 14 | 24 | 34 |
| CONTROL | 9 | 24 | 17 | 30 | 11 | 42 | 26 | 42 | 11 | 12 | 26 | 43 |

a. As measured using a resistance type moisture meter on each post at 2 points 15 cm above (T) or below (B) the groundline. Moisture readings were taken 1.0 and 6.5 cm from the wood surface

Table I-10. Pilodyn pin penetration of Douglas-fir posts treated with MIT, chloropicrin (CP), Vapam, or left untreated.^a

| CHEMICAL | PILODYN PIN PENETRATION (MM) | | | | | |
|----------|------------------------------|----|------|----|------|----|
| | 1978 | | 1980 | | 1980 | |
| | T | B | T | B | T | B |
| MIT | 13 | 16 | 15 | 20 | 12 | 28 |
| Vapam | 12 | 18 | 15 | 26 | 12 | 38 |
| CP | 12 | 16 | 13 | 28 | 13 | 35 |
| CONTROL | 11 | 16 | 13 | 33 | 12 | 40 |

a. Pilodyn pin penetration was measured at 2 locations 15 cm above and below the groundline using a 6 joule Pilodyn equipped with a 2.5 cm pin.

Table I-11. Residual fumigant vapors in Douglas-fir posts treated with MIT, chloropicrin, Vapam, or left untreated as measured using a closed tube bioassay with P. placenta as the test fungus.P. placenta.

| CHEMICAL | YEAR | PERCENT INHIBITION ^a | | | | | |
|----------|------|---------------------------------|------|-----------|------|-----------|------|
| | | 0-0.25 U | CM L | 2.5-5.0 U | CM L | 5.0-7.5 U | CM L |
| MIT | 1980 | 100 | 78 | 100 | 96 | 100 | 93 |
| | 1986 | 16 | 47 | 19 | 22 | 25 | 22 |
| VAPAM | 1980 | 70 | 66 | 57 | 93 | 48 | 27 |
| | 1986 | 13 | 6 | 6 | 16 | 9 | 6 |
| CP | 1980 | 100 | 78 | 87 | 78 | 100 | 87 |
| | 1986 | 6 | 13 | 56 | 19 | 84 | 19 |

a. Percent inhibition is based upon growth of the test fungus in the absence of wood where 100 percent inhibition represents no growth in the presence of the treated wood.

Figure I-3. Basidiomycete colonization of control posts and fumigant treated Douglas-fir posts as shown by culturing of increment cores.

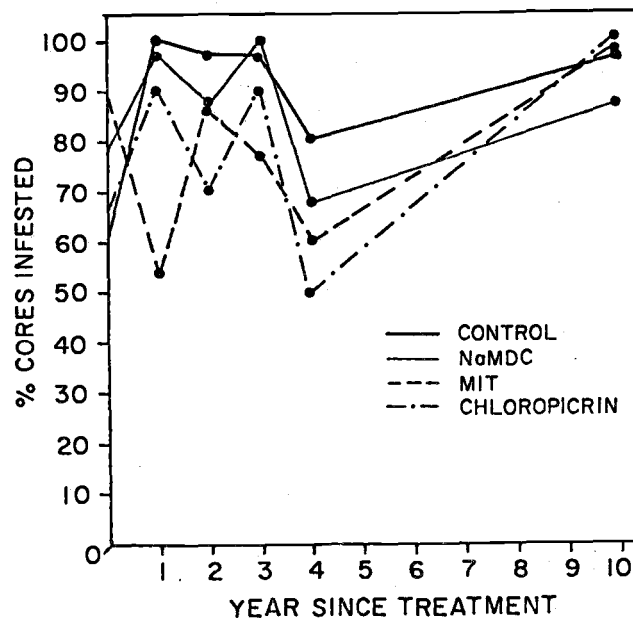
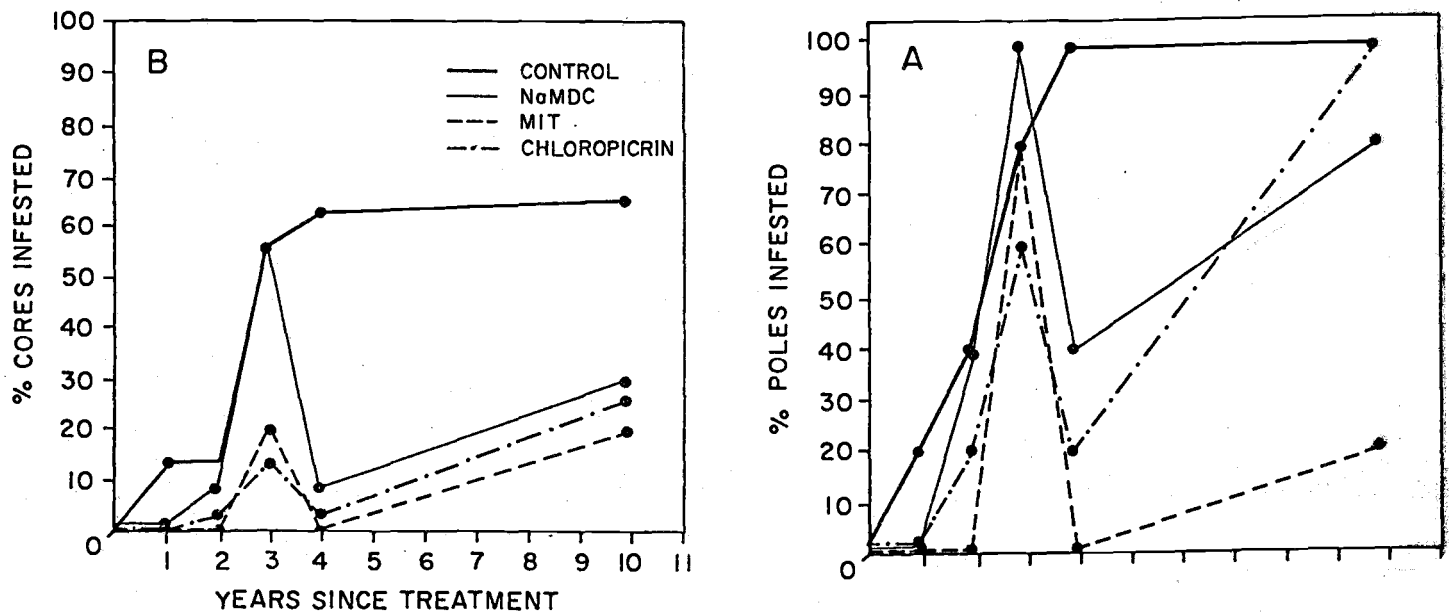


Figure I-4. Non-Basidiomycete colonization of increment cores removed from fumigant-treated and untreated Douglas-fir posts.

B. EVALUATE NEW FUMIGANTS

Ability of pH to control decomposition of Mylone and Tridipam for fungal control.

Last year, we reported preliminary results of tests to control the decomposition of 2 solid fumigants, Mylone (3,5-dimethyltetrahydro-1,3,5,2H-thiadiazine-2-thione) and Tridipam (N,N' dimethylthiuramdisulfide). These stable crystalline solids slowly decompose in the wood to release MIT and other potentially fungitoxic compounds. In soil, Mylone decomposes to produce formaldehyde, hydrogen sulfide, methylamine, and carbon disulfide, and has produced reasonable fungal control in wood in long term laboratory and field tests. Tridipam has not been tested for its ability to control decay fungi, but has produced control of several plant pathogens under laboratory conditions. Unfortunately, the slow decomposition rates of these compounds normally decompose will not rapidly arrest decay. This problem is compounded by the need for more basic conditions for rapid chemical decomposition and the low pH of wood. To overcome this problem, we evaluated methods to enhance the decomposition rate of these compounds in wood.

The ability of pH to enhance decomposition of Mylone and Tridipam was initially investigated in a non-wood system to determine conditions necessary for breakdown. Mylone was obtained from Stauffer Chemical Co. (Westport, CT), while tridipam was synthesized from Vapam.

TEST TUBE EVALUATION: 20 or 50 mg of Mylone or Tridipam were placed in the bottom of 2.5 cm diameter x 20.0 cm long glass test tubes containing Douglas-fir infested with P. carbonica or P. placenta and 0.3 cm diameter agar plugs from the edge of actively growing cultures of the same test fungi. The tubes were sealed with a tight fitting rubber serum cap and 2 ml of phosphate buffer at pH 4.0, 7.0, 10.0, or 12.0 were injected through the serum cap. The tubes

were incubated at room temperature for 7 days and 1 ml air samples were withdrawn from each tube using an air-tight syringe and injected into a Varian 3700 Gas Chromatograph equipped with an flame photometric detector for elemental sulfur to determine the levels of MIT, carbon disulfide, and carbonyl sulfide.

Following chemical analysis, the tubes were opened and the wood and agar samples were removed and placed onto fresh malt agar in petri plates to measure fungal survival and chemical effectiveness. These results were compared with similar tests using 50 mg of Vapam.

BLOCK TESTS: Sterile Douglas-fir heartwood blocks (2.5 cm x 2.5 cm x 10.0 cm long) were end-sealed with tape, dipped in paraffin to retain moisture, soaked in sterile distilled water to raise the wood moisture content to about 50 percent, and inoculated at each end with the test fungus, *P. carbonica*. The inoculum was held in place by two Douglas-fir heartwood (2.5 cm X 2.5 cm X 1.25 cm) blocks which were in turn secured using a rubberband and the assembled blocks were incubated for 1 month, then a 0.98 cm by 2.2 cm deep hole was drilled in the center of each block. Mylone or tridipam dosages ranging from 10 to 600 mg were added to 4 block per treatment. Some holes received 1.8 ml of the previously described pH 4.0, 7.0, 10.0, or 12.0 buffers, and the holes were sealed with a tight fitting rubber serum cap and the blocks were incubated for 1 or 4 weeks at room temperature.

After incubation, the smaller blocks were removed and the fungal survival in the larger block was sampled by culturing. In the fungal tests, the inner 4 pieces from the middle section from each block end were placed onto potato dextrose agar amended with 10 ppm benomyl to retard growth of non-basidiomycetous fungi and the wood was observed for evidence of fungal growth

which was used as a measure of chemical effectiveness. In the chemical tests, the inner 4 pieces from the inner section were extracted in 5 ml of ethyl acetate and analyzed for MIT and carbon disulfide.

The results from the individual chemical tests were compared with the cultural results to determine the relationship between chemical dosage, MIT production, and fungal survival.

RESULTS

TEST TUBE EVALUATIONS: Preliminary tests indicated that Mylone and tridipam were affected by increased pH, although MIT levels detected in the Mylone treated tubes did not appear to increase with the increased pH level (Tables I-12, 13). Lower pH's were associated with higher levels of fungal survival in tridipam treatments and lower levels in Mylone treatments. In addition, high levels of CS_2 were detected in the Mylone tubes, while only trace amounts of this chemical were detected in the tridipam tubes. These results indicate that the rate of Mylone or tridipam decomposition can be controlled by addition of the appropriate pH buffer.

One effect that was not studied was the role of the buffer base in chemical decomposition, since each buffer used a different chemical to achieve the appropriate pH. While studies using acids such as hydrochloric acid or bases such as sodium hydroxide in place of the buffers might eliminate these potential interactions, wood acidity would probably lower the pH to the degree that it had little effect on decomposition. Conversely, the buffers can moderate this acidity and should be more effective decomposition agents.

SMALL BLOCK TESTS: The rate of MIT production was closely correlated with the pH of the buffer added at the time of treatment, with more basic pH's resulting in higher levels of MIT production 1 week after treatment (Figure I-

5, 6). These results differed from the preliminary Mylone tests, suggesting that the presence of wood altered the decomposition products. Blocks incubated for 4 weeks exhibited similar effects, although the levels of MIT detected per oven-dried (OD) gram of wood declined by 50 to 80 percent.

After 1 week, fungal survival in the Mylone treated blocks differed little from untreated control blocks in spite of MIT levels that ranged from 20 to 160 mg per OD gram of wood. These results suggest that the high levels of MIT were only present for a relatively short time and could not effect control. Test results after 4 weeks indicate that addition of buffers at pH 4, 7, or 10 had little effect on fungal control; however, addition of pH 12 buffer resulted in complete control of P. carbonica at dosages greater than 50 mg per block. At this time point, only 20 mg of MIT per OD gram of wood was detected. It was interesting to note that MIT levels in pH 7 and 10 treatments at the 50 mg dosage were 50 and 75 percent, respectively of the pH 12 treatment, but had little influence on fungal survival. Previous Mylone studies have shown that fungal control is achieved only after 3 months in blocks receiving the dry chemical. In our studies, the rate of fungal control varied with pH, indicating that chemical effectiveness can be tailored to particular decay situations. The application of either Mylone or tridipam with a high pH buffer can rapidly release MIT to arrest active decay, while application of these chemicals with pH 7 or 10 buffers at pH 7 or 10 would provide long term decay protection in sound wood.

Mylone decomposition has previously been shown to be pH sensitive, with methylamine, formaldehyde, and carbon disulfide under acidic conditions and hydrogen sulfide, methylamine, formaldehyde, and methylisothiocyanate forming under neutral conditions. Although MIT was detected in pH 4 treatments, the

TABLE I-12. Role of pH in decomposition of tridipam to methylisothiocyanate in glass tubes and its effect on fungal control compared to sodium n-methyldithiocarbamate (NaMDC).

| CHEMICAL DOSAGE (mg) | BUFFER pH | Fungal survival (%) ^a | | MIT LEVEL (ug/ml air) ^b |
|----------------------------|--------------|----------------------------------|------|---------------------------------------|
| | | WOOD | AGAR | |
| 20 (Tridipam) | 4 | 78 | 0 | 10 |
| | 7 | 100 | 0 | 10 |
| | 10 | 0 | 0 | 90 |
| | 12 | 0 | 0 | 211 |
| | DRY | 78 | 90 | 15 |
| 50 (Tridipam) | 4 | 100 | 33 | 7 |
| | 7 | 89 | 0 | 15 |
| | 10 | 0 | 11 | 150 |
| | 12 | 0 | 0 | 589 |
| | DRY | 100 | 100 | 15 |
| 50 (NaMDC) ^c | 4 | 0 | 0 | 15 |
| | 7 | 0 | 0 | 15 |
| | 10 | 34 | 11 | 20 |
| | DRY | 0 | 56 | 15 |
| CONTROL | - | 100 | 100 | - |

a. Based upon exposure of 9 P. carbonica and P. placenta infested wood or agar discs.

b. Trace amounts of carbon disulfide were detected in all of the tridipam treatments containing pH buffer.

c. Vapam contains 32.7 percent sodium n-methyldithiocarbamate in water.

TABLE I-13. Role of pH in decomposition of Mylone to MIT and CS₂ in glass test tubes and its effect on fungal survival.

| CHEMICAL DOSAGE (mg) | BUFFER pH | FUNGAL SURVIVAL (%) ^a | | MIT (ug/ml) | CS ₂ (ug/ml) |
|----------------------------|--------------|----------------------------------|------|----------------|----------------------------|
| | | WOOD | AGAR | | |
| 20 | 4 | 0 | 16 | 482 | 2.670 |
| | 7 | 0 | 0 | 452 | 0.064 |
| | 10 | 100 | 22 | 603 | 0.093 |
| | 12 | 100 | 22 | 324 | 0.133 |
| | DRY | 100 | 100 | 91 | 0.133 |
| 50 | 4 | 0 | 0 | 774 | 3.965 |
| | 7 | 84 | 84 | 759 | 0.073 |
| | 10 | 0 | 6 | 673 | 0.058 |
| | 12 | 0 | 0 | 583 | 0.004 |
| | DRY | 100 | 100 | 27 | TRACE |
| CONTROL | - | 100 | 100 | - | - |

a. Based upon exposure of 9 cubes of P. carbonica or P. placenta infested wood or agar discs.

levels were extremely low after 1 week and not detectable after 4 weeks, suggesting that small variations created localized environments conducive to MIT production in the pH 4 treatments that apparently disappeared during the longer incubation periods.

The results of the tridipam tests indicate that pH had a similar effect on MIT production by this chemical, although the degree of fungal control varied. Only one of the pH treatments (pH 10, 100 mg) eliminated P. carbonica from the infested wood after 1 week and there appeared to be little difference between the pH 7, 10, and 12 levels. Incubating the blocks for an additional 4 weeks produced some degree of fungal control in the pH 10 and 12 treatments. Exposure to tridipam for 4 weeks at pH 12 resulted in complete fungal control at dosages above 150 mg per block, while pH 10 treatments only reduced fungal survival by 30 to 40 percent.

Although not as thoroughly tested, tridipam appears to follow decomposition pathways similar to Vapam. As a result, there are a multitude of pathways by which decomposition occurs and at least 14 potential decomposition products. In addition to the production of volatile fungitoxins such as MIT, deposition of non-volatile chemicals may also occur in the wood. Although these compounds may not eliminate established fungal infestations, they may prevent other organisms from colonizing the wood.

The initial presence of a large wave of fumigant followed by a gradual decline in chemical concentration in both the Mylone and tridipam treatments at pH 10 or 12 was consistent with previous findings. These results suggest that there is some delay between passage of the chemical front and fungal control. It is unclear why this chemical front in the Mylone treated wood was so effective at pH 12 but not at pH 10; however, previous studies indicate

Figure I-5. Effect of pH on the MIT levels detected in Douglas-fir heartwood following treatment with Mylone (A,B) or tridipam (C,D) and incubation for one (A,C) or four weeks (B,D) as measured by gas chromatographic determinations of wood samples extracted for 24 hours in ethyl acetate.

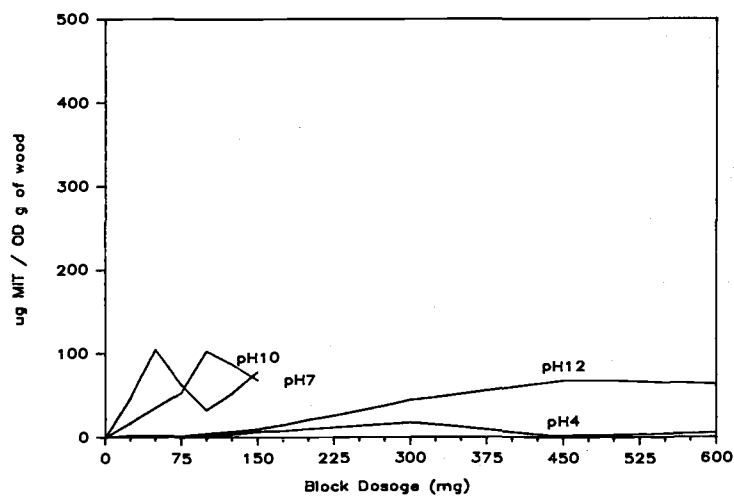
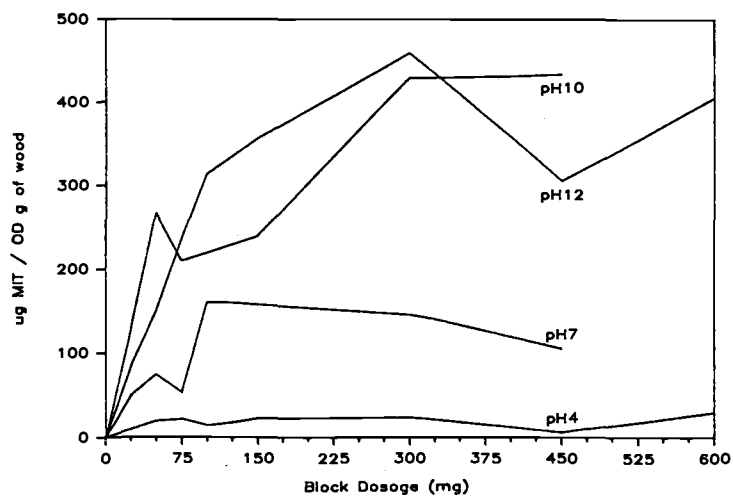
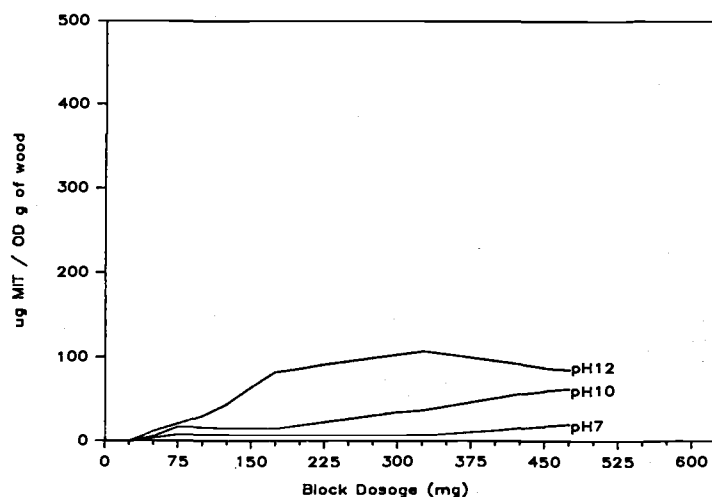
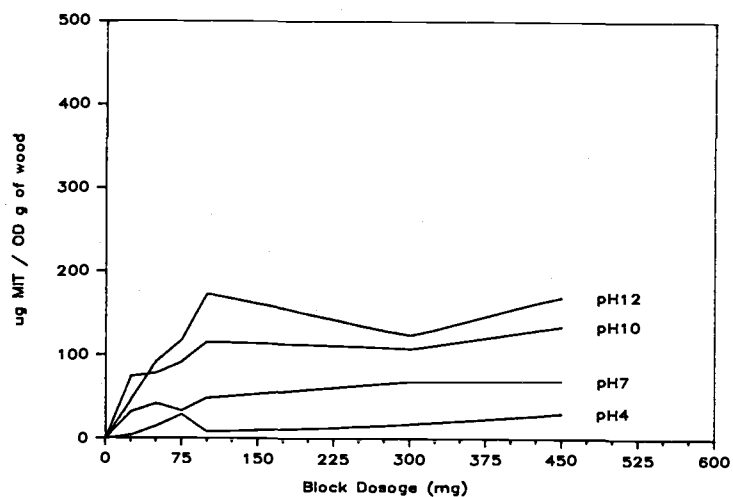
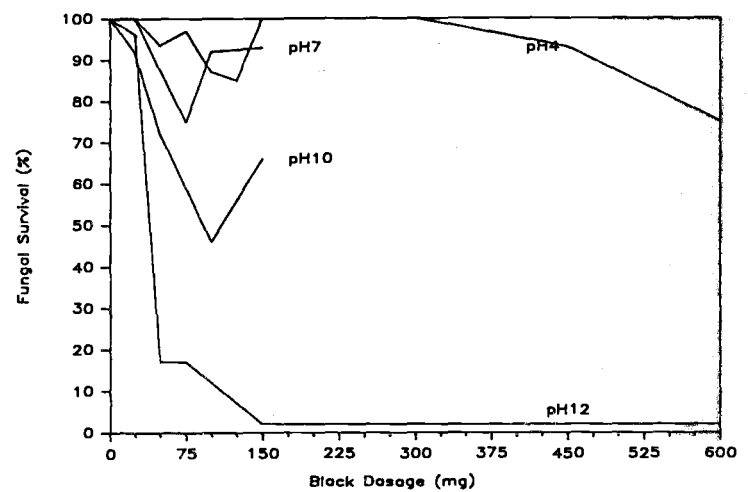
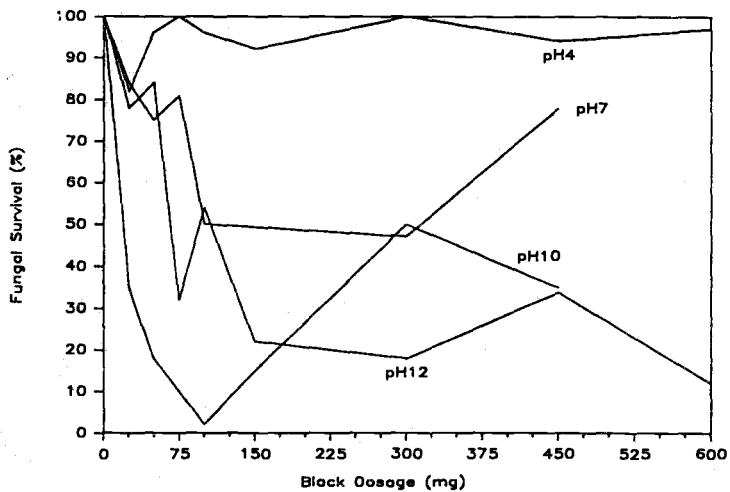
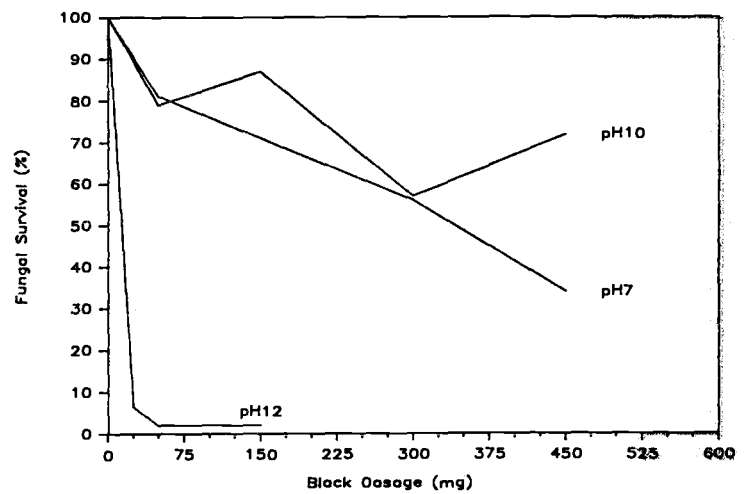
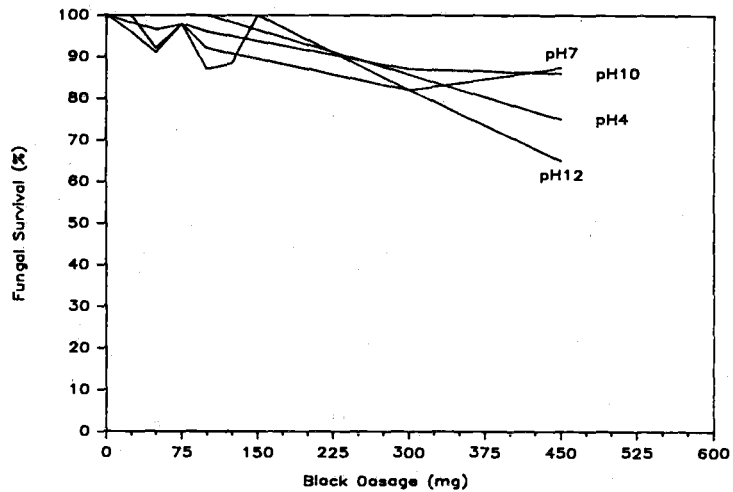


Figure I-6. Effect of pH and dosage of Mylone (A,B) or tridipam (C,D) on control of *P. carbonica* established in Douglas-fir heartwood blocks after 1 (A,C) or 4 weeks (B,D), as measured by culturing wood removed from the affected blocks.



that fungal control will eventually occur with all of the treatments.

The results of the tridipam treatments also indicated that the addition of the pH 12 buffer enhanced fungal control; however, the variation in MIT levels in blocks treated with pH 7 or 10 buffers after 4 weeks suggests that these treatments will also result in long term fungal control. Unfortunately, moisture conditions in our block test made it difficult to maintain constant conditions for more than 4 weeks and larger scale tests are now underway.

The results indicate that the decomposition rate of Mylone and tridipam to MIT can be controlled by varying the pH of simultaneously applied buffers. Generally, pH 12 buffers provided the greatest levels of MIT emission and fungal control, although pH 7 and 10 buffers also produced substantial amounts of MIT. The latter 2 treatments may also provide long term fungal control, but the procedures could not allow for testing this hypothesis.

Ultimately, these chemicals, in combination with selected buffers, could be used to tailor remedial decay control treatments to particular decay situations. This approach, coupled with the use of solid chemicals could substantially improve the precision of wood management programs.

