

## ABSTRACT

Field tests of currently registered fumigants continue to demonstrate the long-term performance of these Vapam, Vorlex, and chloropicrin. Methylisothiocyanate (MITC) and Vorlex treated poles have low levels of fungal infestation and closed-tube bioassays show that residual volatile fungitoxic residues remain in the wood 11 years after treatment.

The search for controlled release, solid fumigants is continuing, with testing of solid sodium n-methyldithiocarbamate (NaMDC), the active ingredient of Vapam, and Mylone (Basamid). These compounds are crystalline solids at room temperature, which slowly decompose to produce MITC and other volatile compounds. Our tests indicate that the rate of decomposition can be altered by the addition of various buffers. The presence of various metals, which was reported to influence decomposition, had little effect on chemical performance. The rates of decomposition of the solid chemicals remain slower than those found for conventional liquid compounds, but the levels of MITC produced are sufficient for fungal control.

In addition to fumigants, fused borate rods were also investigated for their ability to migrate through Douglas-fir heartwood at various wood moisture contents to control established decay fungi. Boron was able to migrate through wood at or above 40 percent moisture content, but exhibited little migration at 20 percent moisture content. Borate rods were capable of controlling both Postia placenta and Antrodia carbonica in our small block test, although the chemical levels required varied with the two fungi.

Based upon laboratory tests, we have established 3 field tests of new chemicals or chemical formulations. In the first, the efficacy of glass

encapsulated MITC (as MITC-FUME) is being evaluated on southern pine and Douglas-fir pole sections. After 6 months, fumigant movement is most rapid through the Douglas-fir poles. This effect was the opposite of the expected result and further evaluations of these poles are currently underway.

Douglas-fir poles have also been treated with Mylone or fused borate rods to evaluate the effectiveness of these two chemicals. In the first test, the effect of buffers and other additives on decomposition of Mylone will be investigated at the OSU test site. In the second, fused borate rods at two dosages will be evaluated at OSU; Hilo, Hawaii; and Charlotte, NC.

Basic studies of fumigant chemistry in wood are also underway. We continue to study the chemistry of NaMDC decomposition with the goal of improving the performance of this chemical. We are also continuing efforts to determine the effects of voids