Effect of pH on Mylone treatment of Douglas-fir poles

Based upon the promising laboratory results, a series of Douglas-fir pole sections similar to those described under the void fumigation tests were prepared. A series of five 2.1 cm diameter by 20 cm long holes were drilled near the mid-point of each pole and 15 grams of dry chemical was added per hole (75 g/ pole). Three poles received only the dry chemical and the holes were plugged with wax-coated, tight fitting dowels. Another 3 poles received a total of 300 ml of a pH 10 buffer along with the Mylone. The buffer was

equally distributed between the 5 treatment holes. A third group of 3 poles received 300 ml of pH 12 buffer. Treatment effectiveness will be assessed on a semi-annual basis by removing increment cores for extract and gas chromatographic analysis. Fungitoxicity will be assessed by exposing dowels infested with P. carbonica in holes drilled at selected sites along the posts. These dowels will be removed semi-annually, returned to the laboratory, and cultured to determine fungal survival, which will be used as measure of chemical effectiveness. If our laboratory results are correct, we should see the most rapid fungal control occurring with the pH 12 treatments and the slowest with the dry chemical treatments.

C. EVALUATION OF THE MOST PROMISING FUMIGANTS IN POLES

New York field test of encapsulated MIT

In 1981 twenty-four 9 year old, chromated copper arsenate poles in a line near Hamburg, New York were found to be colonized by high levels of decay fungi and were used to evaluate the effectiveness of gelatin encapsulated MIT. Details of this test have been presented previously ('86 Ann. Rept., pg. 25-28). Last year, the control poles in this test were treated with 950 ml of encapsulated Vorlex. The poles have been sampled on an annual basis by removing increment cores for closed tube bioassays and culturing.

The results indicate that low levels of decay fungi continue to survive in all of the poles, although none of the isolates was identified as P. carbonica (Table I-14). This species was the most commonly isolated species prior to fumigant treatment. The presence of low levels of decay fungi in these poles continues to be a concern, but the sporadic isolation within the poles suggests that these are isolated colonies that may not be causing any significant damage. These poles should be closely monitored in the future to insure continued protection.

Evaluation of residual fumigant vapors by the closed tube bioassay indicate that fungitoxic vapors are present in the inner cores of both the MIT and Vorlex treatments, but not in the Vapam treatment (Table I-15). The lack of fungitoxicity in the Vapam treated wood closely follows previous results. In the outer wood zone, only the Vorlex and 0.95 liter MIT treatments produced nearly complete inhibition of the test fungus, while the low dosage MIT treatment was associated with decreased inhibition at 1.2 meters above the groundline. The lack of inhibition in the low level treatment indicates that this dosage may require shorter retreatment cycles than the higher dosage.

TABLE I-14

INCIDENCE OF DECAY FUNGI IN DOUGLAS-FIR POLES IN NEW YORK STATE PRIOR TO AND AFTER TREATMENT WITH VAPAM OR GELATIN ENCAPSULATED METHYLISOTHIOCYANATE (MIT).^a

| SAMPLING DATE | METERS ABOVE GROUNDLINE | CORES WITH DECAY FUNGI(%) | | | |
|------------------------|-------------------------|------------------------------|--------------|-------------------------------|--------|
| | | NO FUMIGANT | VAPAM 950 ML | ENCAPSULATED MIT ^b | |
| | | | | 475 ML | 950 ML |
| June 1981 | 0 | 83 | 61 | 78 | 78 |
| | 0.6 | 61 | 72 | 61 | 56 |
| Oct. 1981 | | Poles treated with fumigants | | | |
| July 1982 | 0 | 94 | 22 | 22 | 6 |
| | 0.6 | 67 | 17 | 0 | 6 |
| | 1.2 | 22 | 6 | 6 | 6 |
| July 1983 | 0 | 44 | 6 | 0 | 0 |
| | 0.6 | 61 | 11 | 0 | 6 |
| | 1.2 | 33 | 0 | 0 | 0 |
| July 1984 | 0 | 67 | 0 | 0 | 0 |
| | 0.6 | 78 | 0 | 0 | 0 |
| | 1.2 | 33 | 6 | 0 | 0 |
| July 1985 ^c | 0 | 39 | 0 | 0 | 6 |
| | 0.6 | 61 | 0 | 11 | 0 |
| | 1.2 | 28 | 17 | 6 | 0 |
| July 1986 | 0 | 6 | 0 | 0 | 0 |
| | 0.6 | 0 | 0 | 6 | 0 |
| | 1.2 | 0 | 17 | 11 | 6 |

^a A total of 18 cores (three per height) were removed from six poles for each sampling date.

^b About 1 liter of water per pole was added along with the capsules for the 475 ml MIT treatments, and about 900 ml of water was added with capsules for the 950 ml treatments.

^c Control poles were retreated with gelatin encapsulated Vorlex after the 1985 sampling.

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TABLE 1-15

CLOSED-TUBE BIOASSAYS OF CORES REMOVED FROM NEW YORK POLES
5 YEARS AFTER TREATMENT WITH VAPAM OR GELATIN ENCAPSULATED MIT^a

| CHEMICAL | DOSAGE (ML) | SAMPLING HEIGHT (FEET) | AVERAGE GROWTH OF <i>P. PLACENTA</i> (AS A % OF CONTROL) | |
|--------------------|----------------|------------------------------|---|-------|
| | | | CORE ZONE ^b | |
| | | | OUTER | INNER |
| MIT | 475 | 0 | 9 | 0 |
| | | 0.6 | 22 | 3 |
| | | 1.2 | 44 | 0 |
| MIT | 950 | 0 | 0 | 0 |
| | | 0.6 | 5 | 0 |
| | | 1.2 | 0 | 0 |
| VAPAM | 950 | 0 | 101 | 72 |
| | | 0.6 | 105 | 85 |
| | | 1.2 | 107 | 93 |
| VORLEX (1 year) | | 0 | 13 | 5 |
| | | 0.6 | 7 | 0 |
| | | 1.2 | 12 | 0 |

Control tubes (no wood): Avg = 8.3
mm^c

- ^a The close tube bioassay uses a 1 inch wood segment removed from the pole. These segments are placed into agar tubes pre-inoculated with an assay fungus, *Poria placenta*. Fumigant effectiveness is then evaluated as the ability to inhibit radial growth of the fungus and cores with lower numbers have higher fumigant levels.
- ^b Increment cores were divided into three segments, 0-2.5 cm, 2.5 to 12.5 and 12.5-15 cm. The middle segment was discarded and the outer (0-2.5 cm) and inner (12.5-15 cm) segments were used for closed tube assays.
- ^c Control tubes showed poor growth, ranging from only 5 mm to 20 mm after 7 days growth.

Treatment of through-bored Douglas-fir poles with gelatin encapsulated MIT or chloropicrin

The through-bored Douglas-fir poles located on the Dorena Tap line that were treated in 1982 with gelatin encapsulated MIT or chloropicrin were not sampled this year ('83 Ann. Rept., pg. 33-35). They will be inspected in the summer of 1987 to insure continued fumigant performance.

Treatment of Douglas-fir poles with encapsulated MIT: effect of moisture on chemical release.

In addition to the Dorena Tap study, a second test of encapsulated fumigant was installed in 1983 to evaluate the effect of moisture on performance of encapsulated MIT ('86 Ann. Rept., pg. 30-32). The poles in this test were

TABLE I-16
 FREQUENCY OF DECAY FUNGI ISOLATED FROM DOUGLAS-FIR
 POLES TREATED WITH GELATIN ENCAPSULATED METHYLISOTHIOCYANATE (MIT)^a

| SAMPLING DATE | METERS ABOVE GROUND-LINE | CORES WITH DECAY FUNGI (%) ^b | | |
|------------------|-----------------------------|---|-------|-----|
| | | DRY | MOIST | WET |
| Sept. 1983 | 0 | 80 | 60 | 50 |
| | 0.9 | 100 | 100 | 83 |
| | 1.8 | 80 | 100 | 83 |
| | 2.8 | 60 | 67 | 67 |
| | 3.7 | 20 | 80 | 33 |
| | 4.6 | 20 | 40 | 17 |
| Sept. 1984 | 0 | 60 | 0 | 20 |
| | 0.9 | 40 | 20 | 20 |
| | 1.8 | 0 | 20 | 0 |
| | 2.8 | 20 | 20 | 0 |
| | 3.7 | 40 | 20 | 40 |
| | 4.6 | 60 | 0 | 0 |
| Sept. 1985 | 0 | 0 | 0 | 0 |
| | 0.9 | 0 | 0 | 0 |
| | 1.8 | 0 | 0 | 0 |
| | 2.8 | 0 | 0 | 0 |
| | 3.7 | 0 | 0 | 0 |
| | 4.6 | 20 | 0 | 0 |
| Sept. 1986 | 0 | - | - | - |
| | 0.9 | 40 | 0 | 0 |
| | 1.8 | 0 | 40 | 60 |
| | 2.8 | 20 | 0 | 20 |
| | 3.7 | 40 | 0 | 20 |
| | 4.6 | 20 | 0 | 0 |
| | 5.5 | 40 | 0 | 0 |

^a The initial decay estimates were based on culturing of shavings collected during treatment hole drilling. The 1 year data was based on culturing increment cores removed from sites opposite from the treatment holes.

^b Either 0 ml (dry), 40 ml (moist), or 70 ml (wet) of water was added to each treatment hole to aid in fumigant release.

treated by drilling holes in a spiral pattern with treatment holes offset by 90° around the pole at 1 meter intervals from 0 to 5 meters above the ground line. The holes received gelatin encapsulated MIT along with 0, 40, or 70 ml of water per hole.

The poles have been sampled annually by removing increment cores from locations 0, 0.9, 1.8, 2.8, 3.7, 4.6, and 5.5 meters above the groundline for

culturing and closed tube bioassays. Three years after treatment, the poles continue to be colonized by low levels of decay fungi. This past year, the levels of colonization increased slightly in all of the treatments (Figure I-16); however, the cores are removed in different quadrants of the pole each year. Thus, a slight shift around the pole would be expected to yield slightly different results. Based upon previous experience, the levels of

TABLE I-17
RESIDUAL FUMIGANT EFFECTIVENESS IN DOUGLAS-FIR
UTILITY POLES FOLLOWING APPLICATION
OF GELATIN ENCAPSULATED METHYLISOTHIOCYANATE
AS MEASURED BY THE CLOSED TUBE BIOASSAY^a

| METERS ABOVE GROUND | CORE LOCATION INSIDE TREATED SHELL (cm) | AVERAGE GROWTH OF ASSAY FUNGUS (as % of control) IN ENCAPSULATED MIT TREATED POLES ^b | | |
|---------------------------|---|--|----------|----------|
| | | DRY | MOIST | WET |
| 0 | 0-2.5 12.5-15 | - - | - - | - - |
| 0.9 | 0-2.5 12.5-15 | 7 0 | 12 19 | 0 17 |
| 1.8 | 0-2.5 12.5-15 | 0 16 | 5 0 | 0 21 |
| 2.8 | 0-2.5 12.5-15 | 15 17 | 0 0 | 17 0 |
| 3.7 | 0-2.5 12.5-15 | 19 0 | 8 16 | 0 0 |
| 4.6 | 0-2.5 12.5-15 | 44 25 | 5 8 | 25 0 |
| 5.5 | 0-2.5 12.5-15 | 39 18 | 14 8 | 26 14 |
| Control | (no wood) | 26 mm | | |

^a Four capsules, each containing 22 ml of MIT, were placed in 2.3 cm diameter, treatment holes 44 cm deep. Treatments involved adding either 0 ml (dry), 40 ml (moist), or 70 ml (wet) to each treatment hole to aid in fumigant release from capsules.

^b The closed tube bioassay uses 2.5 cm wood segments removed from the pole. These segments are placed into agar tubes inoculated with an assay fungus, *Poria placenta*. Fumigant effectiveness is then evaluated as the ability to inhibit radial growth of the fungus and cores with lower numbers have higher fumigant levels.

colonization should continue to decline, since the closed tube bioassay continues to demonstrate the presence of fungitoxic vapors in nearly all of the cores removed from these same poles (Table I-17). In general, the results continue to indicate that the moderate addition of water at the time of treatment provided the most effective control, although there is still some variation within the treatments.

Preinstallation fumigation of Douglas-fir poles

Last year we reported on the fumigant treatment of 23 pentachlorophenol treated Douglas-fir poles prior to installation in a line located near Coos Bay, Oregon ('86 Ann. Rept., pg. 33-35). These poles were treated by drilling holes in a spiral pattern from either 0 to 7.2 meters above the groundline or 1.2 m below or 6.0 meters above the groundline. Each pole received 1.15 liters of chemical distributed between the six treatment holes. These poles will be sampled this coming summer to insure that the chemical has migrated through the wood.

In addition to the Coos Bay test, a second pre-installation test was established in cooperation with the Central Lincoln PUD at Newport, Oregon was established. While the first tests was performed in the treatment plant yard, the treatments for this test was performed in the utility's pole storage yard. A total of 27 Douglas-fir poles were treated using a treatment pattern similar to that use for the Coos Bay test. These poles will also be inspected this summer to insure that the fumigant is migrating at adequate levels to prevent decay fungi from colonizing the wood.

Effect of MIT on corrosion of galvanized hardware in wood.

One of the advantages of using solid fumigants is the ability to apply

chemical above the groundline. In this zone, the chemicals are far more likely to come in contact with galvanized hardware. To insure that corrosion would not be a factor in chemical protection above the groundline, a series of galvanized hardware pieces were attached to the site 0.6, 1.2, or 4.3 m from the bottom of several Douglas-fir and western redcedar poles that had been treated with pelletized or gelatin encapsulated MIT. These poles have been exposed for 2 years and examination of the hardware indicates no evidence of metal corrosion. These results indicate that the levels of chemicals used for these applications are not sufficient to cause corrosion problems; however, we will continue to monitor these tests.

Effect of voids on fumigant movement and effectiveness

In the inspection process, poles that contain large voids are routinely treated with fumigants to arrest decay and prolong service life. Generally, the treatments are applied to holes drilled above and below the void, but it is apparent that some chemical will migrate into the void and be lost from the wood. This is particularly true if the void crosses a seasoning check. A number of utilities have questioned whether the chemical losses are sufficient to decrease long-term fumigant effectiveness. It is difficult to assess this effect in the field due to the wide variation in void sizes and wood condition for particular poles.

To partially answer this question, thirty four 2.4 m Douglas-fir posts (15-25 cm diameter) were Boultonized in pentachlorophenol in P-9 Type A oil to produce a thin, preservative treated shell. One half of these poles were cross cut at the mid-point and a series of 7.5-15 by 7.5 cm in diameter holes were drilled into the cut off end. The holes, which simulated decay voids, were loosely packed with brown-rotted wood removed from other decayed poles.

The decayed wood was added to act as a wick for fumigant that migrated into the void. Once the decayed wood was added, the 2 poles halves were reattached using wood glue on the treated shell and metal brackets. The outer edges of each pole were sealed with silicone rubber sealer to retain fumigant. A series of steep angled holes were then drilled above the void and each pole received either 80 or 160 ml of chloropicrin or Vapam (Table I-23).

Once the chemical was added, each hole was capped with a tight fitting, preservative treated dowel. Fumigant movement through the voids will be compared with similar poles without voids by inserting a series of 7.5 cm long (0.6 cm diameter) dowels that were infested with P. carbonica into holes drilled at selected locations above and below the void along each pole. These dowels will be removed at 6 month intervals, cut into one inch segments, and cultured to determine if the fungus survived the chemical exposure. In addition, a series of increment cores removed from locations near the dowel sites will be extracted in ethyl acetate or hexane for 24 hours. These extracts will be analyzed for methylisothiocyanate or chloropicrin using gas chromatographic techniques. The poles in this test were installed in February and results will be included in future reports.

Table I-23. Treatments evaluated on Douglas-fir posts with and without artificial voids.

| TREATMENT | VOID | FUMIGANT DOSAGE (ml) |
|--------------|------|----------------------|
| Vapam | + | 80 |
| | - | 80 |
| | + | 160 |
| | - | 160 |
| Chloropicrin | + | 80 |
| | - | 80 |
| | + | 160 |
| | - | 160 |

D. EVALUATE PROPERTIES OF FUMIGANTS IN RELATION TO IMPROVED PERFORMANCE

Potential Fumigants from Vapam Decomposition

In the course of investigating Vapam decomposition, a number of the decomposition products formed from the sodium salt have shown some promise as fumigants. These chemicals are mostly solid, covalent organic compounds that decompose to produce MIT. Among this group are DMTU, MMDT, DTD, TDDT, MTU, DMTM, DMTD, and TTT (see Table I-18 for abbreviations). All of these compounds may play a role in the long-term Vapam effectiveness of wood, but there are many unanswered questions concerning the stability and long-term effects of each chemical in a wood system. To help answer these questions, the chemicals were evaluated for their long-term stability in the presence of air and for their ability to generate MIT in closed systems. The first four chemicals were obtained from Stauffer Chemical Co., while the remaining group was synthesized.

MTU was prepared by mixing 3.7 g of MIT with 60 ml of methanol and 20 ml of aqueous ammonia and concentrating the mixture after several days incubation. DMTM was prepared by acidifying an equimolar mixture of MIT and NaMDC in acetic acid. This latter compound was unstable and had to be prepared shortly before use.

DMTD was prepared by treating 160 ml of Vapam with an aqueous solution of iodine and potassium iodide. The mixture was filtered, dissolved in 750 ml dichloromethane and 50 ml of acetic acid, then filtered through carbon black and a silicic acid-Decalite mixture prior to concentration and crystallization. While the pure solid was stable, solutions of DMTD in methanol, or ethanol decomposed rapidly. Previous studies using ethanol as a solvent for this chemical to

evaluate fungicidal capabilities may be unreliable because of DMTD decomposition. It is highly likely that these studies actually evaluated the effectiveness of sulfur as a fungicide.

TTT was prepared by heating a mixture of MIT, triethylene amine, and dimethylsulfoxide under nitrogen. As temperature increased from 75 to 120° C, sodium hydride in mineral oil was added, then the reaction mixture was cooled and acidified with acetic acid. The resulting crystals were collected and recrystallized.

In addition to the various decomposition compounds, attempts were made to polymerize MIT and to synthesize metallic salts of the dithiocarbamate salt. The polymerization was performed by mixing 3.5 ml butyl-isocyanate (BIC), 2.4 g MIT and 20 ml dimethylformamide (DMF), protected under a nitrogen stream, and cooling to -50° C. A small amount of initiator (0.5 ml of a saturated solution of sodium cyanide in DMF) was added to the mixture, and polymerization was detected by the immediate presence of a thick white slurry. This slurry was blended in 200 ml of methanol and 3 ml of acetic acid prior to filtration. Sulfur digest indicated the presence of just 1 unit of MIT for 7500 BIC units. This level was deemed unacceptable, and this method was not further examined.

Solid NaMDC was prepared by mixing Vapam (32.1% NaMDC) with 10 times its volume of cold acetone. After several minutes, a colorless crystal formed in the solution, and the mixture was frozen. Additional purification involved dissolving in a 1:1 mixture of ethanol:methanol, filtration and reisolation by rotary evaporation. The filtered mixture was then washed with dichloromethane.

Preparation of the various metallic MDC salts was accomplished by reaction of NaMDC with calcium, magnesium, manganese, copper, iron

(+2), iron (+3), or zinc in water. Little or no solid was formed with the calcium, magnesium, or manganese, and these elements were not further examined.

The stability of all of the materials was examined using 0.03 to 0.10 g samples which were weighed into glass beakers. The samples were exposed to laboratory atmosphere under a fume hood and were weighed at regular intervals to determine mass loss. After 2 to 5 months under these conditions, the samples were transferred to a chamber at 50 percent relative humidity (RH) for 6 days, weighed, and transferred to a chamber at 75 percent RH for 13 days. After weighing, the samples were returned to 50 percent for 15 days, weighed, and returned to laboratory air.

The results of the air exposures indicated that several of the Vapam decomposition products were stable for long periods (Figures I-7). Only TDTT and MMDT lost significant amounts of chemical over the 380-day incubation period, with MMDT losing considerably more weight over the time period. The remaining chemicals were all fairly stable. Conversely, most of the metallic salts of MDC were more volatile than the decomposition products. Of the 6 salts tested, iron (+2) was the most volatile, and the zinc salt was least volatile. The remaining salts all lost variable quantities of chemical over a 220-day period. The slow rate of decomposition of NaMDC was surprising and suggests that use of NaMDC dihydrate may be useful as a solid fumigant, since it can reversibly convert to the anhydrous salt, which may be more stable for long-term storage. Tests are now underway to explore this possibility.

The results also indicate that several Vapam decomposition products are capable of remaining in the wood for long periods and may

provide long-term protection against fungi reinvading the wood. This effect would help to explain the long-term performance of Vapam in spite of its short-term ability to produce volatile fungitoxins.

The ability of the test compounds to generate MIT in a closed system was evaluated by placing 0.25 mg of Douglas-fir sawdust, 0.4 ml of pH 4, 7, or 10 buffer, and 0.04 g of the test chemical into a 15 ml Teflon-capped glass test tube. For comparison, tubes were examined which contained only dry fumigant. After selected time periods, headspace gas analysis of the test tubes was performed, and the samples were injected into the gas chromatograph for sulfur analysis. The results were used to estimate the rate of MIT production for each test compound.

The compounds were divided into 5 categories of MIT formation:

- Very Rapid: Weight losses exceeding 5% per day.
- Moderate: 5 ul headspace analysis produced off-scale reading after 5 days.
- Slow: 20-500 ul samples gave detectable MIT level after 5 days.
- Very Slow: 1000 ul sample showed detectable MIT after 5 to 100 days.
- Below Detection: MIT not detected after 100 days.

The results indicate that only one compound, DMTM produced MIT at a very rapid rate, but 7 compounds produced MIT at moderate rates (Table I-19). The latter group including NaMDC, FeMDC, and ZnMDC, and illustrates the effectiveness of metallic salts for producing MIT from reasonably stable compounds. Of these salts, the iron compounds were by far the most active. The remaining compounds all produced MIT at much slower rates but might prove useful for long-term wood

Table I-19. Relative rates of MIT production by decomposition of potential fumigants in a closed test tube for up to 100 days as determined by gc analysis of headspace samples.^a

| VERY RAPID | MODERATE | SLOW | VERY SLOW | BELOW DETECTION |
|---------------|---|---|--|---|
| DMTM | Fe(+2)MDC Fe(+3)MDC CuMDC NaMDC (4, 7, 10) DMTD (7, 10) TDTT (10) ZnMDC (7, 10) | NaMDC (D) DMTD (4) TDTT (4, D, 7) ZnMDC (4, D) | DMTD (D) DMTU (D, 10) MMDT (4, 7, 10) DTD (7, 10) | DMTU (4,7) MMDT (D) DTD (D) MTD (4) TTT MTU S |

^a Numbers in parentheses next to abbreviations represent pH of buffer added along with the dry chemical. The letter D stands for dry chemical without buffer.

protection. The results also illustrated the effects of pH on decomposition, with more acidic buffers generally decreasing MIT production. The production of MIT from DMTU, DTD, and MMDT has not been reported previously, but these compounds are formed from MIT under suitable conditions and the reverse reaction may also occur. The decomposition of these compounds to product MIT may once again help explain long-term performance.

Figure I-7. Loss of selected Vapam decomposition products as measured by weight changes in aerated containers. A) Losses for TDDT, DMTD, DTD, MMDT, and DMTU. B) Losses for selected metallic salts.

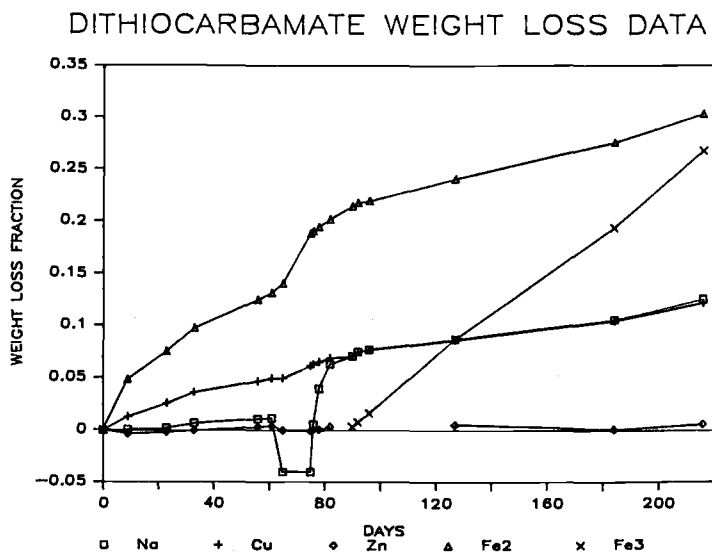
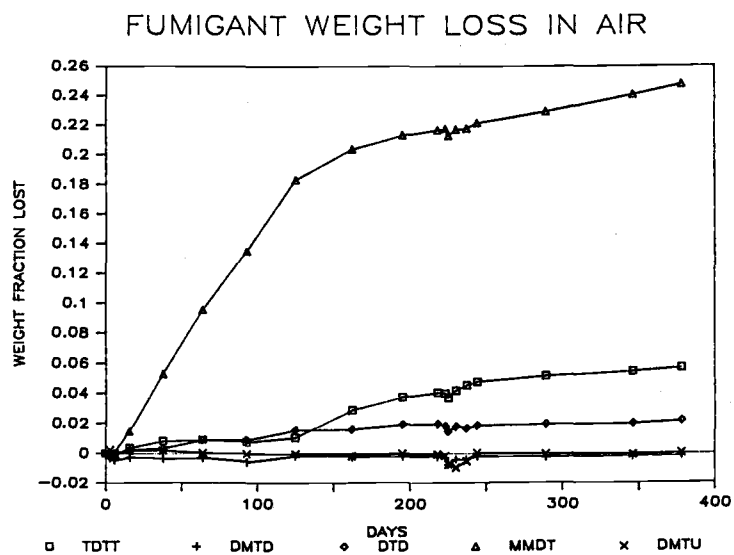


Table 1-18. Characteristics of Metallic Salts of MDC and Potential Decomposition Products Produced From NaMDC.

| SHORT ID | CAS NAME* | CAS NO. | FORMULA | FW | SULFUR FRACTION | MP |
|-------------------------|--|------------|----------------------|-----|-----------------|----------|
| MDC | (methyldithiocarbamate anion) | | $C_2H_4NS_2^-$ | 106 | .604 | -- |
| NaMDC | Sodium methycarbamodithioate | 137-42-8 | $C_2H_4NS_2Na$ | 169 | .496 | -- |
| NaMDC-2H ₂ O | Sodium methycarbamodithioatedihydrate | | | | .213 | -- |
| MTU | Methylthiourea | 598-52-7 | $C_2H_6N_2S$ | 90 | .356 | 119 |
| DMTU | N,N'-dimethylthiourea | 534-13-4 | $C_3H_8N_2S$ | 104 | .308 | 61 |
| MMC | O-methyl-N-methylcarbamothioate | 14128-35-9 | C_3H_7NOS | 107 | .299 | -- |
| MEMC | O-(1-methylethyl)-N-methylcarbamothioate | 20753-31-5 | $C_5H_{11}NOS$ | 135 | .237 | -- |
| MIT | isocyanato-Methane | 556-61-6 | C_2H_3NS | 73 | .438 | 37 |
| TDDT | Tetrahydro-3,5-dimethyl- | 533-74-4 | $C_5H_{10}N_2S_2$ | 162 | .395 | 103 |
| (Mylone) | 2-H,1,3,5-thiadiazine-2-thione | | | | | |
| DMTM | N,N'-dimethyl-thiodicarbonyl- thioic diamide | 5437-22-9 | $C_4H_8N_2S_3$ | 180 | .533 | 75(d) |
| DMTD | N,N'-dimethylthioperoxy dicarbonyl diamide | 2438-90-6 | $C_4H_8N_2S_4$ | 212 | .604 | 96-8(d) |
| DTD | 2,4 dimethyl-1,2,4-thiadiazolidine- 3,5-dithione | 6317-20-0 | $C_4H_6N_2S_3$ | 178 | .539 | 120 |
| MMDT | 4-methyl-5-(methylimino)- 1,2,4-dithiazolidine-3-thione | 20042-85-7 | $C_4H_6N_2S_3$ | 178 | .539 | 84 |
| Sulfur | Sulfur | 7704-34-9 | S ₈ | 256 | 1.00 | 113, 119 |
| TTT | 1,3,5-Trimethyl-(1H,3H,5H)- S-triazine-2,4,6-trithione | 938-65-8 | $C_6H_9N_3S_3$ | 219 | .438 | 168, 70 |
| Fe ₂ MDC | | 37611-74-8 | Fe(MDC) ₂ | | | |
| Fe ₃ MDC | | | Fe(MDC) ₃ | | | |
| CuMDC | | | Cu(MDC) ₂ | | | |
| 2nMDC | | 37611-73-7 | 2n(MDC) ₂ | | | |

*Underlined letter determines position in CAS alphabetical list.

Decomposition of NaMDC in the Presence of Wood, Cellulose, or Glass

The ability of NaMDC to bind to or react with selected wood components may play an important role in decomposition. To evaluate this process, the reaction of NaMDC with Douglas-fir heartwood, cellulose filter paper, or glass beads was evaluated under controlled laboratory conditions.

The formation of non-volatile decomposition products was examined by placing 1 g of NaMDC per 3 g of Douglas-fir heartwood sawdust, 3 g of cellulose filter paper, or 30 g of glass beads in a closed glass container. The chambers were incubated for 75 or 135 days at room temperature, then extracted in dichloromethane (DCM) (Extract A), methanol (Extract B), and water (Extract C) for a minimum of 24 hours in a soxhlet. DCM is incompatible with reverse phase HPLC and was removed by evaporation. The residue was redissolved in methanol for analysis. Any MIT present in the extract was lost at this point.

Because the elution times of the compounds differed widely, mobile phases of different strengths were required. For sulfur determination, 100% methanol was used. DTD, MMDT, and MIT were eluted with 16% acetonitrile, 36% methanol, 48% water. DMTU, MMC, and MIT were eluted with 7% acetonitrile, 13% methanol, and 80% water. At 1 ml/min., these elements gave retention times of 2-10 min. for the listed products. LC columns were (1) C_{18} on 5 μ m silica, 4.6 x 250 mm, (2) C_{18} on 3 μ m silica, 4.6 x 150 mm, and (3) μ RP1 -5 μ m, 4.6 x 200 mm. A Shimadzu LC6A pump, SPD6A (UV) detector operated at 250 nm, SCL 6A system controller, and CR3A data processor were used. The detector was operated at 250 nm.

Only minor amounts of covalent compounds were found in the methanol extract, and despite considerable effort, determination of

NaMDC by LC was unsuccessful. The large amount of wood extractives probably prevented isolation of the sulfur containing salts in this fraction. As a result, total sulfur in this fraction was determined by atomic absorption analysis. Extract B from treated cellulose and glass did not contain interfering extractives. The two major components of these extracts, NaMDC and sodium thiosulfate (both hydrates) were separated by their differential solubilities. NaMDC is readily soluble in 50% methanol: 50% ethanol, while sodium thiosulfate is essentially insoluble in this mixed solvent. A finely ground sample of the mixed salts was stirred with the solvent mixture for at least 30 min. at 25° C. NaMDC and sodium thiosulfate were identified using X-ray diffraction by comparison with known samples. Water Extract C was analyzed for sulfur by atomic absorption spectroscopy (AA), and this sulfur was assumed to be sulfate. At the conclusion of the 3 extractions, the remaining wood and cellulose were digested in nitric acid, and the digests were also analyzed by AA. The sulfur in these digests was assumed to be bound to the wood or cellulose.

The results indicated that the wood retained higher quantities of NaMDC and its decomposition products (Table I-20). In general, cellulose filter paper retained the next largest amount of each component, while glass retained the least. The difference in product concentrations between wood and cellulose suggests that lignin or hemicellulose may play an important role in NaMDC reactivity; however, the structure of wood may act as a trap that protects the NaMDC and its decomposition products from volatilization. Previous tests using pure MIT indicate that large quantities of this chemical are retained by the wood structure. Additional tests are now underway to identify the NaMDC decomposition products present in soiled wood.

Table I-20. Deposition of Selected NaMDC Decomposition Products in Wood, Cellulose, or Glass following 75 or 134 Days of Incubation.

| Reaction Product | Percent Yield of Selected Compounds (as sulfur) ^a | | | | | |
|--|--|---------|--------|--------------|--------|-------------|
| | Wood | | Paper | | Glass | |
| | 75 dys | 134 dys | 75 dys | 134 dys | 75 dys | 134 dys |
| Sulfur | 20.0 | 30.0 | 5.5 | 1.8 | 9.7 | 5.7 |
| DTD-MMDT | 1.1 | 3.3 | 1.3 | 0.03 | BD | 0.02 |
| MIT-MMC | BD ^b | 0.7 | BD | 0.2 | BD | 2.5 |
| DMTU | 4.0 | 9.5 | 6.2 | 5.8 | 4.0 | 3.7 |
| NaMDC + Na ₂ S ₂ O ₃ | 25.0 | 10.0 | 44.0 | 20.0 23.0 | 35.0 | 4.0 33.0 |
| Sulfate | 11.0 | 4.9 | 2.5 | Tr | BD | BD |
| Unextractable sulfur in wood | 4.7 | 3.5 | 0.9 | 0.7 | - | - |
| Total | 65 | 62 | 60 | 51 | 49 | 49 |

^a Numbers represent percent of sulfur yields for the various products. Because the number of sulfur atoms in the products may not be the same as in NaMDC, the molecular yield may be different. For example, a 100% yield of MIT would represent a 50% yield based on sulfur.

^b Below detectable limits.

The emission of MIT from combinations of wood, cellulose, and glass treated with NaMDC was tested using 2 oz. bottles with PTFE-lined screw caps. Each bottle contained a 1-dram vial with 2 ml of a EEE-KOH trapping mixture for MIT. Each bottle received 0.2 g of round wood or cellulose or not substrate and 50 ml Vapam solution. MIT was collected in the trapping solution and analyzed by LC as described in Section I. These tests could not evaluate emission of

COS or CS₂, since the trapping mixture was non-reactive with these components.

When 0.2 g of wood was added to 50 ml of Vapam, 30-45 percent of the theoretical potential MIT product was trapped after 24 hours. In the absence of wood, only 1 percent of the potential MIT was trapped, and a small amount of light-colored residue was left in the bottles, suggesting that the Vapam may have dehydrated before it could decompose. The cellulose filter paper also failed to stimulate MIT production, once again, suggesting that lignin or hemicellulose may play more important roles in Vapam decomposition.

One interesting phenomenon was the enhanced MIT emission when water was added to the Vapam-wood mixtures. MIT recovery increased to 55 to 65% of the theoretical yield when 50 or 100 ml of water was added. This effect was more variable when higher levels (200 or 300 ml) of water were added. The effect of added moisture suggests that Vapam decomposition will be greatest where wood moisture levels are higher. Since decay will be more likely to occur in these zones, the moisture effect should enhance fungal control. The effect of water on MIT emission glass or cellulose-NaMDC mixtures was less uniform, suggesting that other factors may be important in the absence of wood.

Development of a Trapping Procedure for Determining MIT Emission

In the process of determining the rate at which Vapam reacts to produce MIT and other decomposition products, we discovered that volatile chemicals sometimes escaped through tubes used to retain the chemicals. Although it is easily retained using gelatin, MIT is an extremely difficult chemical to contain and will readily move through most materials.

To overcome this problem, we developed a trapping method to prevent the volatile MIT from moving out of the chamber. MIT, in the presence of alcohol, reacts slowly to form stable, non-volatile thiourethanes (Ethoxythiourethane or ETU). These compounds can then be quantified using high-performance liquid chromatography (HPLC).

In selecting the trapping compound, several properties were sought, including: high reactivity with MIT to produce a single, stable reaction product that absorbs at 250 nm, non-interference with UV detection, minimal volatility or toxicity, and solubility (along with the reaction product) in standard HPLC solvents. After some experimenting, ethoxyethoxyethanol (EEE) was identified as the chemical which most closely fit these requirements. In pure solutions, EEE normally reacts too slowly with MIT to be useful, but this reaction occurs rapidly (<20 min.) in the presence of sodium or potassium hydroxide.

To evaluate this method, trapping mixtures were prepared by mixing 20 mg of sodium acetate, sodium hydroxide, or potassium hydroxide per ml of EEE. Two ml of the trapping mixture, in a 2-dram vial, was placed in a 2-ounce, wide-mouth bottle, and 10-20 μ l of melted MIT was added to the bottle with a syringe. The chamber was sealed and incubated for up to 10 days at room temperature. At selected time points, the trapping liquid was removed, diluted 100 to 1000 times with water and analyzed using a Shimadzu HPLC equipped with a 5-mm RP-1 column (20 cm long by 4.6 mm in diameter). The mobile phase was acetonitrile:water (1:3) at a flow rate of 1 ml/minute, and UV detection was used at 250 nm.

Of the 3 salts added to the EEE, sodium acetate trapped only 10 percent of the MIT, while sodium hydroxide and potassium hydroxide

both resulted in 100 percent conversion of the MIT to ETU in the trapping mixture. The traps removed 95 percent of the MIT after only four hours and 100 percent after 24 hours. In addition, the sensitivity of the HPLC for ETU was found to be 16 times greater than for MIT. This sensitivity will permit MIT detection using HPLC methods at much lower levels than previously used methods.

In addition to the evaluation of salts for the trapping mixture, the effect of excess moisture on trapping efficiency and the stability of the trapping mixture were also examined. Although the presence of 10 percent moisture in the trapping mixture only reduced MIT trapping efficiency by 1 to 5 percent, a moisture level of 50 percent reduced trapping efficiency by 60 percent. These results indicate that the trapping procedure will be less effective for measuring MIT release from wood that contains excess moisture. In addition, other tests indicate that these same high moisture levels will result in rapid releases of MIT that the trap could not effectively retain.

The final parameter examined, trap stability, indicated that acidified trapping mixtures lost MIT at a rate of 1 to 2 percent per day, while more basic mixtures experienced MIT losses of 0 to 0.24 percent per day.

The results indicate that the trapping mixtures can be used to effectively retain MIT emitted from fumigant-treated wood. This procedure will be employed to examine MIT emissions from Vapam-treated wood.

Emission of MIT, CS₂ and COS from Vapam or MIT Treated Douglas-fir Heartwood

At present, fumigant applications are limited to uninhabited structures or utility poles because of their volatility and toxicity, and because there is little information available on how the chemicals are released from the wood over time. Preliminary studies suggest that most of the fumigant is rapidly bound to the wood, but more information is needed on the expected levels of fumigant emissions from treated wood structures and the residual fumigant levels in wood intended for disposal.

Douglas-fir heartwood blocks (20.32 x 15.24 x 9.16 cm) were conditioned to 9% moisture and end-coated with epoxy resin. One or two 15 cm long (1.27 cm diameter) holes were drilled at one end, and 20 ml of either Vapam or MIT was poured into each hole. The holes were then plugged with rubber stoppers and sealed with silicone caulk. In addition, 3 blocks were prepared without chemical to serve as controls. The finished blocks were immediately placed into polyethylene tanks 24.3 cm in diameter and 29.2 cm in length which had been fitted with glass rods to suspend the blocks 5 cm above the tank floor.

Each polyethylene tank had inlet and outlet ports on opposite ends, as well as a septum to allow gas sampling. The tanks were sealed and a continuous air flow had been filtered through distilled water and diatomaceous earth was passed through the chamber. Flow rates ranged from 0.110 to 0.189 mls per second, and were measured each time a gas sample was removed.

Gas samples periodically drawn from the tanks were injected directly into a gas chromatograph equipped to detect sulfur compounds including carbon disulfide (CS₂), carbonyl sulfide (COS) and MIT. Peaks detected from the compounds were identified and quantified by comparison with standard solutions.

Vapam tanks: COS was only detected after 1600 to 1750 hours after treatment (Figure I-8). Emission levels in 2 tanks are still increasing, while levels in the other tanks appear to be steady or decreasing. Because of the difficulty of producing COS standards, the peak areas for this chemical were normalized and used as a relative measure of this compound. At this time COS values range from 19 to 360, although a previous sampling resulted in a value of 458 (Tables I-24, 25).

CS₂ was detected at or near the time of installation in all 4 Vapam tanks. Emissions appeared to increase rapidly for the

Table I-24. Emission levels from Douglas-fir treated with Vapam or MIT as measured by GC analysis of air samples.

| Tank # | Total Hours Exposed | Current Air Flow Level (mls/sec) | COS ^a Current Emission Level ^b | CS ₂ ^a Current Emission Level (ul/ml x 10 ⁻⁷) | MIT ^a Current Emission Level (ug/ml) |
|-------------|---------------------|----------------------------------|--|---|---|
| Vapam Tanks | | | | | |
| 1 | 5380 | 0.16 | 19 | 10 | 0.006 |
| 4 | 5352 | 0.15 | 460 | 35 | 0.033 |
| 10 | 5352 | 0.06 | 30 | 35 | 0.012 |
| 14 | 5380 | 0.17 | 25 | 11 | 0.010 |
| MIT Tanks | | | | | |
| 2 | 5253 | 0.19 | 2100 | 80 | 0.642 |
| 6 | 4653 | 0.15 | 1500 | 388 | 1.218 |
| 9 | 4653 | 0.18 | 500 | 200 | 0.721 |
| 15 | 5253 | 0.21 | 200 | 70 | 0.654 |

a. COS = carbonyl sulfide, CS₂ = carbon disulfide, and MIT = methylisothiocyanate.

b. Values represent square root of peak area after adjustment for injection size and detector sensitivity.

first few hundred hours, then leveled off until adjustment of the air flow to a lower rate caused the CS₂ to be detected at higher levels (Figure I-9). All four tanks now appear to have stabilized at this higher level. At the last sampling, emissions of CS₂ in the four tanks varied from 10 to 35 x 10⁻⁷ ul/ml

(Table I-24), while the maximum level detected at any previous sampling was 37×10^{-7} ul/ml (Table I-25).

MIT, although present initially in 2 tanks, was not detected again in any of the tanks until 2000 hours. MIT was not detect in one tank until 4500 hours after treatment (Figure I-10). Emission levels appeared to stabilize soon after detection, although levels in one tank have only been monitored a short time. Levels detected at the last sampling ranged from 0.005 to 0.033 ug/ml of air (Table I-25).

MIT Tanks: COS was detected immediately after installation, remaining fairly constant except for changes caused by fluctuations in air flow (Figure I-9). As with the Vapam tanks, COS levels were adjusted for injection size and detector sensitivity. Current levels vary from 200 - 2100 (Table I-24,) while the maximum level previously measured was 3375 (Table I-25).

CS₂ was detected immediately after tank installation, with levels remaining fairly constant or gradually increasing until decreased air flow rate caused a corresponding increase in emission levels (Figure I-9). All but one tank has stabilized at the new air flow rate, with current emission levels ranging from 70 to 390×10^{-7} ul/ml (Table I-25).

Table I-25. Maximum levels of carbonyl sulfide (COS), carbon disulfide (CS₂) and MIT detected in Douglas-fir heartwood treated with Vapam or MIT as measured using GC analysis of air samples.

| (Hours) Tank # | COS | | CS ₂ | | MIT | |
|-------------------|---|--|---|---|--|------------------------------|
| | Max. Emiss. Level ^a (mls/sec) | Air Flow At Max Level (ul/mlx10 ⁻⁷) | Max. Emiss. Level (mls/sec) (Hours) | Air Flow At Max. Level (ug/ml) | Max Emiss. Level (mls/sec) (Hours) | Air Flow At Max. Level |
| Vapam Tanks | | | | | | |
| 1 | 26 (3792) | 0.14 | 20 (3792) | 0.17 | 0.006 (5380) | 0.16 |
| 4 | 458 (5352) | 0.15 | 37 (4608) | 0.17 | 0.045 (4608) | 0.17 |
| 10 | 399 (3980) | 0.09 | 34 (5352) | 0.06 | 0.013 (3980) | 0.09 |
| 14 | 29 (3125) | 0.19 | 11 (5380) | 0.18 | 0.010 (5380) | 0.18 |
| MIT Tanks | | | | | | |
| 2 | 2481 (3881) | 0.19 | 98 (4509) | 0.20 | 1.250 (1888) | 0.40 |
| 6 | 3375 (2920) | 0.14 | 388 (4653) | 0.15 | 1.557 (1440) | 0.21 |
| 9 | 548 (3281) | 0.15 | 200 (3909) | 0.17 | 1.759 (3281) | 0.15 |
| 15 | 2501 (3354) | 0.19 | 71 (4509) | 0.25 | 0.844 (3881) | 0.21 |

a. Values represent square root of peak area after adjustment for injection size and detector sensitivity.

MIT was detected immediately after installation, with levels rising rapidly for 200 - 500 hours, (Figure I-10). These emissions have either remained constant or declined to levels ranging from 0.69 - 1.25 ug/ml (Table I-24). Although air flow rates vary between the tanks, MIT emissions were similar in all 4 tanks, with a maximum level of 1.760 ug/ml (Table I-25).

Emission levels in the tanks varied with small changes in the air flow rate, making interpretation of the results somewhat difficult; however, several trends were evident. MIT treated wood began to emit all three types of gasses almost immediately, while the Vapam tanks produced only CS₂ initially, and never have produced any of the gasses at levels as high as those emitted by

Figure I-8. Emission of carbonyl sulfide from Douglas-fir heartwood treated with Vapam (a, b) or MIT (c, d) as measured by GC analysis of air samples.

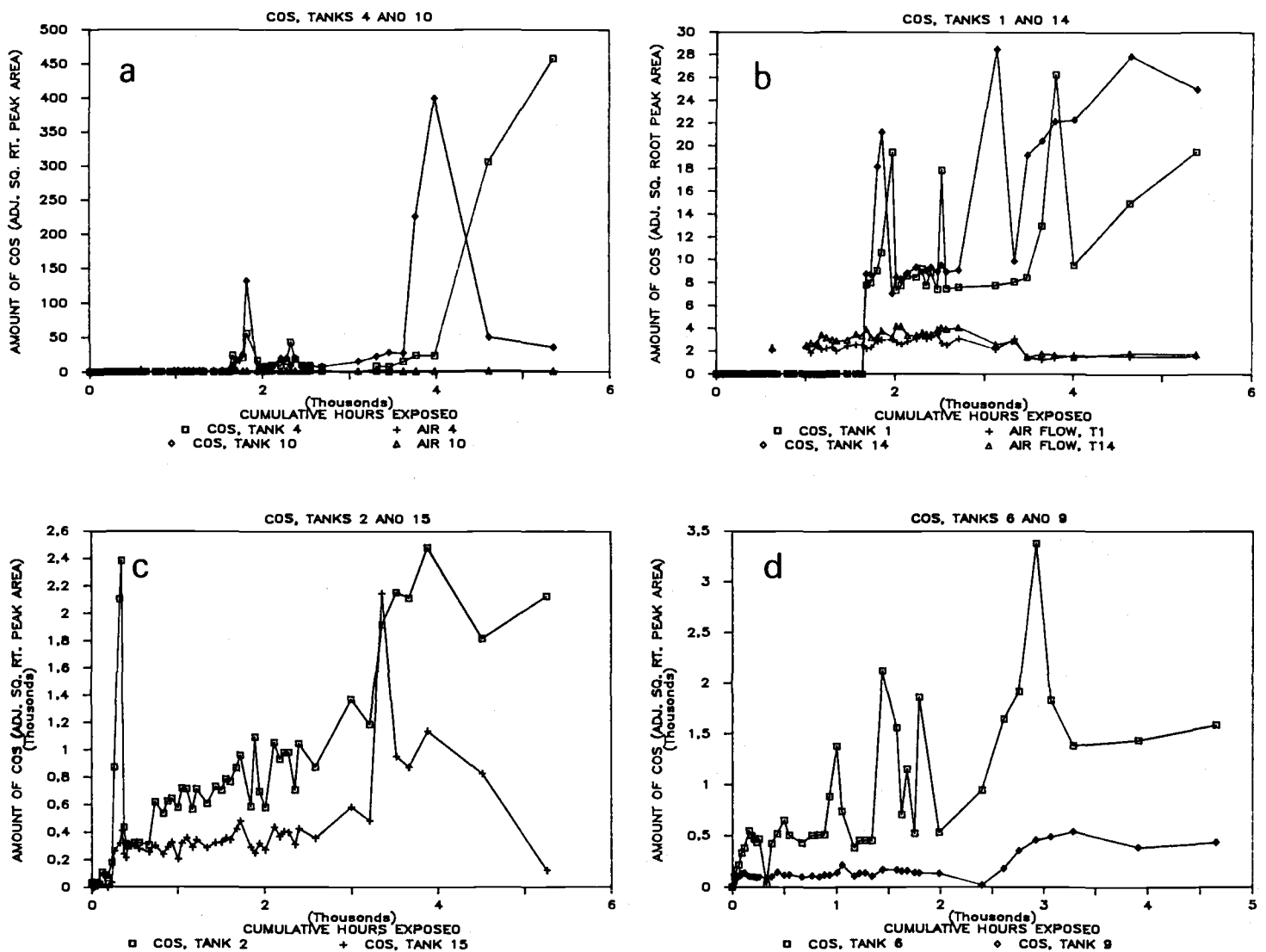


Figure I-9. Emission of carbon disulfide from Douglas-fir heartwood treated with Vapam (a, b) or MIT (c, d) as measured by GC analysis of air samples.

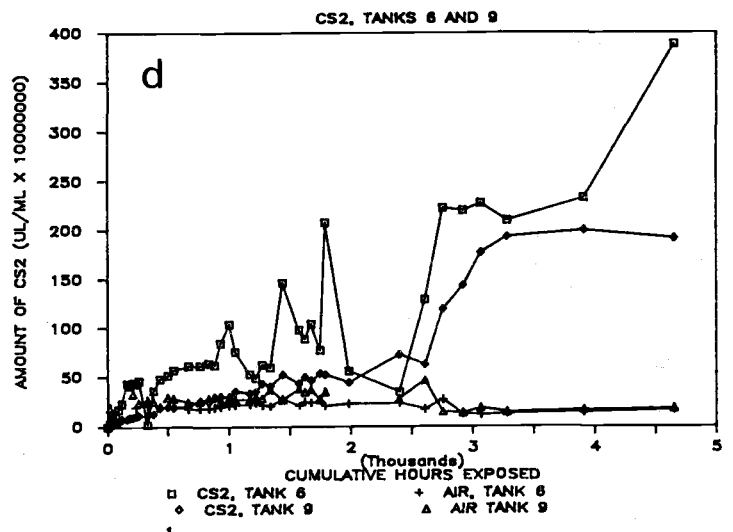
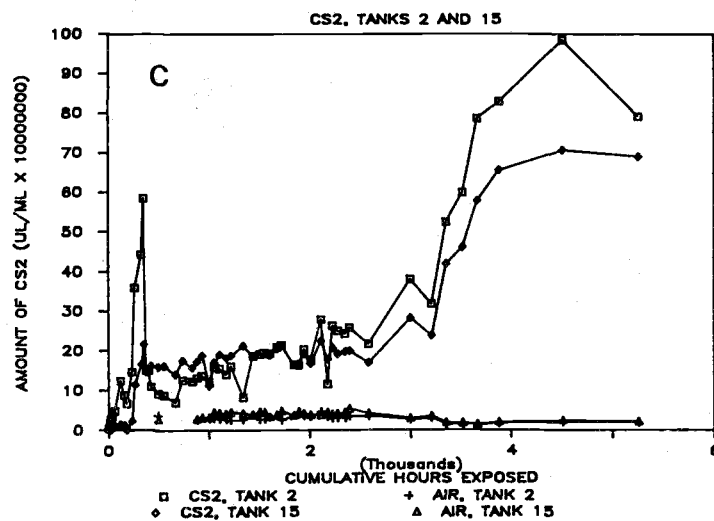
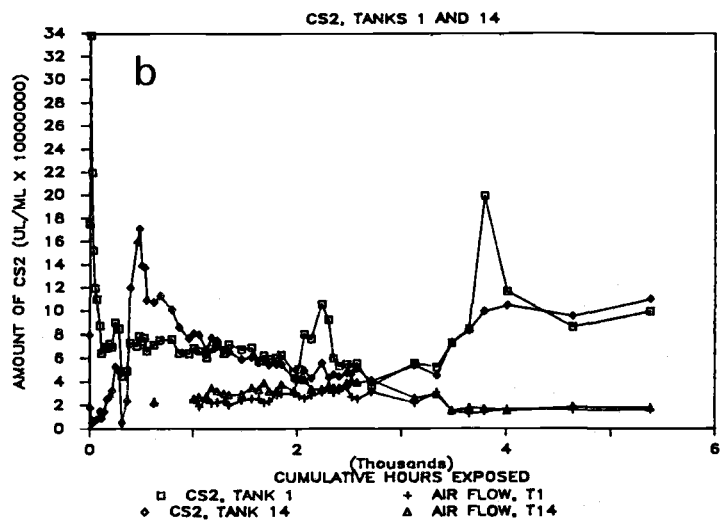
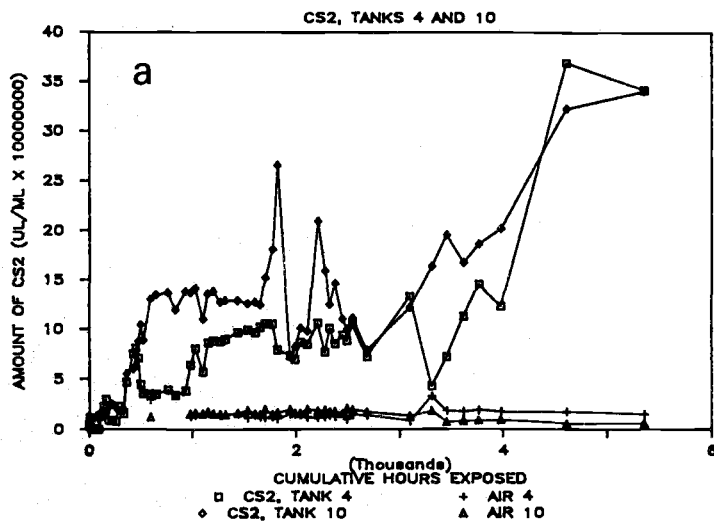
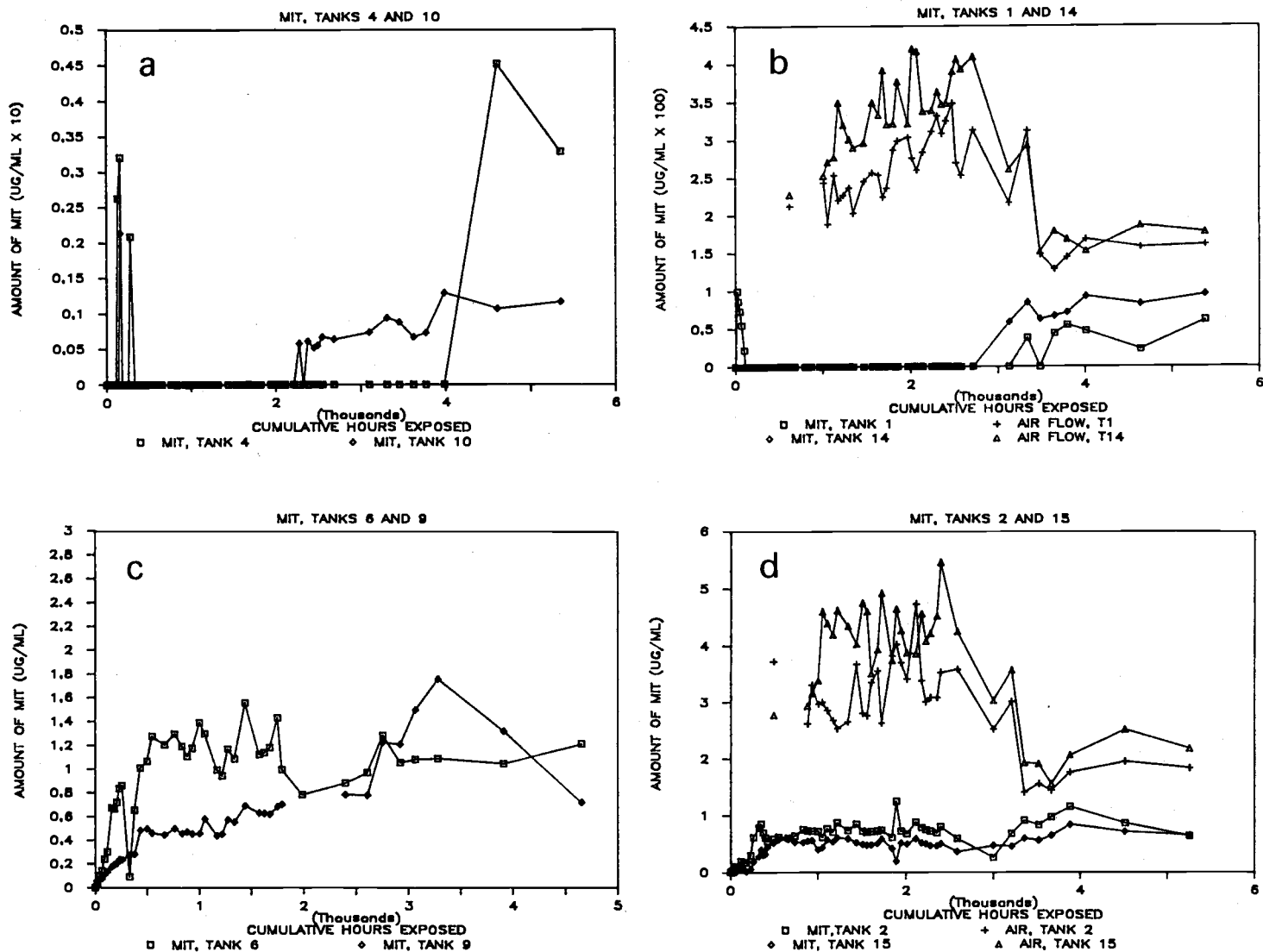


Figure I-10. Emission of MIT₁ from Douglas-fir heartwood treated with Vapam (a, b) or MIT (c, d) as measured by GC analysis of air samples.



the MIT tanks. In addition, except for the CS₂ level in tank 6 and the COS levels in tanks 1 and 4, all emissions appear to have stabilized in accordance with their respective air flow rates. It seems likely that all three types of emissions, in a stable environment, would reach a constant level that might

slowly decline over an extended period.

At present, it is unclear what these emission rates mean in terms of long term fumigant performance; however it is clear that the wood does not completely trap all of the fumigant. As a result, remedial treatment of exposed beams in buildings should be performed in a manner that limits risk of chemical migration through the wood into inhabited areas.

Effect of wood moisture content on fungitoxicity of MIT in Douglas-fir Heartwood

Although fumigant treatment of utility poles with MIT will effectively control internal decay, there are still many questions concerning the ultimate fate of this chemical in wood. MIT fungitoxicity can be lost by diffusion out of the wood, or by reactions within the wood to form new chemicals. The amount of MIT lost by diffusion processes will determine the safety of fumigant application in poorly aerated areas, while losses from decomposition may provide limited decay control if the resulting products are fungitoxic. Both types of losses will determine the effective duration of MIT treatments.

MIT vapors remain in wood for at least 5 years after an MIT or Vorlex treatment, allowing ample time for chemical interactions with wood that can influence fumigant effectiveness (Table I-26). Improving our understanding of the fate of MIT in wood, including decomposition rates and the residual fungitoxicity of decomposition products, will help determine retreatment schedules and identify any disposal hazards associated with fumigant-treated wood. The following experiments investigated the formation and fungitoxicity of MIT residues in Douglas-fir heartwood following fumigation and extensive aeration.

Table I-26. Potential reaction products that may form during methyl-isothiocyanate fumigation of wood.

| Substrate | Potential Products |
|-----------------------|---|
| Water | DMTU (Dimethylthiourea), CS ₂ , CO ₂ |
| Water, O ₂ | DTD (2,4 dimethyl-1,2,4 thiadiazolidine-3,5 dithione) |
| | MMTD (4-methyl-5-methylimino-1,2,4-dithiazolidine-3-thione) |
| Alcohols | Carbamothioates |
| Carboxylic Acids | Amides & COS |
| Amines | Thioureas |

Initial MIT Fumigant Treatment: Small blocks (0.8 cm grain direction x 1.0 cm x 3.0 cm) containing 3 to 6 growth rings per cm were cut from the heartwood of an unseasoned Douglas-fir log (30 cm in diameter). The blocks were oven-dried, weighed, and then groups of 90 blocks were adjusted to either 0%, 12%, or 60% moisture content (MC). Each group of blocks was enclosed in a glass jar with a Teflon-lined screw-top cap along with excess solid MIT to produce a saturated MIT atmosphere (about 42 ug MIT/ml air) and stored at 20°C. Ninety additional blocks were left untreated as controls.

After 15 and 36 weeks fumigation, 43 blocks at each moisture content were removed and initially aerated in a fume hood for 36 and 15 weeks, respectively. The blocks were then further aerated at 20°C and 50% relative humidity until they were required for the experiments below. Four blocks were removed from each jar following 30 weeks fumigation and extracted in ethyl acetate and analysed by gas chromatographic (GC) procedures to determine the initial MIT concentrations present in the blocks during fumigation.

GC analyses were conducted on a Varian 3700 Gas Chromatograph equipped with a flame-photometric detector and a sulfur filter. A glass column (3 m x 4 mm

inner diameter) packed with 10% Carbowax 20M on 80/100 Supelcoport solid support was operated at: nitrogen-flow rate, 75 cc/min; detector temperature 200°C, injection temperature 60°C or 200°C; column temperature, 135°C or 50°C programmed to 150°C. The lower injector and column temperatures were used for analysis of extracts that decomposed to volatile sulfur compounds at higher temperatures. MIT and CS₂ were identified and quantified based on retention times and peak areas of standard solutions in ethyl acetate. COS concentrations were estimated based on peak areas and COS sulfur content.

Non-volatile Residues in Fumigated Blocks: The amount and type of MIT residues remaining in aerated blocks initially fumigated for 15 or 36 weeks at either 0%, 12%, or 60% MC were investigated in 3 experiments. These experiments quantified the residues based on block weight gain, specific fumigation residues, and total sulfur content.

A. Weight Gain- Groups of 6 to 8 blocks from each treatment group were analysed for weight increases indicative of MIT residues not removed by aeration. Blocks aerated for 37 weeks at 50% relative humidity (RH) were exposed to 100% RH for 3 weeks in closed containers above distilled water. Blocks were weighed and then sequentially equilibrated at 93% RH, 76% RH and 55% RH above saturated salt solutions of NH₄H₂PO₄, NaCl, and Mg(NO₃)₂, respectively, to determine if MIT residues influenced wood equilibrium moisture contents (EMC). The final oven dry weights of blocks were determined by drying at 65°C for 3 days, followed by 70°C for 1 day in a closed container over anhydrous calcium sulfate. Final block dry weights were used to calculate EMC's and the mass of MIT residues remaining in the wood.

B. Total Sulfur Content- The total sulfur content (all compounds) remaining in blocks following 12 weeks aeration at 50% RH was determined for

each fumigation treatment exposure. Blocks were analysed both before and after solvent extraction to determine whether the MIT residues were loosely deposited or tightly bound (possibly covalently) to the wood.

Eight blocks from each treatment group were ground in a Wiley mill (20 mesh screen) and then one-half of them were extracted in: cold ethyl acetate (3 times in 25 ml for 18 hr); cold methanol (3 times in 25 ml for 18 hr); hot (85°C) water (3 times in 125 ml for 12 hr); hot (65°C) 80% methanol (3 times in 125 for 18 hr), and finally in acetonitrile (12 hr Soxhlet extraction). One gram samples of extracted and non-extracted blocks were digested in 10 ml of concentrated nitric acid and analysed for total sulfur content at the Oregon State University Plant Analysis Laboratory using a Jarrell-Ash ICAP-9000 Inductively Coupled Plasma (ICP) spectrometer. The total sulfur content was used to estimate rates of formation of extractable and non-extractable MIT residues in the wood.

C. Specific MIT Fumigation Residues- The extracts from blocks initially fumigated for 36 weeks were concentrated in a rotary evaporator and then analysed for specific MIT decomposition residues on a Shimadzu High Performance Liquid Chromatograph using a 15 cm long (4.6 mm ID) Econosphere C-18 (3 µm particle size) column and a wave length of 250 nm. Extracts were analysed using isocratic mobile phases of: 100% methanol (MeOH); 16% acetonitrile, 36% MeOH, and 48% water; or 6.7% acetonitrile, 13.3% MeOH, and 80% water at elution rates of 1 ml/min. Decomposition products were identified based on retention times using the different mobile phases with standards of known MIT decomposition products (see Table 1). Standards were made using DMTU (N773-A63), DTD (N1045-B63), and MMTD (N1044-A63) obtained from Stauffer Chemical Co. (Westport CT), as well as sublimed sulfur.

Fungitoxicity of MIT Residues in Wood: A series of experiments were conducted to determine if the residues deposited in MIT fumigated wood imparted any resistance to decay by P. carbonica Overh., a major brown-rot fungus of Douglas-fir heartwood.

A. All Residues- The combined toxicity of all MIT residues remaining in aerated wood (8 weeks at 50% RH) was investigated by infiltrating 10 blocks from each fumigation exposure group with water and sterilizing them using a reciprocal tyndallization process. The blocks were adjusted to 60% MC, inoculated with a water suspension of fragmented P. carbonica mycelium, and placed in petri dishes on glass rods over wet filter paper to maintain humidity. The plates were sealed with parafilm and incubated for 10 weeks at 20-25°C to allow fungal colonization.

B. Specific Extractable Residues- The 3 MIT decomposition residues identified in extracts of fumigated wood, DMTU, DTD, and sulfur (Table I-30), were tested for their influence on fungal colonization and subsequent decay of Douglas-fir heartwood blocks. Groups of 8 blocks (0.5 cm grain length x 2.5 cm x 2.5 cm) were oven-dried and infiltrated with solutions of test chemicals to produce a range of chemical retentions. Water was used as a carrier for DMTU, while ethanol was used for DTD and sulfur. Ethanol was removed by drying the blocks at 70°C for 48 hr. The blocks were then infiltrated with sterile water under vacuum, adjusted to 70% MC, and inoculated with suspensions of fragmented P. carbonica mycelium. After 12 weeks, the blocks were observed for fungal growth, oven-dried, and weighed to determine weight loss due to fungal decay.

C. Non-extractable Residues- Groups of 8 blocks from each fumigation exposure (24 week aeration) were extracted in MeOH (36 hr), water (60 hr), and

acetonitrile (36 hr) using a Soxhlet apparatus, and then dried (72°C for 48 hr) to determine initial oven dry weights. These blocks were infiltrated with water, autoclaved (15 min at 15 psi), and Soxhlet extracted for 24 hr in water to remove any water soluble compounds produced by autoclaving. The blocks were adjusted to 70% MC and inoculated with a suspension of fragmented P. carbonica mycelium.

After 6 weeks, P. carbonica was poorly established on control blocks, with some Penicillium sp. contamination. To subject the blocks to a harsher decay treatment, they were reautoclaved (10 min, 15 psi) and placed on glass-rods above 2% malt agar in petri-plates inoculated with P. carbonica. After 10 weeks incubation (20-25°C), blocks were oven-dried to determine weight loss due to decay.

Release of Volatiles from Fumigated and Aerated Wood: Fungitoxicity studies suggested that even after extensive aeration under dry conditions (50% RH), fumigated blocks released volatile fungitoxicants when wetted. This effect was supported by GC analyses of headspace vapors above dry-aerated blocks, which found MIT and COS vapors released only after the wood was wetted (100% MC).

The influence of moisture content on the release of volatile sulfur compounds from MIT fumigated wood was further investigated in blocks from each MIT fumigation exposure. Blocks aerated for 27 weeks at 50% RH were ground in a Wiley mill (20 mesh screen), and immediately sealed in 25 ml chambers. After 2 hrs, headspace gases were analysed to determine if volatile sulfur compounds were released by the grinding procedure. These samples were aerated for 3 days at 50% RH to allow newly released volatiles to dissipate, and then subsamples of the ground wood were extracted in ethyl acetate (7 days) to

determine the initial levels of extractable, volatile sulfur compounds. Wood was either extracted dry, or by first adding an equal weight of water, to determine if water influenced extraction results.

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

RESULTS

Initial MIT Fumigant Treatment: Low levels of CS₂ (20 to 60 ug/g wood) and COS (16 to 240 ug/g wood), and high concentrations of MIT (28 to 31 mg/g wood) were detected in blocks during fumigation. The lowest concentrations of COS and CS₂ were found in blocks fumigated at 0% MC, suggesting that water influenced MIT decomposition.

Blocks fumigated at 12% and 60% MC were distinctly yellowed, while those exposed at 0% MC appeared unchanged. In addition, the surface of blocks fumigated for 36 weeks at 60% MC contained large numbers of clear to yellowish crystals, which HPLC analyses suggest are mostly sulfur. Scanning electron microscopy (SEM) found crystals only on the external surfaces of blocks, but never internally. Energy dispersive X-ray scans found high sulfur contents in all cell wall layers.

Non-volatile Residues in Fumigated Blocks

A. Weight Gain- Wood moisture content during fumigation greatly influenced the mass of MIT residues remaining after extensive aeration (Table I-27). Blocks did not gain detectable weight when fumigated at 0% MC, but as the wood

moisture content and length of exposure were increased, block weight gains also increased. These weight gains represent the deposition of fumigant residues including extractable MIT residues, MIT decomposition products, and non-extractable covalently bound products. Deposition of MIT fumigation residues in wood also influenced the EMC of blocks during desorption (Table I-28). These same patterns were also observed in blocks following 15 weeks fumigation, but all EMC influences were minor and should not influence behavior in wood.

Table I-27. Mass of non-volatile residues^a remaining in Douglas-fir heartwood blocks following exposure to a saturated methylisothiocyanate atmosphere for 15 or 36 weeks.

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

^a Blocks were aerated for 37 weeks (50% RH), wetted to the fiber saturation point (3 weeks), and then dried at 70°C.

^b Values represent the means and standard deviations (in parenthesis) of 6-8 blocks corrected for a 0.8 mg average weight loss in controls.

Table I-28. The influence of methylisothiocyanate fumigation residues on wood equilibrium moisture content (EMC).^a

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

^a Douglas-fir heartwood blocks were exposed to a saturated MIT atmosphere for 36 weeks and then aerated extensively.

^b Groups significantly different from controls at $\alpha=0.01$ based on least significant difference calculations.

B. Total Sulfur Content- MIT fumigation greatly increased the total sulfur content of blocks, which gives a quantitative measure of sulfur containing MIT residues remaining in aerated wood (Table I-30). A large portion of this sulfur was extractable, especially in wood at higher moisture contents. Non-extractable sulfur residues, which may represent MIT reactions with wood alcohol groups to form carbamothioates, were present at low concentrations in wood fumigated at 0% MC. In wood fumigated at 12% and 60% MC the higher levels of non-extractable sulfur were independent of wood moisture content, and dependent only on the length of fumigation.

The rate of formation of MIT residues in wood was estimated based on the total sulfur content remaining in the fumigated blocks. Based on the sulfur contents of blocks fumigated for 36 weeks in a saturated MIT atmosphere (Table I-29), MIT decomposed at about 0.17%, 0.94%, and 1.6% of the total sorbed MIT per week for wood at 0%, 12%, and 60% MC, respectively. Non-extractable sulfur residues were produced at a rate of 0.36% of the sorbed MIT per week in wood fumigated at both 12% and 60% MC.

Although MIT apparently decomposes slowly in wood, the long periods that fumigants remain in poles may permit deposition of substantial concentrations of MIT residues. Wood in ground contact is generally above 12% MC, which is sufficient to deposit these extractable and non-extractable MIT residues in the wood. Decomposition will influence fumigant effectiveness by reducing fumigant concentrations in wood, but the products formed may also provide residual decay control.

C. Specific MIT Fumigation Residues- HPLC analysis of extracts of wood initially fumigated for 36 weeks found DMTU and DTD (MIT decomposition in water, see Table I-26), along with elemental sulfur (Table I-29). All three

products were formed at concentrations dependent on the wood moisture content during fumigation, with minimal concentrations formed in wood fumigated at 0% MC, and much higher concentrations found in wood fumigated at 12% and 60% MC. Although wood at 12% MC is well below the FSP of Douglas-fir, and free water should not be present, substantial amounts of these MIT-water reaction products were still formed. Even after the 19 weeks aeration, significant amounts of MIT were extracted from these blocks, suggesting that some MIT is tightly sorbed to wood components, and is not easily removed by dry aeration.

Both DMTU and DTD are highly soluble in ethyl acetate and methanol, but only about 1/3 of each compound was removed by ethyl acetate extraction, with the rest removed in cold methanol. The increased wood swelling ability of methanol may have been necessary for the improved removal of these MIT decomposition products, suggesting that they were deposited within the cell walls.

Decomposition products identified from the extracts (Table I-30) accounted for only a portion of the total extractable sulfur removed from these blocks (Table I-29). This was not unexpected, since MIT reacts with a large number of chemical groups, but only some standards for known MIT decomposition products were available for HPLC peak comparisons.

Fungitoxicity of MIT Residues

A. All Residues- MIT fumigated blocks aerated for 8 weeks at 50% RH were resistant to colonization and decay by P. carbonica, with fungal growth only on control blocks. These blocks were then exposed to harsher decay conditions by transferring them onto glass rod supports above 2% malt agar plates containing actively growing P. carbonica cultures. After 6 weeks, only control blocks and blocks initially fumigated for 15 weeks at 0% MC were

Table I-29. Average sulfur content of Douglas-fir heartwood blocks exposed to a saturated methylisothiocyanate atmosphere for 15 or 36 weeks, and then aerated for 40 or 19 weeks, respectively.^a

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

^a Sulfur contents determined by ICP analysis of acid digestions of wood.

^b Values represent the means and standard deviations (in parenthesis) of duplicate blocks.

Table I-30. Concentrations of non-volatile methylisothiocyanate residues extracted from ground Douglas-fir heartwood blocks.^a

| Wood MC During Fumigation | ug/g Oven Dry Wood ^b | | | | |
|---------------------------|---------------------------------|--------|-----|-----|------------|
| | DMTU | Sulfur | DTD | MIT | Total as S |
| Untreated Controls | 0 | 2 | 0 | 0 | 2 |
| 0% | 2 | 13 | 0 | 67 | 43 |
| 12% | 1750 | 360 | 102 | 140 | 1020 |
| 60% | 6000 | 2170 | 840 | 170 | 4540 |

^a Blocks were fumigated in a saturated MIT atmosphere at selected moisture contents (MC) for 36 weeks, and then aerated for 19 weeks before analysis.

^b Values represent the average of two replicates, which except for MIT concentrations, were very similar for each replicate.

colonized by P. carbonica. The remaining colonies were killed in all plates except one containing blocks initially fumigated for 36 weeks at 0% MC, even though there was no direct wood-agar contact. Although these blocks were aerated extensively under dry conditions, volatile fungitoxicants were apparently released when the wood was wetted.

B. Specific Extractable Residues- All 3 MIT decomposition products inhibited the ability of P. carbonica to colonize and decay blocks (Table I-31). DTD was the most fungitoxic, preventing visible fungal growth on wood at concentrations above 0.24 mg/g oven dry wood. Although DMTU was less fungitoxic, requiring 4.8 mg/g oven dry wood to prevent fungal growth, it was also produced in much higher concentrations in wood (Table I-30). Sulfur, on the other hand, reduced wood weight loss independently of the concentrations tested, but never completely inhibited fungal growth, which is probably related to its poor water solubility.

The decay hazard in this test was relatively mild, as the fungus had to colonize and decay wood without any external nutrients. This resulted in low weight losses, but may better approximate actual decay hazards. DMTU and DTD offer the potential for long term residual protection in fumigated products, depending on the concentrations deposited in wood by MIT decomposition. These products are formed at the highest concentrations in wet wood, where their ability to prevent re-establishment of decay is most needed, but the stability of these compounds is not known.

C. Non-extractable Residues- Those MIT residues not removed by solvent extraction can impart some decay resistance to the wood (Table I-32). Although all blocks were colonized, blocks fumigated at high moisture contents (high sulfur residue concentrations) suffered substantially lower weight

Table I-31: Influence of methylisothiocyanate decomposition products on the ability of *Poria carbonica* to colonize and induce weight loss in Douglas-fir heartwood blocks.^a

| MIT Decomposition Product ^b | Concentration mg/g OD Wood | Fungal Growth | Block Wt. Loss Percent ^c | Percent of Control Wt. Loss |
|--|-------------------------------|------------------|---|-----------------------------------|
| DMTU ³ | 4.8 | - | 0.32 (0.11) | 13 |
| | 1.1 | + | 1.19 (0.20) | 49 |
| | 0.21 | ++ | 2.41 (0.41) | 99 |
| | 0.00 | ++ | 2.44 (0.37) | 100 |
| DTD ⁴ | 0.93 | - | 0.30 (0.05) | 16 |
| | 0.46 | - | 0.36 (0.06) | 20 |
| | 0.24 | - | 0.63 (0.09) | 35 |
| | 0.12 | ++ | 2.03 (0.17) | 52 |
| | 0.03 | ++ | 3.64 (0.61) | 94 |
| | 0.00 | ++ | 3.89 (0.95) | 100 |
| Sulfur | 1.2 | + | 1.15 (0.16) | 63 |
| | 0.62 | + | 1.02 (0.15) | 56 |
| | 0.23 | + | 1.15 (0.17) | 63 |
| | 0.12 | + | 1.41 (0.37) | 36 |
| | 0.00 | ++ | 3.89 (0.95) | 100 |

^a Blocks were incubated at 75% moisture content were inoculated with a mycelial fragment and spore suspension and then incubated for 12 weeks at 20-23°C.

^b Abbreviations are: Dimethylthiourea (DMTU), 2,4-dimethyl-1,2,4-thiadiazolidine-3,5-dithione (DTD). DTD was dissolved in ethanol for infiltration into the blocks, and consisted of about 90% DTD and 10% MMTD.

^c Figures represent means (standard deviations in parenthesis) of 8 replicate blocks.

losses. This decay test was severe, with an external carbon source supplied to the fungus, but these residues provided some decay protection.

Release of Volatiles from Fumigated and Aerated Wood: The release of volatile sulfur compounds from wetted blocks was similar for blocks initially fumigated for 15 and 36 weeks, but only the 36 week results will be described.

Grinding of dry-aerated blocks released detectable concentrations of MIT and CS₂, but not COS (Table I-33). Even after an additional 3 days of dry-

Table I-32. Influence of non-extractable MIT fumigation residues on the ability of *P. carbonica* to decay Douglas-fir heartwood^a.

| Fumigation Conditions | | Estimated Residue Concentration ug S/g wood ^b | Block Wt. Loss (%) ^c | Wt. Loss as % of Control |
|-----------------------|---------|--|---------------------------------|--------------------------|
| Exposure Duration | Wood MC | | | |
| Control | -- | 0 | 23.8 (1.9) | 100 |
| 15 Week | 0% | 140 | 20.3 (1.2) | 85 |
| | 12% | 770 | 15.2 (3.2) | 64 |
| | 60% | 770 | 13.2 (2.1) | 55 |
| 36 Week | 0% | 480 | 11.8 (1.2) | 50 |
| | 12% | 1730 | 8.3 (3.4) | 35 |
| | 60% | 1740 | 8.4 (4.0) | 35 |

^a Blocks weighing about 1 g were decayed in an agar block method for 10 weeks.

^b Residue concentrations (sulfur basis) were estimated from Table I-29.

^c Values represent mean and standard deviation of 8 replicate blocks.

aeration, substantial amounts of extractable MIT, COS, and CS₂ were present in the blocks (Table I-34). These concentrations were dependent on whether the blocks were extracted dry or with the addition of water, and suggests that water may swell wood for better extraction, or may be involved in chemical reactions forming these gases.

The rate of MIT release from ground blocks that were wetted to 100% MC was influenced by wood moisture content during the initial MIT fumigation (Fig. I-11). High rates of MIT release were initially observed in wood that was fumigated at 0% MC, but these rates decreased rapidly and MIT concentrations declined below detectable levels (0.05 ug MIT/hr/g wood) after 2 days. The rates of MIT release were initially lower in wood fumigated at higher moisture contents, but high concentrations of MIT continued to be released for a longer time. Low concentrations of COS and CS₂ were also initially released from wetted wood, but rapidly declined below minimum detection concentrations.

Table I-33. Release of volatile fumigant residues immediately after grinding methylisothiocyanate treated Douglas-fir heartwood blocks.^a

| Fumigation Moisture Content | Volatile Release (ug/g Oven Dry Wood) | | |
|--------------------------------|---------------------------------------|-----------------|------|
| | COS | CS ₂ | MIT |
| 0% | 0.00 | 0.23 | 0.46 |
| 12% | 0.00 | 0.55 | 0.15 |
| 60% | 0.00 | 0.09 | 0.07 |

^a Blocks at three moisture contents were initially exposed to saturated MIT vapors for 36 weeks, and then aerated for 33 weeks under dry (50% RH) conditions.

Table I-34. Extractable concentrations of volatile methylisothiocyanate fumigation residues in dry-aerated wood before and after aeration for 3 days at 100% moisture content (MC).^a

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

^a Blocks were initially exposed at 3 moisture contents to saturated MIT vapors for 36 weeks and then aerated for 33 weeks.

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

The concentrations of extractable MIT remaining in wood after the 3 day wet aeration were greatly reduced, especially in wood initially fumigated at 0% MC (Table I-34). Dry aeration for 33 weeks (50% RH) did not remove all volatile MIT residues from the blocks, but these residues were rapidly volatilized as the wood moisture content was increased. Wet wood is required for active fungal growth and decay, and moisture content dependent release offers a potentially beneficial fumigant reservoir for decay fungus control.

The rapid release of MIT when dry-aerated blocks were wetted may represent

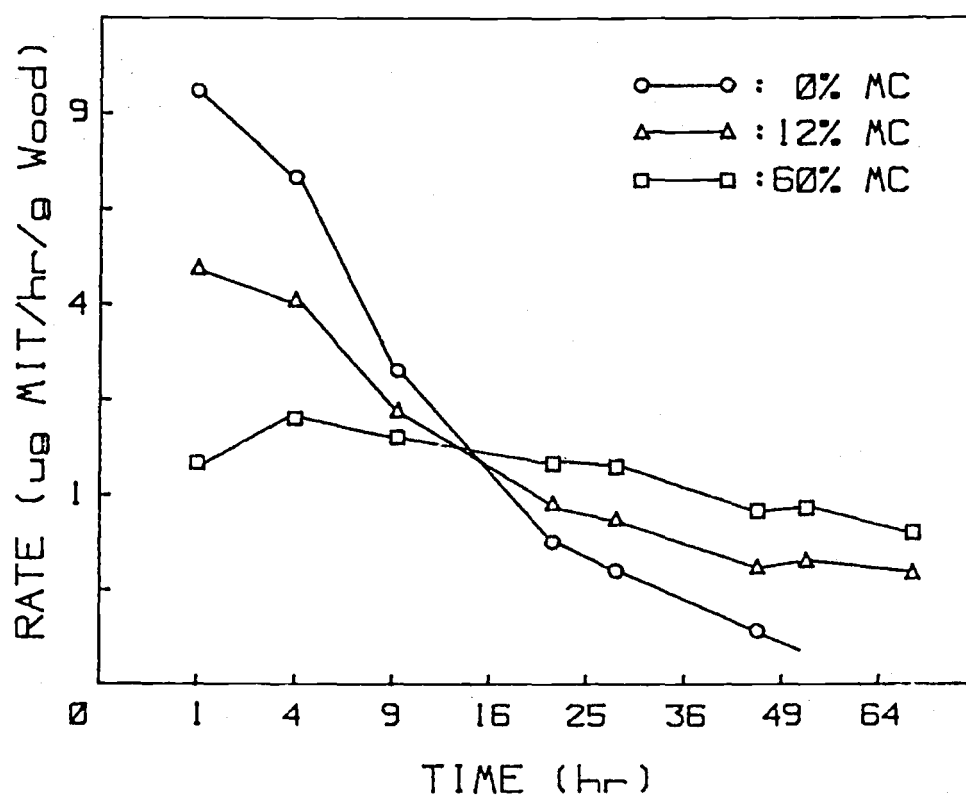


Figure I-11. Rate of Methylisothiocyanate release from ground Douglas-fir heartwood blocks when moistened to 100% moisture content (MC) and aerated at a flow rate of 30 ml/hr. Blocks at 0%, 12%, and 60% MC were initially fumigated for 36 weeks and then aerated for 34 weeks at 50% relative humidity.

MIT that was sorbed to the wood, or a regeneration of MIT from decomposition products formed in the initial fumigation. The release of MIT and CS₂ following wood grinding suggests a physical sorption of these compounds to the wood. The increased concentrations extracted when ground wood was wetted may be the result of the water swelling the wood structure to enhance solvent accessibility, but the presence of COS only in wetted wood suggests that chemical reactions involving water may also produce these compounds.

Decomposition of MIT in Douglas-fir heartwood may play a significant role in determining the overall effectiveness of this fumigant. MIT decomposition will reduce internal fumigant concentrations, but the compounds formed may also provide some residual protection against fungal recolonization.

Understanding MIT decomposition rates and products formed in wood should help predict its long-term performance and allow informative decisions on their most effective applications.

E. MOVEMENT AND EFFECTIVENESS OF MIT

Decomposition of methylisothiocyanate in Douglas-fir heartwood

Previous research (Third Annual Report, 1983, pg 23-30) has shown that wood moisture content influences both MIT fungitoxicity and sorption in Douglas-fir heartwood during short exposures at high fumigant concentrations. Similar information is lacking for long exposures at low fumigant concentrations, which is needed to determine how long fumigant treatments will remain effective (retreatment schedules) and the most effective fumigant treatment conditions for continued fungal control. This report describes preliminary results describing MIT fungitoxicity to P. carbonica and sorption properties in Douglas-fir heartwood blocks following long exposures to low MIT concentrations.

Fungitoxicity Studies: These studies use previously described techniques (see also Third Annual Report, 1983, pp. 23-30), which were modified for longer fumigations at lower concentrations.

A. Sample Preparation- Groups of 30 coastal Douglas-fir heartwood blocks (0.5 cm grain direction by 2.5 cm square) were oven-dried, weighed, infiltrated with water, and sterilized by autoclaving for 20 min (15 psi). Blocks were then adjusted to 75% MC by aeration in a laminar flow hood and inoculated with an aqueous suspension of fragmented P. carbonica mycelium. Blocks were placed on glass rods above wet filter paper (humidity source) in

petri plates, and incubated for 4 to 7 months (20-25°C). The moisture content of blocks were adjusted to either 10%, 20%, 40%, or 70% MC at least 1 week prior to use in fumigation experiments. These prefumigation moisture content adjustments assumed 5% block weight losses due to decay. Initial block moisture contents were estimated by comparing the wet and oven-dry weights of small pieces of each block (0.5 cm by 0.8 cm square) removed just prior to fumigation.

B. Fumigation Apparatus- Blocks adjusted to the desired moisture contents were fumigated in a continuous flow apparatus that produced an air stream containing constant MIT vapor concentrations. This air stream was then split to flow into 3 identical fumigation chambers at 15 ml/min/chamber.

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

C. Fungitoxicity Estimates- Prefumigation fungal population densities in blocks were estimated by cutting six radial sections (1.5 cm by 0.5 cm by 60 um) from each block with a microtome. The wood sections were homogenized for 1 minute (20,000 rpm) in 16 ml of water. The homogenized wood suspensions were mixed with 60 ml of potato-dextrose-agar amended with 2ppm benomyl at 50°C (pH 4.5), which was distributed between 5 petri plates. Plates were incubated at 20-25°C and resulting P. carbonica colonies were counted.

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

After 7 days fumigation, small pieces of wood (0.5 cm x 0.8 cm square) were removed to estimate wood moisture content and total MIT sorption. These wood samples were weighed and then extracted in 2 ml of ethyl acetate for 7 days. Extracts were analyzed for MIT content on a Varian 3700 gas chromatograph as described in the section above.

MIT Sorption Studies: Fumigant sorption in the Douglas-fir blocks used in the fungitoxicity studies described above was greatly influenced by wood moisture content. This influence of wood moisture content and decay by P. carbonica on MIT sorption in wood was investigated further by inoculating 24 Douglas-fir heartwood blocks (0.5 cm grain length by 2.5 cm by 0.8 cm) with P. carbonica and incubating at 20-25°C for 6 months. Blocks were then oven-dried, and their weight losses due to decay determined. These blocks, along with 24 sound (undecayed) blocks were divided into 4 groups of 6 decayed and 6 sound blocks which were adjusted to either 12%, 20%, 40%, or 70% MC, and then fumigated for 7 days at 0.25 ug MIT/ml air in the same apparatus used for the fungitoxicity studies. Blocks were then removed from the fumigation chambers, weighed, and extracted in 5 ml of ethyl acetate for 7 days. Total MIT

sorption was then determined by GC analysis of the extracts.

RESULTS

MIT Fungitoxicity at Constant Wood Moisture Content: MIT fungitoxicity to P. carbonica in Douglas-fir heartwood blocks was strongly influenced by wood moisture content at low MIT vapor concentrations (< 1.0 ug/cc air) (Figure I-12). Because survival was based on sequential estimates of fungal populations in small subsamples of each block, fluctuating population estimates, coupled with limited fungal kill could result in apparent population increases during fumigation. This effect was observed during short MIT exposures at low moisture contents, and these graphs are more accurate at low survival levels (below 60% survival).

Poria carbonica was more sensitive to MIT fumigation in wet wood than in wood below the FSP at all 3 MIT vapor concentrations. In wood fumigated at 0.25 ug MIT/cc air, about 4 times the exposure length was required to control fungi in dry wood than in wet wood (Figure I-12A). A similar relationship was observed in wood fumigated at 0.72 ug MIT/cc air (Figure I-12B), although, as expected, shorter fumigant exposures controlled decay fungi. In addition to fungitoxicity effects, wood moisture content also influenced the amount of extractable MIT, with higher MIT concentrations in wood below the FSP than in wood above the FSP (see Table I-36).

The product of MIT concentration (ug/cc air) and exposure times (hr) required to kill 90% (CT₉₀ values) of the P. carbonica propagules in wood were calculated and compared with results from an earlier study that used MIT concentrations above 2 ug/ml air (Table I-35). In wood at 14-20% MC, CT₉₀ values were comparable with earlier results, and remained constant at about 90 ug MIT/cc air/hr throughout the range of MIT vapor concentrations tested.

Table I-35. Estimated MIT concentration X exposure times necessary to kill 90% (CT₉₀ values) of the *P. carbonica* propagules in Douglas-fir heartwood blocks fumigated under dry or wet conditions.

| Wood Moisture Content Range (%) | CT ₉₀ values ^a in wood fumigated at MIT concentrations of: (ug MIT/cc air) | | | |
|---------------------------------------|---|------|------|------|
| | 3.0 | 0.70 | 0.25 | 0.10 |
| 14-20% | 93 | 82 | 105 | -- |
| 40-60% | 54 | 28 | 18 | 9.4 |

^a CT₉₀ values in units of ug MIT/cc air/hr.

However, in wood at 40-60% MC, CT₉₀ values declined with decreasing fumigant vapor concentrations (or increasing fumigation length). As MIT vapor concentrations decreased in 40-60% MC wood fumigations, the length of exposure required to control decay fungi increased (Figure I-12C), but the decreasing CT₉₀ values indicate, this increase was proportionally lower than the decrease in MIT concentration. This suggests that very low MIT concentrations, which may not be toxic to inactive decay fungi in dry wood, become more toxic in wet wood. This increased toxicity may be very important in long-term wood protection, since fungal growth and active decay will only occur in wood above the fiber saturation point.

MIT Fungitoxicity with Changing Wood MC: The reduced fungitoxicity of MIT in dry wood may be due to lower MIT sensitivity of dessicated or inactive fungal propagules. To further investigate wood moisture content influences on MIT fungitoxicity, dry *P. carbonica* infested blocks (below the FSP) were fumigated at high RH to increase block moisture contents during fumigation.

MIT fungitoxicity was greater when blocks initially at 18% MC were fumigated at 100% RH (0.70 ug MIT/cc air) than in blocks maintained dry during

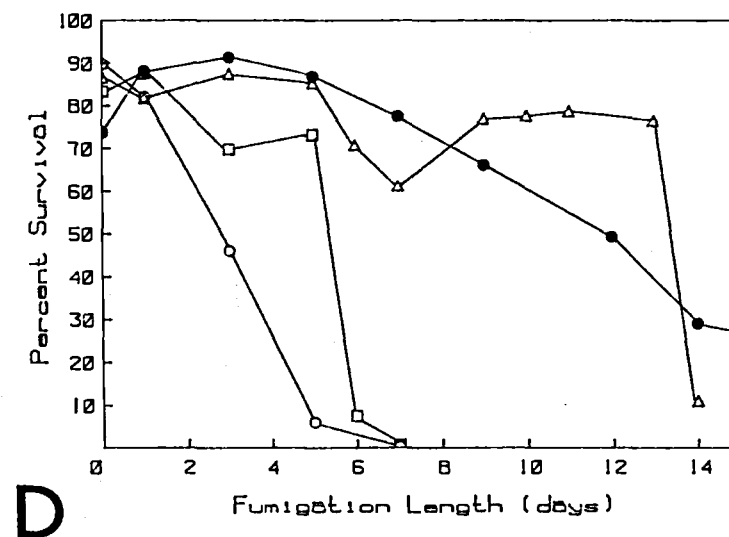
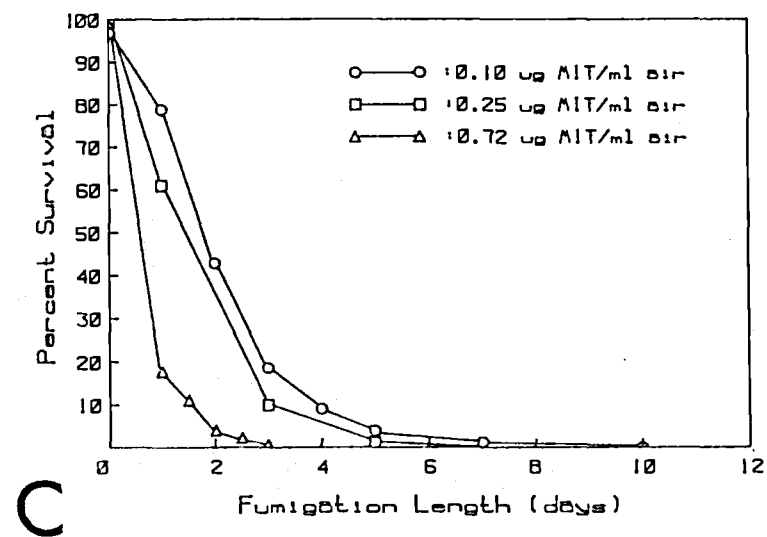
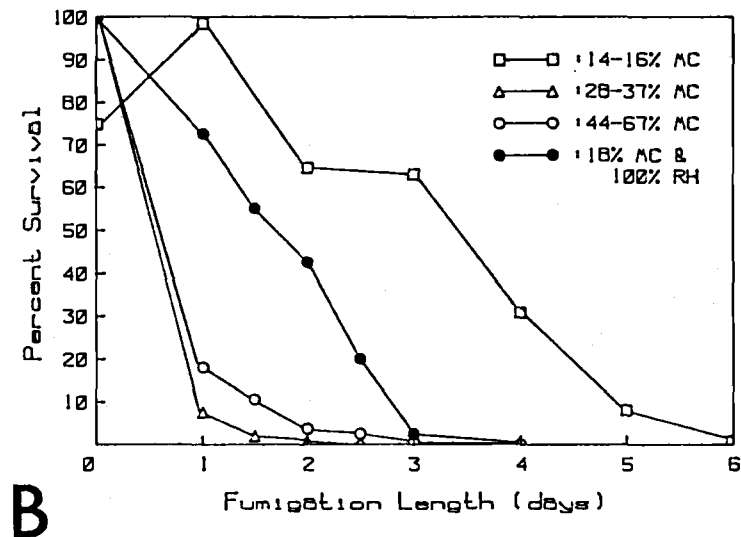
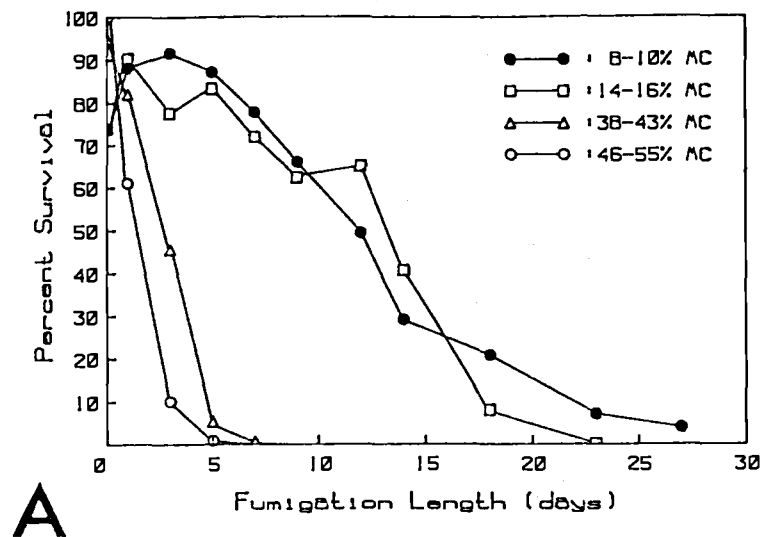


Figure I-12. Dosage-response relationships describing the influence of wood moisture content on the fungitoxicity of MIT to *P. carbonica* in Douglas-fir heartwood blocks. Infested wood blocks were exposed at: A) 0.25 ug MIT/cc air at 4 wood moisture contents (MC); B) 0.70 ug MIT/cc air at 3 wood moisture contents, with one set at 18% MC exposed at 100% relative humidity (RH); C) 40-60% MC at 3 different MIT vapor concentrations; D) 0.25 ug MIT/cc air at either 44% MC, 18% MC, or 18% MC with the relative humidity increased to 100% at 5 days, or at 13 days. Each point represents the average fungal survival in 5 blocks expressed as the percent of the maximum population density measured in each block.

fumigation, but lower than in blocks initially above the FSP (Figure I-12B). After fumigation for 5 days, the final block moisture contents were very close to the FSP of Douglas-fir (28-30% MC). The increased MIT fungitoxicity in dry blocks exposed to high RH conditions suggests that fungi in dry wood may not be more resistant to MIT, but that resistance may be dependent on the moisture content of the fungus.

The influence of increasing wood moisture content during fumigation on MIT fungitoxicity was more pronounced when blocks were initially fumigated under dry conditions (Figure I-12D). In this fumigation, 2 groups of blocks at 10% MC were fumigated at 0.25 ug MIT/cc air for either 5 days (5 blocks) or 13 days (2 blocks) before the RH of chambers was increased to 100%. The survival of P. carbonica in blocks decreased sharply after only 1 day at 100% RH, with survival less than 0.5% by the second day. This drastic decrease in survival occurred at a rate that was faster than in blocks initially fumigated at 38-43% MC. Wood blocks adjusted quickly to the new RH conditions, with blocks increasing to about 28% MC, and sorbed MIT concentrations decreasing from about 700 to 150 ug MIT/g oven dry wood after only one day at 100% RH. Increased wood moisture content during fumigation resulted in a substantial release of sorbed MIT from the dry wood. The rapid kill of P. carbonica in blocks when the RH was increased to 100% probably resulted from an increased susceptibility of the fungus, along with a temporary increase in MIT vapor concentrations within the wood. The greatly increased fungitoxicity of MIT in wet wood may help explain why Vapam (a 32% water solution of sodium N-methyldithiocarbamate), which decomposes to MIT, has performed well as a wood fumigant.

MIT Sorption by Douglas-fir Heartwood: The sorption of MIT by Douglas-fir

heartwood was strongly dependent on wood moisture content during fumigation, but was not greatly influenced by wood decay (Table I-36). Although there were differences in MIT sorption when decayed and non-decayed blocks were fumigated together under the same conditions, wood decay also reduced the final block moisture contents. This moisture content influence was probably more important in explaining the differences in MIT sorption than the decay itself. These results compare favorably with partition coefficients of 700 (18-22% MC wood) and 500 (36-43% MC wood) calculated from previous studies using higher MIT vapor concentrations (1-3 ug MIT/cc air) for 32 hr.

Table I-36. Influence of wood decay and moisture content on MIT sorption in heartwood blocks.^a

| Wood Moisture Content (%) ^b | Wood Decay Wt. Loss (%) ^c | MIT Sorption (ug/g OD wood) | Partition Coeff. ^d |
|---|---|--------------------------------|----------------------------------|
| 9.6 (0.2) | 0.0 | 687 (26) | 2750 |
| 8.0 (0.3) | 10.9 | 601 (63) | 2400 |
| 15.5 (0.3) | 0.0 | 246 (9) | 984 |
| 13.9 (0.8) | 9.8 | 293 (9) | 1170 |
| 32.4 (0.5) | 0.0 | 111 (11) | 444 |
| 29.2 (1.0) | 10.5 | 133 (10) | 532 |
| 60.2 (8.3) | 0.0 | 119 (7) | 476 |
| 67.8 (9.3) | 11.0 | 158 (8) | 632 |

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

^b Blocks were initially adjusted to 10%, 20%, 40%, or 70% MC. Figures represent the final moisture contents at the end of fumigation.

^c Block weight losses from decay ranged from 7% to 14%.

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

CONCLUSIONS: The decay fungus P. carbonica was more susceptible to MIT in wet wood (above the FSP) than in dry wood (below the FSP). This increased susceptibility was apparently dependent on fungal water content, as fungi in dry wood rapidly became more susceptible during fumigation when RH is increased.

These preliminary tests indicate that MIT is much less toxic to decay fungi in dry wood than in wet wood, binding of high MIT concentrations in dry wood may improve overall fumigant effectiveness. The MIT bound in dry wood may serve as a fumigant reservoir which is rapidly volatilized when wood becomes wet and susceptible to active fungal decay. This release may help explain the excellent long term performance of MIT in wood.

OBJECTIVE II

DEVELOP ENVIRONMENTALLY ACCEPTABLE PRESERVATIVE TREATMENTS FOR SAFELY CONTROLLING ABOVE GROUND SAPWOOD DECAY IN CEDAR POLES

A. FIELD EVALUATION OF CHEMICALS ON CEDAR TEST POLES

In 1983, a number of potential penta replacements were applied to cedar test poles in our field test site. The following year, a second set of chemicals was applied to additional poles at this site ('84 Ann. Rept., pg. 26). These poles were sprayed with water each day during the dry summer months to encourage decay and stimulate leaching. Each set of poles was sampled 2 years after treatment. Unfortunately, isolated poles in the second test group appear to have been sprayed with penta prior to installation in our test. To overcome this problem, we have reinstalled the test on smaller samples that have been tested for the presence of penta. The smaller size was chosen because of the difficulty of locating a sufficient number of full size poles for all of the chemicals now in the test.

Six weathered cedar poles removed from service in Idaho were cut into a series of 6 inch cubes that each contained one weather, sapwood face. The transverse and radial faces of each block were coated with epoxy resin to prevent chemical absorption and retard leaching of cedar heartwood extractives. The uncoated, weathered face of each section was dipped in 500 ml of the appropriate test solution for 30 seconds (Table II-1). All chemicals which had performed well in previous tests were evaluated, including those already applied to the cedar poles, and all chemicals that have performed well in more recent laboratory tests were incorporated into this study. The blocks were air dried for 24 hours, then painted on the transverse and radial surfaces to protect the epoxy from UV degradation. The coated blocks were then placed on a south facing test fence at a 30 angle. These

pieces will be watered during the summer months to accelerate the test, which will be sampled after 2 years of exposure.

B. LABORATORY EVALUATION OF NEW CHEMICALS AS REPLACEMENTS FOR PENTACHLOROPHENOL

As in previous years, we continue to screen promising formulations in our laboratory decay test. In these tests, six 3.2 by 3.8 by 7.0 cm Ponderosa pine sapwood blocks were placed end-grain down in the appropriate concentration of the test solution for 30 minutes. This exposure resulted in a gradient of chemical into the wood that is similar to that found on sprayed poles. One half of the blocks in each treatment were immediately sampled by removing 12 mm by 9 mm diameter plugs from the end-grain. These plugs were crosscut into 4 equal sized wafers that were tested in a modified soil block test using P. placenta as the test fungus. The remaining blocks were exposed in a Weatherometer for 4 weeks to accelerate chemical leaching. the weathering cycle consisted of an 8 hour water spray followed by 16 hours of drying. The blocks were heated throughout the weathering by two infrared lamps directed at the treated ends of the blocks. The weatherometer made one revolution per minute, and during each revolution each block was wetted by the spray for 8 seconds, which kept the block wet for the entire eight hour period. After one month, the blocks were removed and sampled in the same manner as the non-weathered blocks.

Previously, we have reported on the performance of over 50 chemicals under laboratory conditions ('86 Ann. Rept., pg. 47-54; '83 Ann. Rept., pg. 25-30). This past year, we evaluated a total of 13 compounds at the manufacturer's recommended concentration and at one half of that level (Table II-2). Eleven compounds were applied alone, while 2 were applied in combination with

Busperse 47, a penetrant additive.

The results indicate that several compounds exhibited potential as penta replacements (Table II-3). Isothiazolone, isothiazolone plus Busperse, IPBC plus Busperse and IPBC alone all limited decay weight losses to less than 15 percent 12 to 15 mm from the wood surface. The presence of the penetrant appears to improve performance of the IPBC and the isothiazolone, but this effect is marginal. The ability of these compounds to migrate into the wood to depths of 15 mm suggests that they will perform most like penta, which also protects the inner wood zone. An additional 3 chemicals limited decay in the 8 to 11 mm zone. Two of these compounds were proprietary quaternary ammonium compounds which have performed well in field tests at other laboratories. The third chemical, Amical 48, is an iodo-sulfone compound that has performed well in stake tests. A third group of 3 chemicals provided decay protection up to 4 to 7 mm from the wood surface. Two of these treatments were lower concentrations of chemicals from the first two groups, while the third was NP-1, which is used to protect lumber from sapstain. This formulation was not designed for decay control but appears to provide very reasonable protection for this application. Although it did not provide protection to the same depth as penta, it did protect the wood to a greater depth than all of the remaining chemicals, which were divided into those that protected only the wood surface, and those that provided little or no protection to any wood zone. As stated last year, it is unclear whether a chemical must protect the wood far below the surface to be an effective sapwood decay control agent or whether some surface protection is sufficient. For this reason, we have included the chemicals from the first 3 performance groups in our field tests.

Table II-1. Summary of chemicals included in field trials of potential cedar sapwood decay control agents.

| TRADE NAME (CHEMICAL) | DISPERSANT CONCENTRATION (%) | |
|--|------------------------------|------------------------|
| Amical 48 (diiodomethyl paratolyl sulfone) | diesel | 1.00 |
| Arquad C-50 (3-trimethylcocammonium chloride) | water | 5.00 |
| Arquad C-50 & IPBC | diesel | 4.00 & 2.50 |
| Busan 1009 (methyl bis(thiocyanate/2(thiocyanomethylthio) benzo-thiazole (MBT/TCMTB) | water | 4.00/2.00 |
| Busan 1009 & Busperse 47 | water | 4.00 & 9.00 |
| Busan 1030 (TCMTB) | water | 4.00/2.00 |
| Busan 1030 & Busperse 47 | water | 4.00 & 9.00 |
| Rodewood SC-503 (Azaconazole) | water | 0.15/0.30 |
| Copper 8 quinolinolate | diesel | 0.12 ^a |
| " " | water | 0.30 ^a |
| Copper naphthenate | diesel | 2.00 ^a |
| CWP-44 (Copper amine) | water | 10.00 |
| Polyphase (3-iodo 2 propynyl butyl carbamate (IPBC) | water | 2.00 |
| Woodlife (IPBC) | diesel | 0.50 |
| IPBC & Busperse | diesel | 1.00 & 5.00 |
| Isothiazolone | diesel | 1.00 |
| Isothiazolone & Busperse 47 | diesel | 1.00 & 5.00 |
| Isothiazolone & Arquad C-50 | diesel | 3.50 & 6.00 |
| N-100-WD [Dodecyl dimethyl ammonium salt of naphthenic acid] (DDBAN) | water | 8.00 |
| N-100-SS (DDBAN) | diesel | 8.00 |
| Pentachlorophenol | diesel | 10.00 |
| Quaternary ammonium A-13 | water | 1.00 |
| Quaternary ammonium A-32 | water | 1.00 |
| Tributyl-tin-oxide (TBT0) | diesel | 5.00 |
| M-Gard 550 (Zinc naphthenate) | water | 4.00 ^a |
| M-Gard 553 (Zinc naphthenate) | water | 4.00/2.00 ¹ |

a. Chemical active ingredient is on a metal basis (copper or zinc).

Table II-2. Chemicals tested under laboratory conditions.

| Chemical | DISPERSANT | % ACTIVE |
|---|--------------------|--------------------------|
| Mercaptobenzothiazole (Nuodex 84) | diesel | 1.00/0.75/0.37 |
| " | water | 1.00/0.50 |
| Isothiazolone | diesel | 1.00 |
| Isothiazolone & Busperse 47 | diesel | 1.00/0.50 & 5.00/2.50 |
| Polyphase & Busperse 47 | diesel | 1.00/0.50 & 5.00/2.50 |
| Polyphase (Woodlife) | diesel | 0.50/0.25 |
| Diiodomethyl paratolyl sulfone (Amical 48) | diesel/ acetone | 1.00/ 0.50 |
| Diiodomethyl paratolyl sulfone (ABG-8001 Flowable) | water | 1.00/0.50 |
| Quaternary ammonium compound # A-13 | water | 1.00/0.50 |
| QAC # A-31 | water | 1.00/0.50 |
| QAC # A-32 | water | 1.00/0.50 |
| QAC # A-34 | water | 1.00/0.50 |
| QAC # A-35 | water | 1.00/0.50 |
| Koppers NP-1 | water | 1.00/0.50 |

Table II-3. Effects of weathering on performance of selected test chemicals near the wood surface.^a

| Preservative | Concentration (%AI) | Wood Weight Loss (%) | |
|--------------------------------|------------------------|----------------------|-----------|
| | | Unweathered | Weathered |
| <u>Waterborne chemicals</u> | | | |
| Nuodex 84 | 0.50 | 8 | 50 |
| Amical ABG-8001 | 0.50 | 5 | 38 |
| QAC # A-35 | 1.00 | 4 | 35 |
| <u>Oilborne chemicals</u> | | | |
| Isothiazolone & Busperse 47 | 0.25 & 2.50 | 10 | 36 |

a. Weight losses represent the average of 4 unweathered and 6 weathered specimens per treatment.

Table II-4. Relative ability of selected preservatives to prevent wood weight loss in ponderosa pine wafers exposed in a modified soil block test.

| Preservative | Dosage | Carrier | Weight Loss (%) at Selected Block Depths (mm) | | | | |
|--|-----------|---------|---|-----|------|-------|-------|
| | | | 0-3 | 4-7 | 8-11 | 12-15 | Total |
| Group A: Weight losses <15% at 12-15 mm | | | | | | | |
| Isothiazolone | 1.0 | oil | 6 | 5 | 7 | 6 | 29 |
| Isothiazolone & Busperse 47 | 1.0 & 5.0 | oil | 5 | 7 | 8 | 6 | 26 |
| Polyphase & Busperse 47 | 1.0 & 5.0 | oil | 5 | 5 | 5 | 5 | 25 |
| " " | 0.5 & 2.5 | oil | 6 | 9 | 11 | 10 | 36 |
| Polyphase | 0.5 | oil | 8 | 7 | 7 | 5 | 27 |
| ----- | | | | | | | |
| Group B: Weight losses <15% at 8-11 mm | | | | | | | |
| QAC # A-13 | 1.0 | water | 5 | 9 | 14 | 31 | 59 |
| QAC # A-32 | 1.0 | water | 6 | 5 | 13 | 30 | 54 |
| Amical 48 | 1.0 | oil | 5 | 10 | 8 | 25 | 48 |
| ----- | | | | | | | |
| Group C: Weight losses <15 % at 4-7 mm | | | | | | | |
| Woodlife | 0.25 | oil | 8 | 7 | 25 | 9 | 49 |
| NP-1 | 1.0 | water | 4 | 5 | 23 | 22 | 54 |
| | 0.5 | water | 5 | 11 | 22 | 33 | 71 |
| QAC # A-32 | 0.5 | water | 6 | 11 | 46 | 46 | 109 |
| ----- | | | | | | | |
| Group D: Weight losses <15 % at 0-3 mm | | | | | | | |
| Isothiazolone & Busperse 47 | 0.5 & 2.5 | oil | 10 | 23 | 31 | 32 | 96 |
| QAC # A-13 | 0.5 | water | 14 | 31 | 46 | 46 | 137 |
| Nuodex 84 | 1.0 | water | 5 | 33 | 15 | 33 | 86 |
| | 0.5 | water | 8 | 43 | 50 | 41 | 142 |
| Amical ABG-8001 | 1.0 | water | 7 | 31 | 39 | 37 | 114 |
| | 0.5 | water | 5 | 54 | 52 | 52 | 163 |
| QAC # A-35 | 1.0 | water | 4 | 32 | 31 | 44 | 112 |
| QAC # A-34 | 1.0 | water | 4 | 21 | 40 | 35 | 100 |
| ----- | | | | | | | |
| Group E: Weight losses >15 % at all depths | | | | | | | |
| Nuodex 84 | 1.0 | oil | 41 | 55 | 51 | 53 | 200 |
| | 0.75 | oil | 34 | 44 | 30 | 34 | 142 |
| | 0.37 | oil | 37 | 28 | 41 | 54 | 160 |
| Amical 48 | 0.5 | oil | 56 | 32 | 59 | 51 | 198 |
| QAC # A-35 | 0.5 | water | 21 | 26 | 32 | 20 | 99 |
| QAC # A-34 | 0.5 | water | 32 | 36 | 57 | 57 | 181 |

OBJECTIVE III

PREVENTING DECAY INITIATION IN FIELD- DRILLED BOLT HOLES IN DOUGLAS-FIR POLES

A. EVALUATION OF TREATMENTS FOR PREVENTING BOLT HOLE ASSOCIATED DECAY.

An experimental field trial to evaluate the ability of initial treatments with Polybor, ammonium bifluoride (ABF), pentachlorophenol (Penta), Patox washers, or Boracol 40 to prevent decay initiation in field drilled bolt holes was established in 1981 ('84 Ann. Rept., pg. 31-32). Briefly, poles were lightly treated with pentachlorophenol in P9 Type A oil to produce a thin, preservative treated shell. A series of holes were drilled in a spiral pattern around each pole to hold hardware normally used to support crossarms or other attachments. The holes in each pole were treated with one of the above mentioned chemicals and the hardware was inserted and secured. A number of poles with untreated bolt holes were included to serve as controls. One half of the control poles in this test have been sampled on an annual basis by removing cores from sites directly beneath the gain plate or above the washer on the opposite side of each bolt hole. These cores were cultured for the presence of decay fungi, which were used as the measure of treatment effectiveness. To accelerate decay, the poles were sprinkled daily during the dry summer months. In the original plan, the treated poles would only be sampled when the control poles contained a sufficiently high level of fungal colonizations.

The annual inspections revealed that 3 of the 4 control poles contained decay fungi after 4 years, but only 9 percent of the cores from these poles were colonized. Although this level was still quite low, we decided to inspect all of the poles after five years of exposure. In this evaluation,

increment cores were removed for culturing and the hardware was removed and examined for evidence of corrosion.

The results indicate that several of the treatments were associated with markedly reduced levels of fungal colonization (Table III-1) including ABF, Boracol, and penta. Eighty percent of the poles treated with Polybor or Patox washers contained decay fungi, and both of these treatments experienced higher degrees of fungal colonization. Of the treatments, only penta lacks the ability to migrate for long distances in the wood, but this chemical is a potent, broad spectrum biocide and the presence of a shallow protective layer may have been sufficient to limit colonization. Both Polybor and Patox washers contain water soluble salts that can migrate with any moisture entering the wood; however, neither provide any degree of protection. Polybor is highly mobile in wood and the constant rewetting may have encouraged migration away from the bolt hole surface. This migration may have decreased the boron levels below the toxic threshold permitting fungi to colonize the wood. The Patox washers were placed on the outside of the bolt hole. In this position, some chemical may migrate along the bolt threads into the hole; however, this migration did not appear to be sufficient for preventing fungal colonization. The remaining chemicals all provided residual protection to the bolt hole.

It is of interest to note the slow rate of fungal colonization in the field drilled bolt holes, even under seemingly optimal conditions for decay development; however, decay fungi do eventually colonize these poles and it is critical that some type of protection be applied to these holes. Our results suggest that Boracol 40 or ABF provided protection that was comparable to 10 percent penta. Until recently, the latter chemical was the main treatment for

protecting field drilled bolt holes.

Examination of the galvanized hardware removed from the test poles indicate that none of the treatments were experiencing corrosion problems. This is particularly important for the ABF treatment, since this chemical has been reported to be highly corrosive. It appears that the low chemical dosage moves rapidly into the surrounding wood, where it is unavailable to interact with the hardware.

Table III-1. Colonization of field drilled bolt holes in Douglas-fir poles by decay fungi five years after exposure.^a

| TREATMENT | (%) Poles Colonized | Cores with Decay Fungi (%) | | |
|---------------------|---------------------------|----------------------------|---------------|--------------|
| | | Lower Site | Upper Site | All Sites |
| Ammonium bifluoride | 25 | 0 | 6 | 3 |
| Patox washers | 100 | 16 | 6 | 11 |
| Boracol 40 | 25 | 0 | 6 | 3 |
| Penta (10%) | 50 | 9 | 3 | 6 |
| Polybor | 100 | 6 | 25 | 16 |
| Controls | 63 | 2 | 19 | 10 |

a. Each treatment was tested on 4 poles, except the control, which contained 8 poles. A total of 32 cores were removed from each site per treatment group, except the controls where 64 cores were removed and tested.

B. ABOVE GROUND FUMIGANT TREATMENT WITH GELATIN ENCAPSULATED MIT OR PELLETIZED MIT

A second method for preventing bolt hole decay involves fumigant treatment above or below the exposed hole. These treatments depend on the commercialization of solid fumigants that can be safely applied above ground. Last year we began an evaluation of pelletized and gelatin encapsulated MIT applied to a series of 15 Douglas-fir poles to which an underbuilt line had been attached. The holes for these crossarms had been field drilled and there

was some doubt that the holes were field treated at the time of drilling ('86 Ann. Rept., pg. 58-59). Samples removed for culturing from sites 2 feet below the treating hole 1 year after treatment indicated that none of the treated poles contained decay fungi. These poles were resampled this past year by removing increment cores from sites 4 feet below the treatment sites. The outer and inner inch of each core were used for closed tube bioassays, while the remaining wood was cultured for the presence of decay fungi. The results indicate that the fumigant has not yet migrated down the pole to a sufficient degree to eliminate established decay fungi, and only the 120 g MIT pellet treatment was free of decay fungi (Table III-2). Liquid fumigants generally move downward at higher dosages than they move upward; however, the movement patterns of solid chemicals have not yet been established. Cultural results suggest that downward migration of the solid MIT has been somewhat retarded. Conversely, closed tube bioassays indicate that inhibitory levels of MIT are present in all of the treated poles (Table III-3). These levels have not yet reached complete inhibition, but suggest that an additional year of migration should produce lower levels of fungal colonization at these sites.

The results indicate that application of fumigants to prevent or control bolt hole decay should be made as close as possible to the exposed wood. Conversely, care should be taken to insure that the hole does not adversely affect pole strength. These poles will be resampled at the same locations this coming year to insure that the chemical has migrated at levels sufficient to control decay.

TABLE III-2. Fungal population near bolt hole attachments in Douglas-fir poles treated with encapsulated or pelletized MIT.

| TREATMENT | DOSAGE | CORES WITH DECAY/NON-DECAY FUNGI (%) ^a | | |
|--------------|--------|---|------|--------|
| | | 1984 | 1985 | 1986 |
| MIT Capsules | 45 ml | 33/33 | 0/70 | 11/100 |
| MIT Capsules | 90 ml | 0/50 | 0/67 | 17/100 |
| MIT Pellets | 60 gm | 50/50 | 0/50 | 17/100 |
| MIT Pellets | 120 gm | 0/20 | 0/46 | 0/100 |

a. In 1984, chips from the original treatment holes were cultured. In 1985, cores were removed at sites 0.6 m below the treatment holes. In 1986, cores were removed from sites 1.2 m below the treatment holes.

TABLE III-3. Presence of fungitoxic vapors at selected sites below field drilled bolt holes treated with encapsulated or pelletized MIT as measured with the closed tube bioassay.

| TREATMENT (DOSAGE) | REPLICATES | INHIBITION OF <i>P. placenta</i> ^a | | | |
|-------------------------|------------|---|------|------------|------|
| | | OUTER ZONE | | INNER ZONE | |
| | | 1985 | 1986 | 1985 | 1986 |
| MIT Pellets (60 g) | 5 | 58 | 62 | 75 | 70 |
| MIT Pellets (120 g) | 2 | 72 | 83 | 60 | 100 |
| MIT Capsules (45 ml) | 6 | 30 | 21 | 65 | 43 |
| MIT Capsules (90 ml) | 2 | 60 | 63 | 70 | 100 |

a. Percent inhibition was measured against the growth of the test fungus in tubes containing no wood, where 100 percent inhibition signifies no growth, while 0 inhibition signifies that no fungitoxic vapors were present.

OBJECTIVE IV

DETECT EARLY DECAY IN WOOD AND ESTIMATE RESIDUAL
STRENGTH OF POLES IN SERVICE

A. USE OF FLUORESCENT COUPLED LECTINS FOR DETECTING DECAY FUNGI IN WOOD

We continue to study the use of fluorescent coupled lectins as probes for detecting fungi in decaying wood sections. These compounds are highly specific for various sugar compounds and one, wheat germ agglutinin (WGA), is highly specific for fungal chitin. This specificity is being used to study the progress of fungal colonization and wood attack at very early stages of decay by Coriolus versicolor, Poria placenta, and Chaetomium globosum. These fungi represent a white rotter, a brown rotter, and a soft rotter, respectively. Preliminary results indicate that substantial changes are occurring prior to the detection of wood weight loss. These changes are accompanied by the presence of a considerable amount of fungal hyphae, which are found passing through pits in the wood cell wall. These hyphae are far less visible using conventional staining techniques and it is hoped that the lectins will allow more detailed study of the early stages of decay.

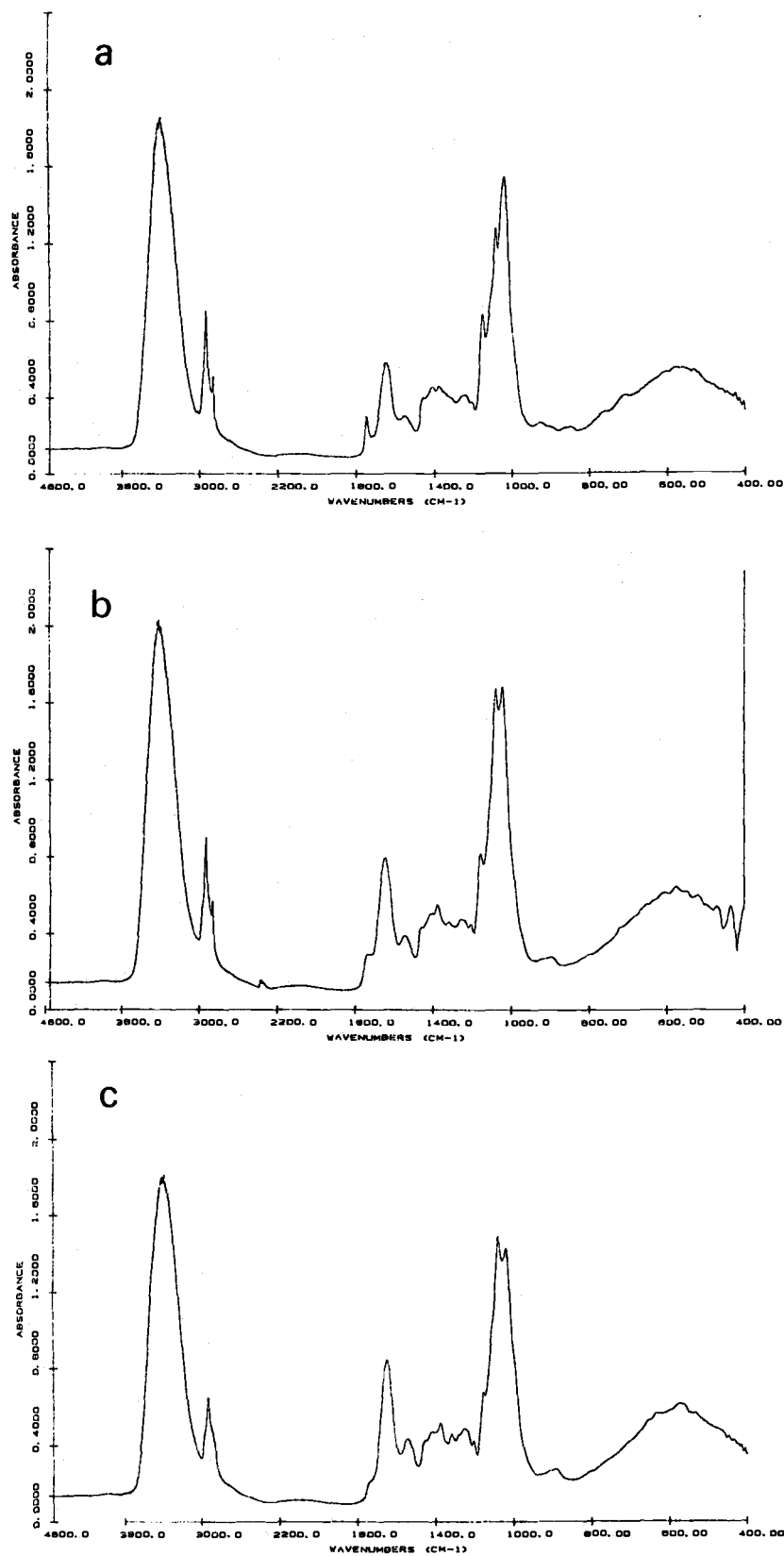
B. DETECTING INCIPIENT DECAY USING INFRA-RED SPECTROSCOPIC ANALYSIS OF WARM WATER EXTRACTS

In previous years, we have reported on the use of infra-red spectroscopic analysis of warm water extracts of wood to detect early decay. This technique identified a characteristic peak at 1720 nm which was present at the early stages of brown rot attack. This past year we acquired a much more sophisticated Fourier Transformer Infra-red (FTIR) Spectrophotometer and are now re-examining a number of previous findings using this equipment. We are presently examining the warm water extracts of Douglas-fir, western hemlock, Ponderosa pine, and red alder exposed to a number of brown, white, and soft

rot fungi for periods ranging from 0 to 16 weeks. These tests indicate that the peak previously detected in extracts from brown rotted wood at the very early stages of decay is not present in wood attacked by a number of soft and white rot fungi. While this negates the use of infra-red spectroscopy for detecting all wood decay, the technique may still be useful for detecting brown rot attack. Since strength losses occur most rapidly with brown rot fungi, early detection of these fungi would limit the amount of wood damage. Further studies are planned on this topic.

In addition to our use of the FTIR for detecting wood decay, we have recently begun tests to use this instrument for identifying wood decay fungi. In this effort, various isolates from our culture collection have been grown in liquid shake culture in malt extract, potato extract, and a variety of simple sugars (maltose, glucose, xylose, and sorbitol) at very low concentrations (0.5 %). The hyphae have been filtered and freeze-dried prior to compression in a potassium bromide pellet for FTIR analysis. Although only a few fungi have been examined, the results indicate that there are distinct differences in the spectra produced by the various test fungi (Figure IV-1) and studies are underway to further quantify these results. If successful, the FTIR could be used to confirm the identification of groups that are extremely difficult to separate using visual characteristics or ability to grow on specific media.

Figure IV-1. Infra-red spectrograph of fungal extracts from a) Poria placenta, b) Coriolous versicolor, and c) Chaetomium globosum.



C. THE USE OF LONGITUDINAL COMPRESSION AS A PREDICTOR OF WOOD STRENGTH

Initial wood strength is a critical factor in designing with wood. Unfortunately, wood is a variable material and designers must cope with this variability by designing for the weakest possible member in a given structure. To overcome this limitation, we have evaluated a number of small scale, semi-non-destructive tests that could be used to predict wood strength. One of these tests is longitudinal compression (compression parallel to the grain). Previous tests ('86 Ann. Rep. 79-81) have shown that LCS of plugs removed from the groundline of used cedar poles was a good predictor of full-length pole bending strength ($R^2 = 0.64$). While these tests were promising, the study involved a limited number of poles and additional tests were needed to verify these results.

The use of LCS as a strength predictor was further assessed using 26 untreated Lodgepole pine (Pinus contorta) posts (8 feet long and 5 inches in diameter) that were chosen for straightness of grain and absence of gross defects that might affect bending strength. The characteristics for the posts were similar to those which might be used for pole selection, in that care was taken to avoid excessive knot clusters, the presence of stained wood, or other defects that would cause pole rejection.

Each pole was used to evaluate a number of strength properties including:

- Acoustic testing (in cooperation with J.B. Wilson's ESEERCO project)
- Pilodyn pin penetration: The surface strength of each pole was measured using a 6-Joule Pilodyn equipped with a 2.5 mm diameter pin to test at 1 foot intervals along the upper face of each pole.
- Static Bending: Each pole was tested in static bending to failure by supporting the pole at each end and applying the load to the mid-point of a 6

foot span. The data was used to calculate modulus of rupture (MOR) and modulus of elasticity (MOE).

-Longitudinal compression strength: The LCS of each post was assessed using two tests. In the first, four 1.27 cm long by 1.27 cm diameter plugs were cut from the upper and lower pole surface, 15 cm from each pole end. These plugs were soaked in water and tested for longitudinal compression using methods previous described ('86 Ann. Rept., pg. 79-81). In addition to the plugs, a series of 1.27 cm cubes, cut from the zones adjacent to the plugs, were sampled for LCS using the same methods, but substituting a flat plate for compressing specimens. At the conclusion of the tests, LCS was calculated on the basis of surface area compressed.

-Specific Gravity: Specific gravity, by itself a reasonable predictor of wood strength, was measured for each plug and cube used in the LCS test by dividing volume by water-immersion of water-soaked specimens into specimen oven-dry weight.

-Knot characteristics: As the tests were performed, it became clear that certain species characteristics of lodgepole pine exerted a significant influence on strength properties. Of these, the characteristic knot clusters in this species exerted the strongest influence. To account for the effect of knots on bending strength, the cumulative knot diameter was measured in a zone 15 cm to each side of the post mid-span. In addition, the number of knots in this same zone were counted.

At the conclusion of the tests, the results were compared and regression analyses were performed to determine which of the methods best predicted post strength as measured by the bending tests.

The results indicate that specific gravity was the best predictor of post

bending strength ($R^2 = 0.622$) (Figure IV-2) and this figure was marginally improved by incorporating cumulative knot diameter ($R^2 = 0.736$). When LCS of plugs was compared to MOR, the correlation was quite low ($R^2 = 0.368$); however, incorporation of knot diameter enhanced the correlation to a value similar to that found for specific gravity ($R^2 = 0.634$) (Figure IV-3). Cutting cubes for LCS testing was much more time consuming than cutting plugs but the tests showed similar abilities to predict MOR (the R^2 of LCS of cubes vs. MOR was 0.302). LCS of plugs is a relatively simple test that can be performed on small samples in the field without the need for elaborate equipment, and might be useful for selecting high strength material for special uses.

The remaining parameters did not appear to be useful for estimating wood strength. Comparisons between Pilodyn pin penetration and post MOR had an R^2 of 0.527 when the knot diameter was included in the regression equation while knot diameter alone vs. MOR had an R^2 of 0.335 (Figures IV-4 + IV-5).

The sonic tests have been inconclusive because of the presence of large knot clusters. Further analysis of this data is underway.

In part, the bending test results reflect the knot clusters present in lodgepole pine and indicate that further tests are required using species that either lack these clusters or have clusters that do not occupy such a large area of the post circumference.

Figure IV-2. Comparison of predicted strength of lodgepole pine posts versus actual MOR using a) specific gravity or b) specific gravity and cumulative knot diameter as predictors.

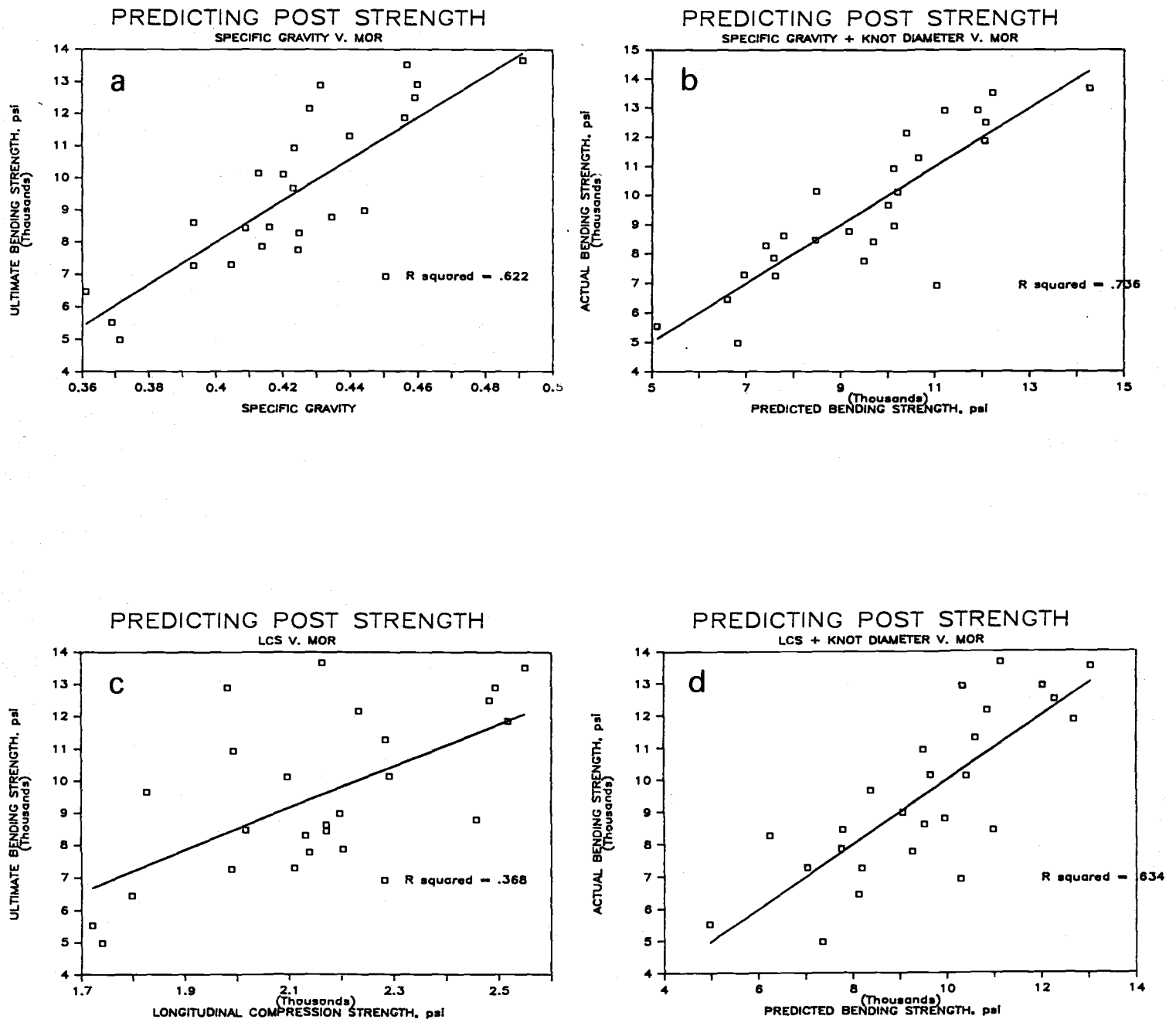


Figure IV-3. Comparison of predicted strength of lodgepole pine posts vs actual MOR using a) longitudinal compression strength (LCS) or b) LCS plus cumulative knot diameter as predictors.

Figure IV-4. Comparison of predicted strength of lodgepole pine posts vs. actual MOR as measured using a) Pilodyn pin penetration or b) Pilodyn pin penetration and cumulative knot diameter as predictors.

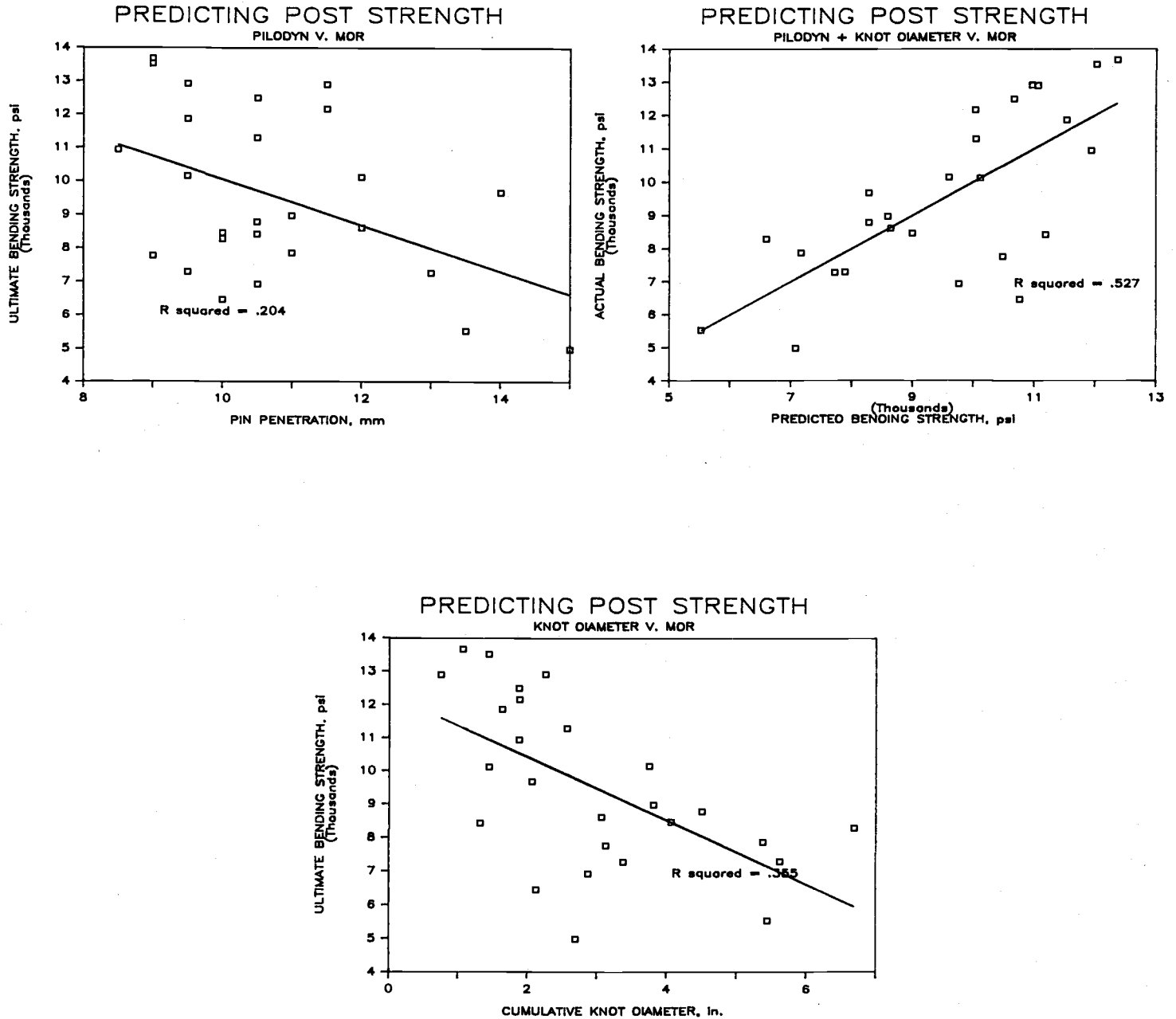


Figure IV-5. Comparison of predicted strength of lodgepole pine posts vs. actual MOR as measured using cumulative diameter of knots with 30 cm of the post mid-span.

D. PREDICTING THE STRENGTH OF WOOD POLE HARDWARE CONNECTIONS

Twenty-four Douglas-fir pole sections pressure-treated with pentachlorophenol were tested by Bonneville Power Administration¹ for ultimate strength in axial and transverse loading for 4 sizes of single-bolt connections. Transverse failure (load perpendicular to grain) was shown to be unrelated to bolt size (Figure IV-6) while axial failure (load parallel to grain), measured at 1/2 inch bolt displacement, was highly dependant on bolt size (Figure IV-7). The following study was made to determine if wood-pole hardware connection strength could be predicted by measuring longitudinal compression strength (LCS) or specific gravity of plugs removed from the pole sections. Previous studies at the Forest Research Laboratory² have shown that these properties can be good predictors of wood strength.

Following wood-pole hardware testing, the pole sections were transported to the Forest Research Laboratory. A 1.25 cm diameter plug was removed from clear wood adjacent to each bolt hole in the 24 pole sections, producing a total of 48 plugs.

Longitudinal compression strength testing: The plugs were cut to 3.8 cm lengths, saturated with water in a vacuum desiccator, and tested for LCS. As the plugs were compressed beyond maximum load failure, preservative was squeezed from the wood. To avoid chemical contamination of equipment, the tests were terminated at maximum load rather than maximum compression, even though LCS at maximum compression has, in the past, been a better wood strength predictor. Rate of compression was 0.2 cm/min and each test was

1 Ultimate Strength Tests of Wood Pole Hardware by C. Ek.
Report No. ERGH-86-35. Sept. 30, 1986.

2 Longitudinal compression: a measure of wood strength.
1987. S.M. Smith and J.J. Morrell. Forest Prod. J. 37(5):49-53.

completed in approximately 1 minute.

Specific gravity measurement: Prior to LCS testing, wet volume was measured by water-displacement. After LCS testing and prior to weighing, the plugs were air-dried for 2 weeks under a ventilated hood to a uniform moisture content. The plugs were not oven-dried, the usual practice for measuring specific gravity, because of the risk of pentachlorophenol fumes being released into the laboratory. Specific gravity measurements, therefore, are relative to each other and can not be compared to previously published values.

Data analysis: Plug LCS, plug specific gravity, bolt size, and pole section diameter were regressed on wood-pole hardware connection strength, in order to evaluate the ability of each variable, or combination of variables, to predict strength.

The wood-pole hardware connection test results showed that 2 pole sections with 2.54 cm diameter bolt holes had low transverse strength. These two sections had low specific gravity, LCS, and annual rings/inch (Table IV-1), compared to the remaining transversely-loaded pole sections. Regressions of LCS and specific gravity against transverse load failure (Figure IV-6) showed that LCS and specific gravity accounted for the 2 low-strength 2.54 cm diameter bolt connections. However, low R^2 values (0.500 and 0.513, respectively) for these regressions and the regression of pole section diameter on transverse load failure ($R^2=0.358$) (Table IV-2; Figure IV-6) indicate that other wood properties may also influence transverse wood-pole connector strength. In addition, variations in preservative retention among

pole sections may have reduced the accuracy of specific gravity measurements.

While transverse wood pole connection strength was poorly correlated with bolt size, axial wood-pole strength was highly dependent on bolt size, predicting 94% of the variation in failure strength (Table IV-2). Specific gravity and LCS were inversely related to axial load failure (Figure IV-7) while pole section diameter had little influence on axial bolt strength (Table IV-2; Figure IV-7).

This study indicates that LCS, specific gravity, and pole section diameter are helpful in predicting transverse wood-pole connection strength but that they have little effect on axial wood-pole connection strength. In order to develop accurate equations for predicting connector strength, pole sections having a wide range of specific gravity, LCS, and diameters need to be tested in each bolt-size group. Untreated poles should be tested to eliminate the effects of preservative retention.

Table IV-1. Wood properties and strength of wood-pole connectors

| POLE SECTIONS | | | PLUGS | | |
|-------------------------|----------------------|-------|------------|------|-----------------|
| BOLT HOLE DIAM., in. | SECTION DIAM. in. | RINGS | LCS psi | SG | STRENGTH lb. |
| TRANSVERSE LOAD | | | | | |
| 5/8 | 8.5 | 11.1 | 3106 | .557 | 8200 |
| 5/8 | 9.0 | 11.1 | 3315 | .616 | 12600 |
| 5/8 | 9.5 | 11.1 | 3608 | .622 | 13400 |
| 3/4 | 10.0 | 11.1 | 3681 | .681 | 12200 |
| 3/4 | 9.1 | 11.0 | 3505 | .582 | 13700 |
| 3/4 | 9.0 | 11.0 | 3498 | .571 | 9220 |
| 7/8 | 10.2 | 11.1 | 3799 | .667 | 14600 |
| 7/8 | 9.0 | 11.0 | 3432 | .630 | 12300 |
| 7/8 | 9.4 | 11.0 | 3542 | .603 | 12200 |
| 1 | 9.6 | 11.0 | 3916 | .669 | 11200 |
| 1 | 8.4 | 3.6 | 2222 | .529 | 8800 |
| 1 | 9.4 | 3.6 | 2347 | .536 | 8100 |
| AXIAL | | | | | |
| 5/8 | 8.3 | 9.3 | 3307 | .572 | 6700 |
| 5/8 | 8.8 | 9.3 | 3014 | .566 | 7870 |
| 5/8 | 9.2 | 9.3 | 2904 | .574 | 6170 |
| 3/4 | 8.8 | 9.3 | 2948 | .554 | 10000 |
| 3/4 | 9.2 | 9.3 | 3007 | .564 | 8940 |
| 3/4 | 9.5 | 9.3 | 3549 | .581 | 9100 |
| 7/8 | 8.8 | 5.0 | 2669 | .474 | 14000 |
| 7/8 | 9.0 | 5.0 | 2681 | .482 | 11500 |
| 7/8 | 9.6 | 5.0 | 2618 | .502 | 12460 |
| 1 | 9.0 | 5.0 | 2666 | .463 | 15200 |
| 1 | 9.2 | 5.0 | 2663 | .502 | 14840 |
| 1 | 9.8 | 5.0 | 2699 | .497 | 16700 |

Table IV-2. Predicting wood-pole connection strength

| PREDICTOR VARIABLE(S) | PERCENT STRENGTH VARIATION EXPLAINED R^2 |
|--|--|
| TRANSVERSE | |
| BOLT SIZE | 0.061 |
| LCS | 0.500 |
| SPECIFIC GRAVITY | 0.513 |
| POLE SECTION DIAMETER | 0.358 |
| LCS + POLE SECTION DIAMETER | 0.548 |
| SPECIFIC GRAVITY + POLE SECTION DIAMETER | 0.518 |
| AXIAL | |
| BOLT SIZE | 0.944 |
| LCS | 0.402 ¹ |
| SPECIFIC GRAVITY | 0.760 ¹ |
| POLE SECTION DIAMETER | 0.191 |

¹ inverse relationship

Figure IV-6. Predicting wood-pole hardware transverse connection strength with (A) bolt size; (B) longitudinal compression strength; (C) specific gravity; (D) pole section diameter.

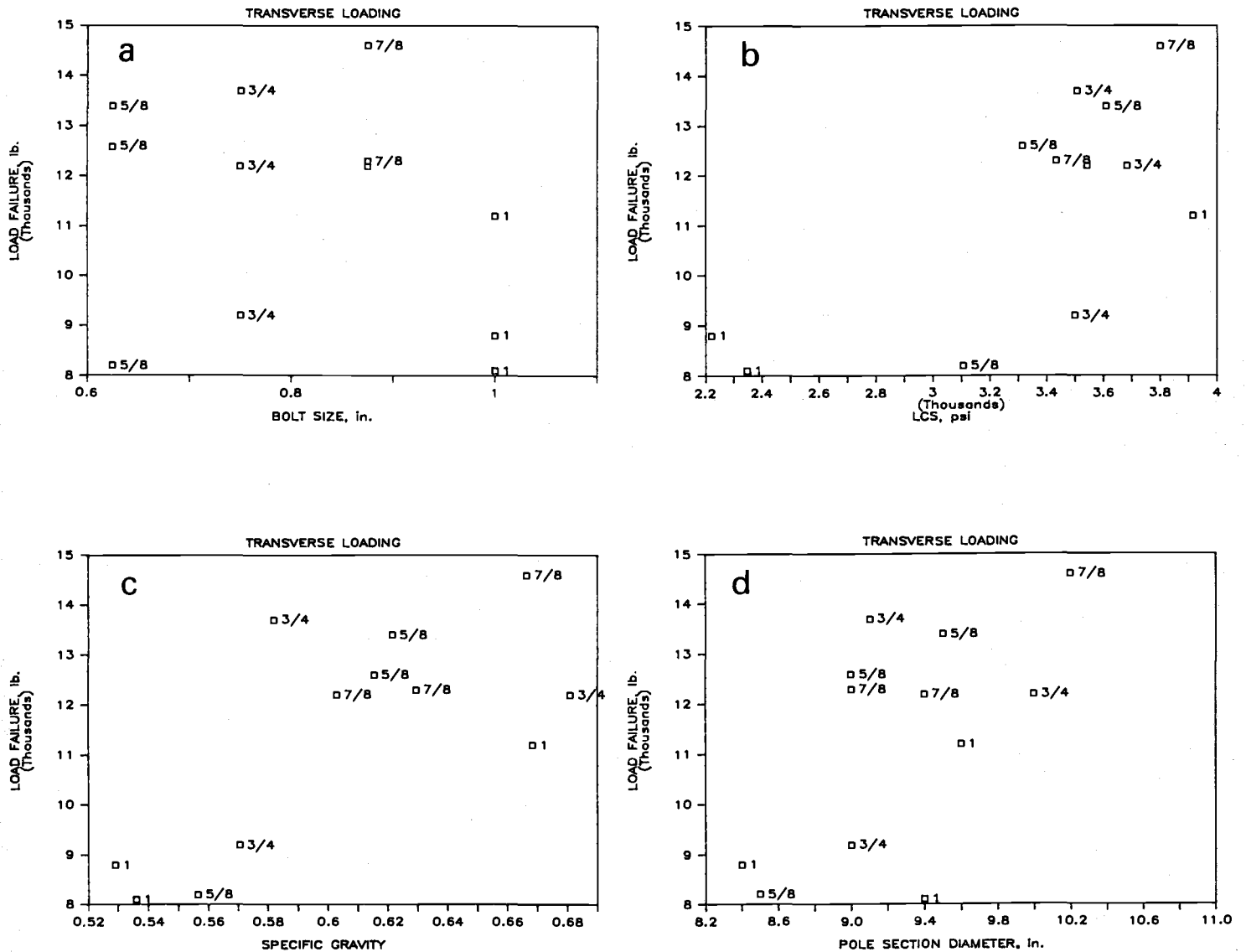
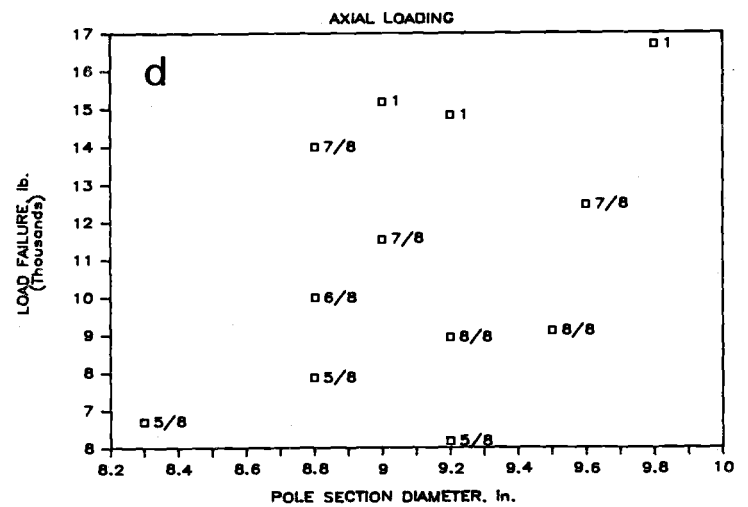
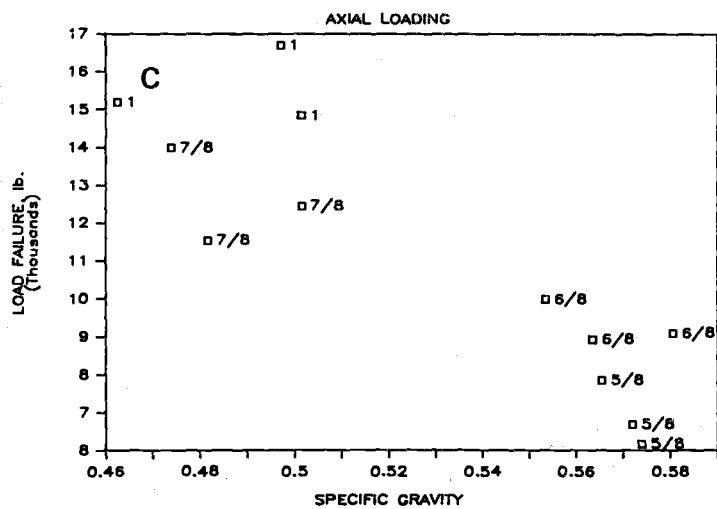
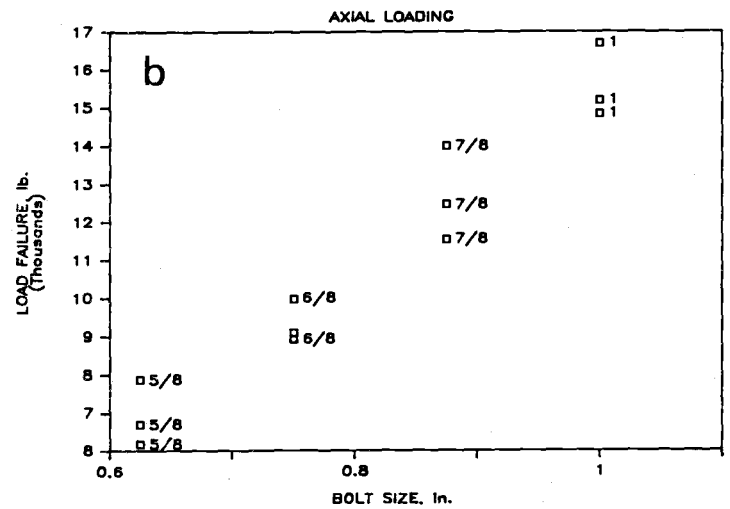
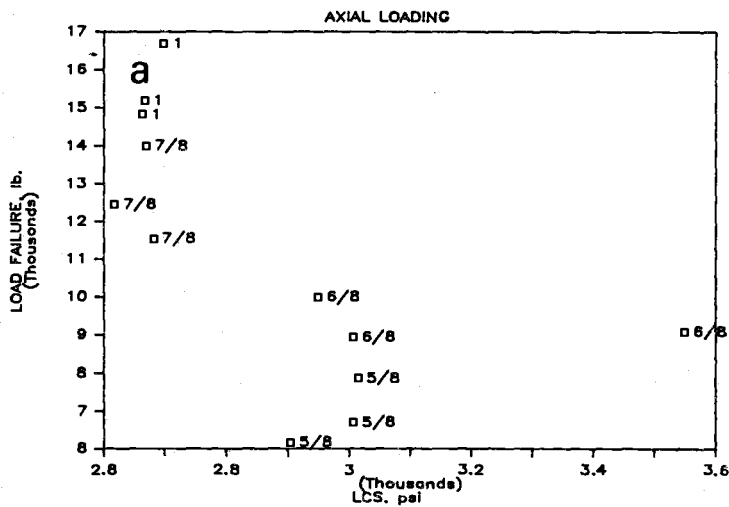


Figure IV-7. Predicting wood-pole hardware axial connection strength with (A) bolt size; (B) longitudinal compression strength; (C) specific gravity; (D) pole section diameter.



OBJECTIVE V

EVALUATE THE POTENTIAL FOR INFECTION AND DECAY DEVELOPMENT
IN AIR-SEASONING DOUGLAS-FIR POLESA. INTERNAL WOOD TEMPERATURE IN DOUGLAS-FIR POLES DURING PRESERVATIVE
TREATMENT

The large number of fungi found in air-seasoned Douglas-fir poles increases the importance of adequate heating to eliminate these fungi during the preservative treatment cycle. While previous studies indicate that oil-borne treatments involving long heating periods should result in complete sterilization, many utilities question whether treatments using relatively short steaming periods eliminate fungi.

To answer this question, we examined the temperature sensitivity of P. carbonica and P. placenta established in Douglas-fir heartwood blocks ('85 Ann. Rept., pg.) and have undertaken a study to determine the internal temperatures in Douglas-fir poles during commercial pressure treatment with oilborne pentachlorophenol or waterborne ammoniacal copper arsenate ('86 Ann. Rept., pg. 82-86).

In the internal temperature study, eighteen 8 foot long pole sections were pressure-treated in a commercial cylinder while the internal pole temperatures were monitored. Briefly, pole sections (30.5-55.8 cm in diameter) that had air-seasoned for about 1 year were cut to 2.44 m lengths. Ten increment cores were removed from each pole for culturing to determine the initial degree of fungal colonization. In addition, wood moisture contents were taken at 1.25, 2.5, and 5.0 cm in from the surface using a resistance-type moisture meter. The cross section of each pole was then coated with a marine grade epoxy resin to retard end-grain penetration of preservative solution that might influence thermocouple readings, and a series of 0.95 cm diameter holes were drilled to

depths of 5, 10, 15, 20, and 25 cm from the surface along the pole length. Each hole was filled with a Dow Corning Silicone Rubber Sealant to within 3.75 cm of the top and a 2.5 cm dowel which had been center drilled was inserted on top of the epoxy. This dowel protected the thermocouple during the pressure cycle. At this point, a copper constantin thermocouple was inserted through the hole in the dowel until it reached the bottom of the drilled hole. Once the resin set, a small dab of Dow Corning 340 Silicone heat-sink compound was placed on the very top of the hole and allowed to cure for at least 24 hours prior to temperature testing. The poles were then placed on top of the tram in a commercial cylinder and the thermocouples were threaded through a specially constructed flange with a Teflon fitting which was connected to a CR-21X Micro Data Logger that collected readings every 10 seconds and averaged this data every 15 minutes to produce one value for a given thermocouple. At the end of a given charge, the thermocouples were removed from the cylinder and reattached to the poles to follow the wood cool down. The collected data was then transferred to an IBM PC-AT for more detailed analyses.

Last year, we presented data from one charge with pentachlorophenol in oil and 2 charges using ammoniacal copper arsenate (ACA). This past year, an additional penta charge and 5 ACA/ACZA charges were evaluated with a particular interest in plants whose cylinders were equipped with heating coils to maintain solution temperature and an emphasis on larger diameter poles. The latter approach was taken since these poles are less likely to be completely sterilized and may be left in the yard for longer periods to air-season prior to treatment.

As expected, penta treatments resulted in internal temperatures at the pole center which were over 67 C for 30 hours or longer, indicating that this

treatment will more than adequately sterilize the wood (Figure V-1). The results of the ACA treatments indicate that small diameter poles (<30 cm diameter) can be adequately heating to sterilize the wood (67 C for 75 minutes at the pith center) using a 6 hour steaming period (123 C) even when the treating solution is used at ambient temperature (25-30 C) (Figures V-2-4). These results indicate that most of the heating occurs during the steaming process, while the remaining vacuum/pressure period results in more uniform distribution of the heat added during the steam period. The need for at least a 6 hour steam period was clearly shown when the steam period was decreased (Figure V-3). In this instance, the center of the pole never reached the required temperature and it is likely that any fungi present could survive to become a problem once the pole was placed in service. One suprising finding was the relatively small effect of using heated solution for the vacuum/pressure period (Figure V-4). While the presence of warmer solution delayed the loss of internal temperature, it did not appear to increase the maximum internal temperature reached. Since the solution was heated to 140 F, it is likely that it only acted as an insulator, thereby delaying the loss of heat from the pole surface. This in turn, provided more heat to maintain internal temperature. Heated solution probably has other benefits including improved penetration and uniformity of treatment.

While the results obtained using smaller diameter poles (<40.6 cm diameter) indicated that careful adherence to the pre-steaming period would result in adequate heating of the pith center, examination of larger poles demonstrated that the current steaming period is inadequate for sterilizing these poles. There are plans for increasing the steam period to 8 hours and this would seem to be particularly useful for larger diameter poles. In our 2 charges, the

center of the pole never reached 150 F, although 145 F was reached for a short period (Figure V-4). The results from all of the temperature studies are currently being analyzed with the goal of producing accurate heating curves for the treatment of poles of various diameters with ACA or ACZA.

One perplexing problem with the results of the heating studies has been the absence of decay fungi in most of the poles following preservative treatment, in spite of the failure to reach the desired internal temperature. Only one core in a single pole contained decay fungi following treatment, although most of the cultured cores contained non-decay fungi. This anomaly suggests that long term exposure to the lower temperatures was sufficient to eliminate decay fungi; however, our previous laboratory results indicated that both P. carbonica and P. placenta were capable of surviving for periods of 6 to 10 hours at 140 F. The results from these tests will be evaluated in more detail over the coming year.

Figure V-1. Internal temperature development in Douglas-fir pole sections during preservative treatment with pentachlorophenol in P-9 Type A oil.

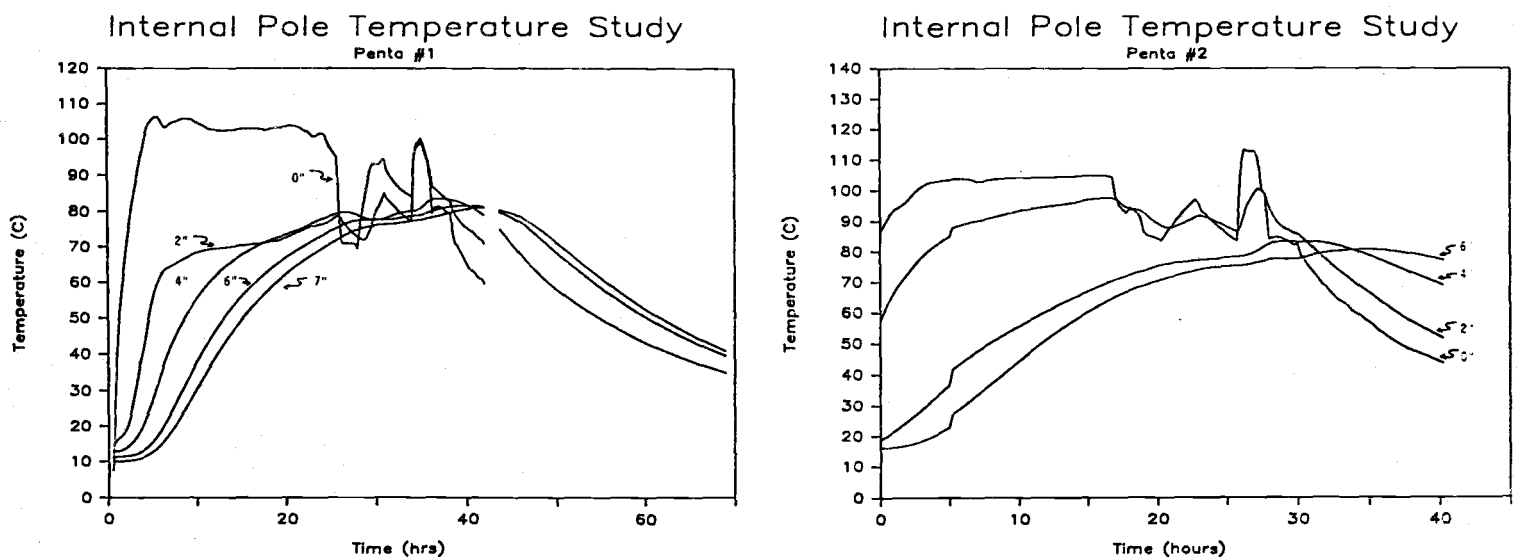


Figure V-2. Internal temperature development in Douglas-fir pole sections during preservative treatment with waterborne ammonical copper arsenate.

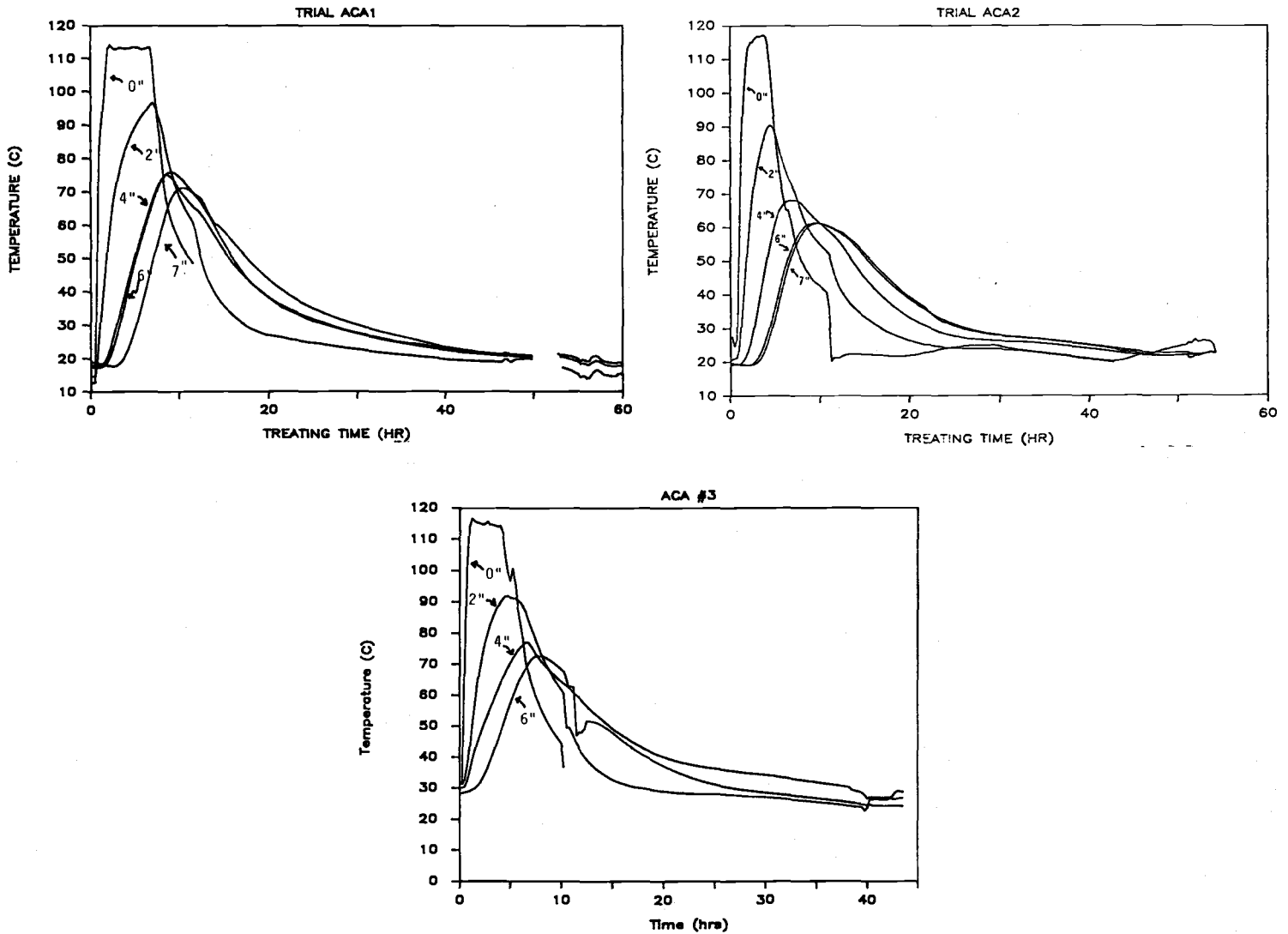


Figure V-3. Internal temperature development in Douglas-fir pole sections during preservative treatment with waterborne ammoniacal copper arsenate.

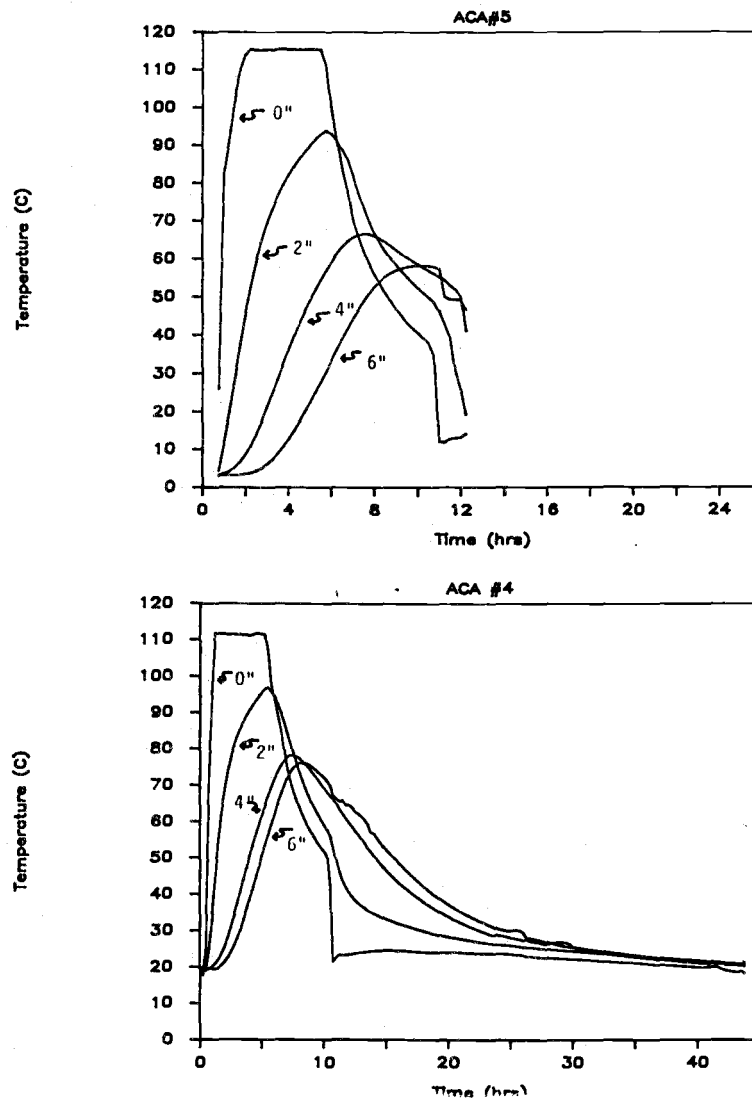
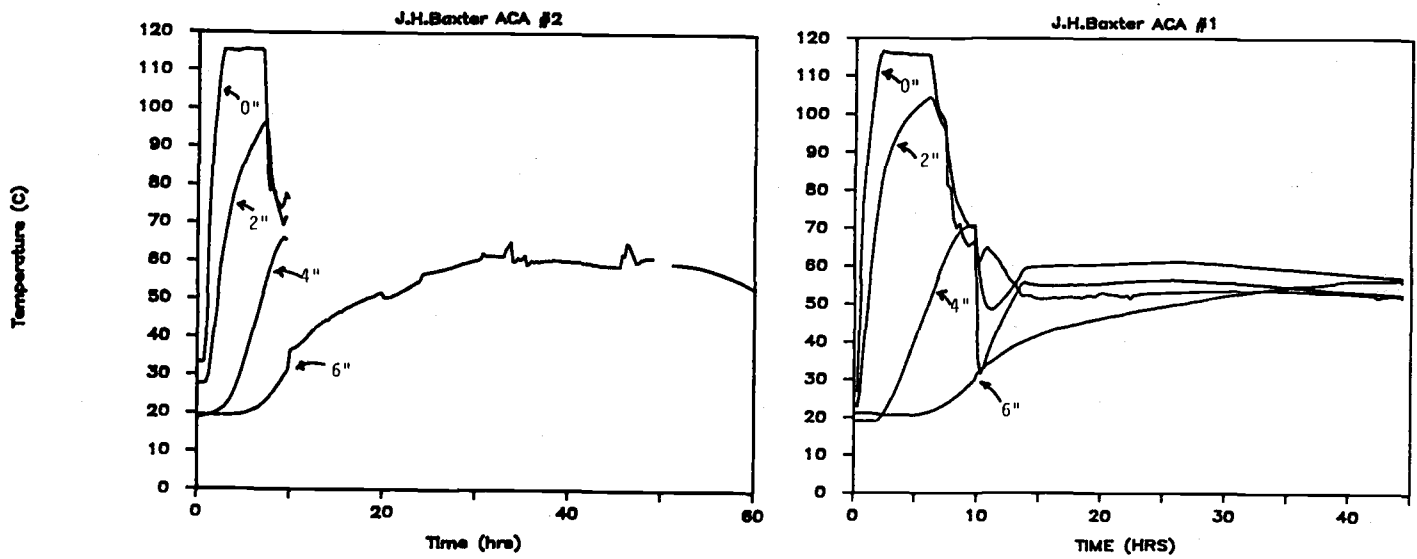


Figure V-4. Internal temperature development in Douglas-fir pole sections during preservative treatment with waterborne ammoniacal copper zinc arsenate.



B. DECAY DEVELOPMENT STUDY

Effect of fungal colony size on wood strength properties. In the course of the air-seasoning study, we have generated a wealth of data on the species of fungi colonizing Douglas-fir, the sequence in which they enter the wood, and the relative volume of wood occupied by each fungus. The latter information could be useful for determining the strength losses associated with fungal colonization. Unfortunately, there is little information on the effect of colony size on wood strength. To develop this information, sapwood and heartwood beams (1.27 by 1.27 by 20.3 cm) were cut from a green Douglas-fir pole section. A 2.0 mm diameter hole was drilled through each beam at mid-

span, from one radial face to within 1.6 mm of the opposite radial face. The beams were vacuum-pressure soaked in water to moisture contents above fiber saturation, wrapped in plastic-wrap and steam sterilized for 20 minutes. Each beam was injected at mid-span (into the pre-drilled hole) with 20 ul of fungal spore suspension. Heartwood beams were inoculated with P. carbonica or P. placenta, while sapwood beams were inoculated with Peniophora spp. or Haematostereum sanguinolentum. These fungi were the species most commonly isolated from the heartwood and sapwood, respectively, of poles in the air-seasoning study. Control beams were not inoculated. All beams were incubated at 28 C to accelerate fungal growth and will be tested at 13 selected time points.

At each time point, 4 beams in each group will be tested to failure in bending. The center 3 inches of each beam will be cut into 16 cross-sectional wafers which will then be sectioned to produce 4 cubes each. The cubes will be plated on nutrient agar and monitored for evidence of fungal growth to determine fungal colony size. Each beam was initially acoustically tested at the start of this study to record "fingerprints" and will be re-evaluated prior to mechanical testing to determine if colonization is associated with changes in acoustic properties.

Longitudinal compression strength and decay colony density- At each time point, 4 inoculated beams and one control beam in each group will be cut into thirteen 1.27 cm cubes. Eight cubes per beam will be compressed parallel to grain at a speed of 0.2 cm/min. A series of 120u thick transverse sections will be cut from each of the remaining cubes. These sections will be placed on nutrient agar and the presence or absence of fungal growth will be used to estimate fungal density at various positions in the beam.

Peniophora spp. has been in test for 6 months and there has been no loss in bending strength (Figure V-5) or LCS loss (Figure V-6). Both decay colony size (Figure V-5) and decay colony density (Table V-1) have declined after two or three months. This decrease may be caused by Penicillium and bacterial contamination or may indicate that the fungus has exhausted the readily available sugars. Poria placenta, P. carbonica, and Haematostereum sanguinolentum have been in test for only two months and results are incomplete for these fungi.

Table V-1. Density of Peniophora spp. in Douglas-fir heartwood beams incubated at 28 C. for selected time periods^a.

| INCUBATION PERIOD (MONTHS) | COLONIZED BEAMS (by beam position in cm) ^b | | | | |
|----------------------------------|---|-----|------|------|------|
| | 1.9 | 5.7 | 10.2 | 14.6 | 18.4 |
| 1 | 1 | 4 | 4 | 4 | 0 |
| 2 | 4 | 4 | 4 | 4 | 4 |
| 4 | 1 | 2 | 0 | 2 | 1 |
| 6 | 2 | 1 | 1 | 2 | 3 |

^a As determined by culturing a 120u thick sections, cut from selected positions in each beam.

^b At each time point, 4 beams were sampled for the presence of decay fungi.

Figure V-5. Effect of *Peniophora* spp. on a) bending MOR and b) bending MOE of beams during the first six months of incubation; c) degree of colonization by *Peniophora* spp., *Penicillium* spp., or bacteria in the middle 3 inches of the beams.

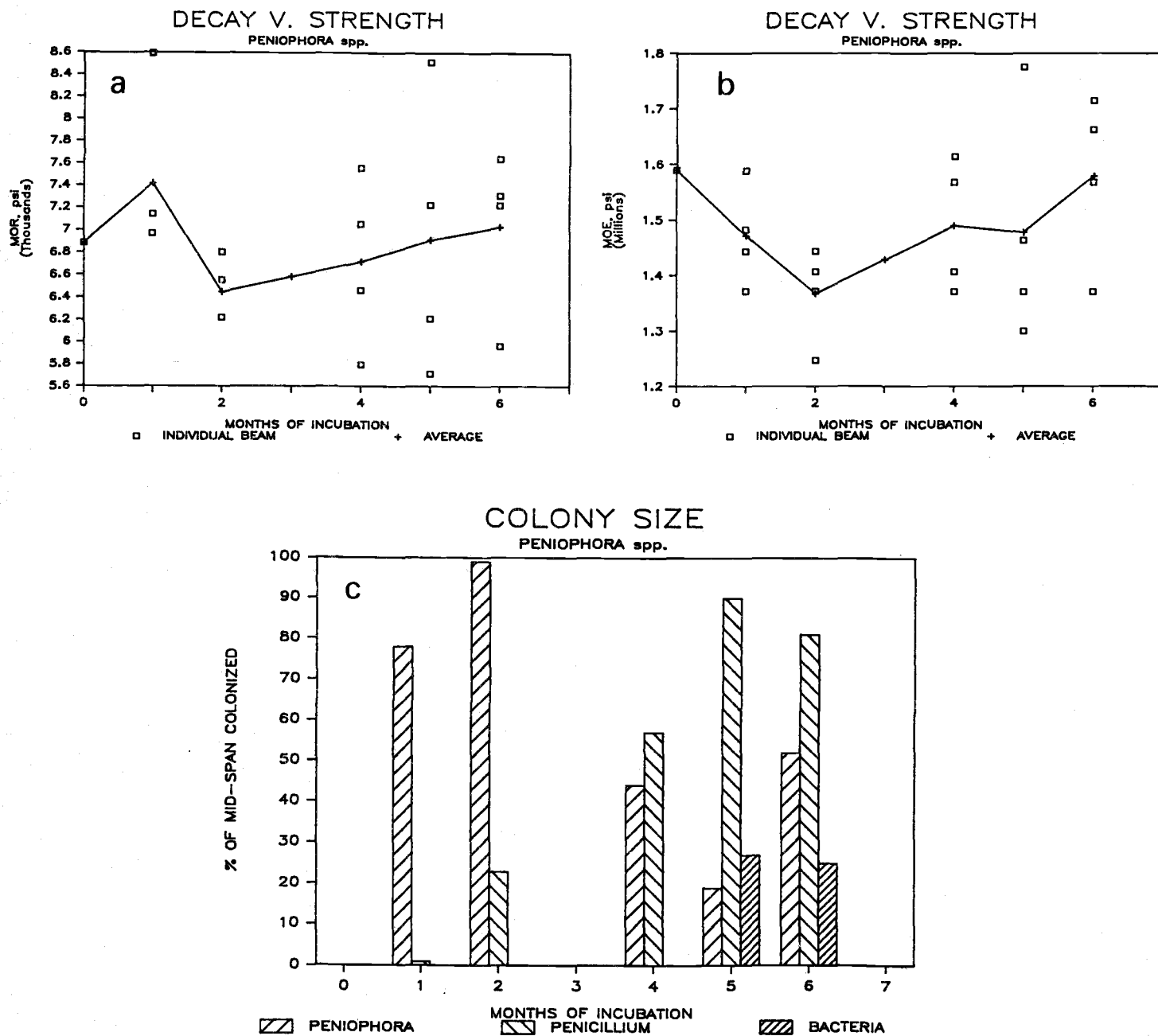
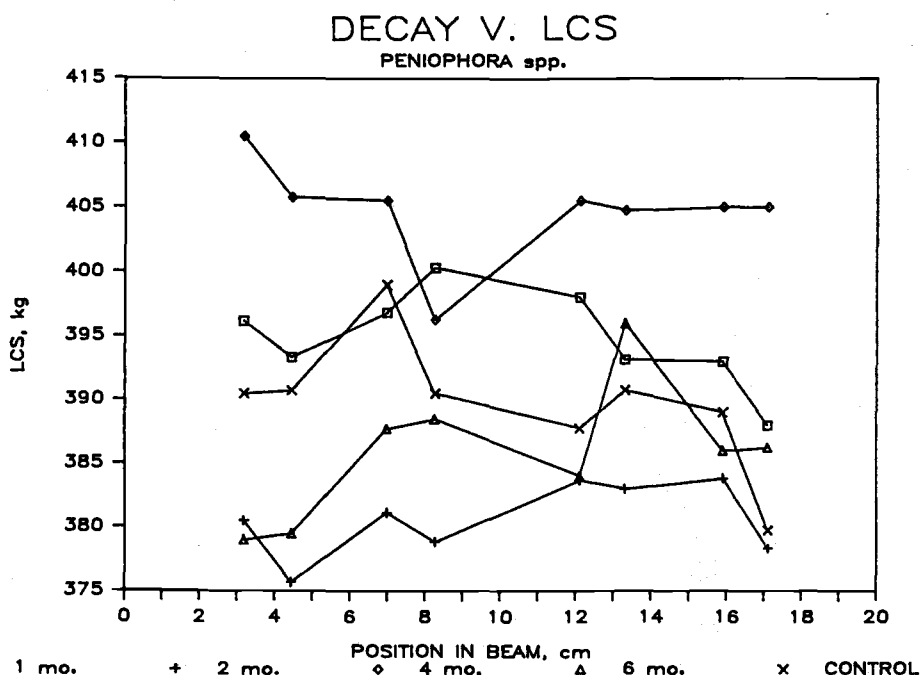


Figure V-6. Effect of *Peniophora* on longitudinal compression strength of beams during the first 6 months of incubation.



C. SAPWOOD THICKNESS OF SECOND GROWTH DOUGLAS-FIR LOGS FROM PACIFIC NORTHWEST AIR-SEASONING YARDS.

Many treaters are concerned that the second growth Douglas-fir logs which are increasingly used for poles will have exceptionally thick sapwood that may not be completely protected during the pressure treatment process. Since sapwood lacks resistance to decay, this untreated wood would become susceptible to internal decay. The standards presently call for 1.90 cm or 85 percent of the sapwood, which ever is greater. It is readily apparent that an increase in sapwood will allow for the presence of more untreated sapwood in a thicker sapwood pole. While one report from the Forest Products Laboratory in Madison examined sapwood thickness, this study evaluated trees with the bark on and did not take into account variations due to peeling. Since a certain amount of sapwood is removed during the peeling process to shape the pole,

measurements at this time will have more significance to treaters.

The sapwood thickness of poles in five yards located in Oregon and southern Washington was examined to provide information on this question. At each seasoning yard, poles from selected sizes and lengths were examined at the top and butt. Since pole stock varied between yards, it was not possible to find representatives for all classes and heights at the 5 yards. At each yard, the top and butt diameter of the poles were recorded, then the sapwood thickness at each end was measured and the average number of rings per inch in the sapwood was counted. A total of 460 poles were measured in these tests and the results were tabulated by yard, pole class, and pole height.

It is difficult to make generalizations for a species based on only a few hundred observations, but the results indicate that sapwood thickness varied by pole height, class and seasoning yard. Within these yards, average sapwood thickness only ranged from 2.90 to 4.78 cm at any given site (Table V-2). The results also indicate that there was little difference in sapwood thickness between Class 1, 2, or 3 poles, nor was there much difference between Class 4, 5, or 6 poles. There was; however, a visible difference between these 2 groups of pole classes. In spite of the variation between pole classes, all of the average sapwood thickness values were well above the 1.9 cm requirement for sapwood penetration of Coastal Douglas-fir poles suggesting that a re-evaluation of the sapwood penetration requirement might be in order to insure continued production of a quality product. This topic is currently under consideration by an AWP Task Force on the Western Species and was one of the reasons for this brief study.

Table V-2. Average sapwood thickness of Douglas-fir poles in five Pacific Northwest air-seasoning yards.

| SITE | SAPWOOD THICKNESS (CM) BY POLE CLASS ^a | | | | | | | | | TOTAL |
|-------|---|-------------|---------------|---------------|---------------|--------------|--------------|-------------|--------------|---------------|
| | H1 | H5 | 1 | 2 | 3 | 4 | 5 | 6 | B | |
| 1 | | | 4.01 (13) | 4.57 (22) | 4.09 (14) | 3.49 (39) | - | 3.81 (3) | - | 3.99 (91) |
| 2 | 3.18 (1) | - | 4.50 (26) | 2.90 (27) | 4.39 (25) | 4.01 (11) | 3.93 (10) | - | 4.98 (11) | 3.96 (111) |
| 3 | - | - | 4.67 (54) | 4.47 (13) | 4.78 (29) | - | - | - | - | 4.64 (96) |
| 4 | | 4.76 (1) | 4.64 (15) | 4.14 (20) | 3.86 (20) | 3.62 (5) | - | - | - | 4.20 (61) |
| 5 | - | - | - | 4.42 (66) | 4.54 (35) | - | - | - | - | 4.49 (101) |
| Total | 3.18 (1) | 4.76 (1) | 4.42 (108) | 4.09 (148) | 4.32 (123) | 3.71 (55) | 3.93 (10) | 3.81 (3) | 4.98 (11) | 4.30 (460) |

a. Values represent averages while figures in parentheses represent number of samples.

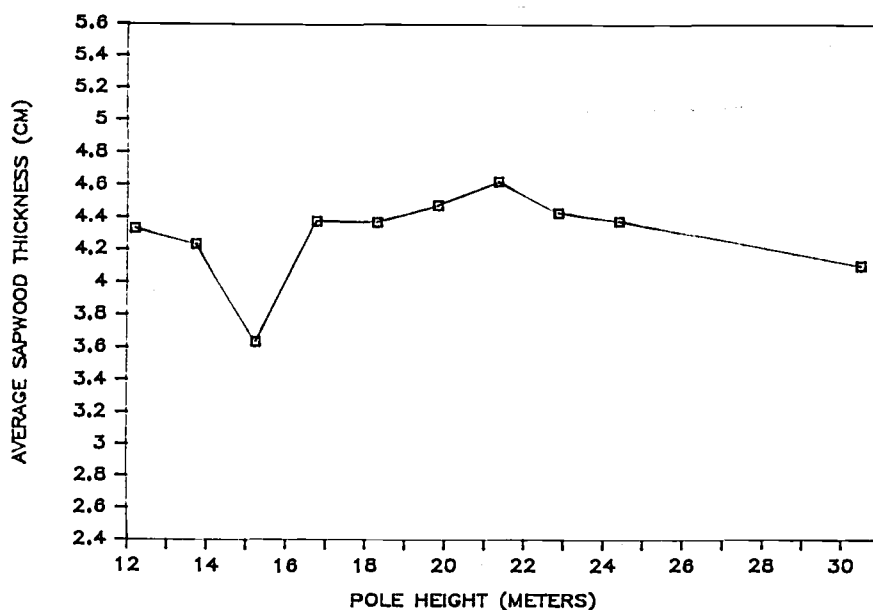


Figure V-7. Average sapwood thickness versus pole height of Douglas-fir poles sampled in five air-seasoning yards in the Pacific Northwest.

OBJECTIVE VI

DETERMINE ROLE OF NON-DECAY FUNGI IN INTERNAL AND EXTERNAL DECAY OF PRESERVATIVE-TREATED DOUGLAS-FIR IN GROUND CONTACT

A. EFFECT OF FUNGI ISOLATED FROM FUMIGANT-TREATED WOOD ON PROTECTION OF DOUGLAS-FIR HEARTWOOD

Five of the most common non-decay fungi isolated from poles treated with fumigants in 1969 (Santiam-Toledo Line) ('85 Annual Report, pg. 114) were evaluated for their ability to affect two decay fungi, P. carbonica and P. placenta. The test was conducted using agar plate and soil-block techniques. The latter was employed to simulate a more natural environment for fungal interactions.

Douglas-fir heartwood blocks (2.0 x 0.3 x 1.0 cm) were conditioned to constant weight and moisture content (25-30 percent) by placing them over water for 3-5 days. The blocks were then exposed to Vapam or chloropicrin to produce retentions of 0.015 and 0.075 mg/cc of wood or 0.0015 and 0.015 mg/cc of wood, respectively. Each treatment was replicated 7 times with 5 blocks for weight loss determination and 2 for GC analysis. In most cases, the blocks were aerated following fumigant exposure to reach the desired level.

The fumigant-treated blocks were aseptically introduced on actively growing cultures of non-decay fungi that included Scytalidium sp. 1, Trichoderma sp. 2, Scytalidium sp. 3, Trichoderma sp. 4, Penicillium sp. 5 and then transferred to cultures of decay fungi using the following sequence:

1. Test blocks exposed to non-decay fungi for 4 and 8 weeks.
2. Test blocks exposed to P. carbonica or P. placenta for 4 and 8 weeks.
3. Test blocks exposed to non-decay fungi and then transferred to P. carbonica or P. placenta.
4. Test blocks exposed to P. carbonica or P. placenta and then transferred to cultures of non-decay fungi.

At the conclusion of the exposure period, weight loss, moisture content, and MIT or chloropicrin content of each block was determined.

At present, only the 0.015 mg/cc Vapam treatment has been completed. The results from this test indicate that exposure to Scytalidium sp. or Trichoderma prior to exposure to P. carbonica or P. placenta resulted in weight losses which were lower than those found following exposure to either of the latter 2 fungi alone (Table VI-1). This effect confirms previous tests using higher concentrations of Vapam (1.5 mg/cc of wood) ('86 An. Rept., pg. 96-100). In addition, the use of the soil-block test resulted in more severe weight losses than the agar-plate test. Soil is capable of considerable fumigant degradation which may have contributed to the higher weight losses. Additional tests on this subject are continuing.

Table VI-1. Average percent weight losses of Douglas-fir test blocks treated with 0.015 mg/cc of Vapam wood using agar-plate and soil-block techniques.

| Fungal Combination | Agar Plate | | Soil Block | |
|-------------------------------|------------|-----------|--------------|--------------|
| | Treated | Untreated | Treated | Untreated |
| A. 1. Scy 1 + P. carbonica | 4.58 | 6.05 | 12.91 | 13.99 |
| 2. P. carbonica + Scy 1 | 5.63 | 6.67 | 13.12 | 16.96 |
| 3. Scy 1 + P. placenta | 6.22 | 6.77 | 14.69 | 17.77 |
| 4. P. placenta + Scy 1 | 7.64 | 8.61 | 25.88 | 57.36 |
| 5. P. carbonica only | 6.29 | 6.98 | 8.64 | ^a |
| 6. P. placenta only | 12.36 | 12.92 | 49.63 | 58.38 |
| 7. Scy 1 only | 2.89 | 4.46 | 5.38 | 5.39 |
| B. 1. Tricho 2 + P. carbonica | 2.82 | 6.10 | ^a | ^a |
| 2. P. carbonica + Tricho 2 | 4.30 | 10.74 | ^a | ^a |
| 3. Tricho 2 + P. placenta | 5.21 | 5.74 | 12.46 | 15.93 |
| 4. P. placenta + Tricho 2 | 7.35 | 8.97 | 33.72 | 34.95 |
| 5. P. carbonica only | 5.42 | 5.74 | 8.64 | ^a |
| 6. P. placenta only | 8.98 | 11.96 | 38.77 | 47.90 |
| 7. Tricho 2 only | 0.88 | 1.96 | 2.31 | 3.24 |

^a No weight losses were determined--blocks were contaminated with Penicillin.

B. EXAMINATION OF CELLON TREATED LAMINATE STOCK REMOVED FROM RICHLAND, WASHINGTON AFTER 12 YEARS OF SERVICE

The use of the Cellon process to deliver pentachlorophenol into wood without creating oily surface deposits was once hailed as a major treating advancement. This treatment has been found to be more susceptible to surface decay by soft rot fungi and many utilities no longer purchase poles treated by this process. Unfortunately, there are numerous decay susceptible Cellon treated poles remaining in service. Most of the problems with Cellon-treated poles has occurred in the wetter regions of the United States, where moisture conditions are more conducive to attack by soft rot fungi. Recently, inspectors from BPA located several Cellon-treated laminated Douglas-fir transmission structures that contained significant amounts of surface decay.

While the occurrence of this type of damage was not new, these poles were located in Richland, Washington, an area with low rainfall and well-drained volcanic soils. These poles contained surface decay that extended up to 3.75 cm in from the surface. Because of the degree of attack and the geographic location where it occurred, the following examination was conducted.

One section from the groundline zone of a laminated Douglas-fir transmission pole was removed and brought to the Oregon State University Forest Research Laboratory. The zones of surface damage were carefully examined and mapped. Once this mapping was completed, a series of plugs were cut from the damaged and undamaged zones. These plugs were cut into 0.3 cm segments and segments from the same zones were combined for analysis using an ASOMA 8610 x-ray emission analyzer for the chlorine in pentachlorophenol.

In addition to the chemical analysis, thin sections cut from selected locations in the damaged and undamaged zones of the pole were examined for evidence of soft rot cavities in the S-2 cell wall layer (Type 1 soft rot) or erosion of the wood cell wall (Type 2 soft rot).

Finally, increment cores were removed from locations adjacent to those sampled for the chemical analysis for culturing. Any fungi growing from the wood were examined microscopically and identified.

Chemical evaluations indicated that nearly all of the undecayed zones contained high levels of penta, while retentions in the decayed zones were substantially lower (Figures VI-1-4). The only exception to this trend was on side D where penta levels in the decayed zone were 25 percent lower than those in the sound wood for the outer 0.3 cm (Figure VI-4). This side was heavily attacked on nearly the entire face and the lack of damage in the zone of low penta retention may have occurred where the wood was not in ground contact

and, therefore, not subject to soft rot activity. This side was also interesting since soft rot attack occurred in wood that was treated to retentions above the threshold for most Basidiomycetes. Soft rot fungi are reported to be less sensitive to toxicants and much higher retentions may be required to adequately protect Cellon treated wood from soft rot attack.

In the remaining analyses, the levels of penta were much higher in the non-attacked zone (Figures VI-1-3). This variation in retention suggests that either the penta was depleted from the wood prior to attack, or the wood was improperly treated prior to installation. While it is difficult to determine which of these factors accounted for the severe surface attack experienced by this wood, the degree of damage and the sharp delineation between sound and decayed wood suggest that the non-uniform treatment contributed to the damage.

Microscopic examination of sections cut from damaged and undamaged zones revealed that most of the cells in the former zone contained evidence of Type 2 soft rot attack. Although some cavities were also noted in the summerwood, this damage was sporadic and did not appear to be significant. No soft rot damage was noted in the undamaged sections examined. Type 2 soft rot attack is generally the more common mode of soft rot attack and laboratory tests indicate that this attack is associated with large losses in wood strength.

Culturing of increment cores removed from the poles revealed that the wood was colonized by a sparse microflora. In general, the wood removed from the decayed zones was heavily colonized by Scytalidium lignicola, a common inhabitant of preservative-treated Douglas-fir. This species has been reported to cause soft rot damage, but only at a very slow rate. This suggests that this fungus may have colonized the wood after the initial attack occurred. Further studies will continue with the other fungi isolated from

these cores to determine if they are capable of causing soft rot damage.

The results indicate that penta retentions were closely correlated with soft rot damage in 3 of the 4 faces examined. This result, along with the sharp delineation between sound and damaged wood in the groundline region suggests that non-uniform distribution of treatment contributed to the rapid soft rot attack. This poor distribution may reflect the use of refractory Douglas-fir, the presence of moisture pockets at the time of treatment, or the loss of penta from the surface when the wood was solvent washed after treatment. The latter practice was commonly used to reduce penta blooming on the surface of Cellon-treated poles.

While penta levels can be used to explain most of the surface attack, evaluating the levels of attack in other poles installed at the same time and determining the nature of the soil surrounding these poles may also help explain this severe attack.

Figure VI-1. Retention of pentachlorophenol in decayed and non-decayed zones in sides A, B, C, OR D of a Cellon-treated Douglas-fir laminated transmission pole as measured using x-ray emission spectroscopy.

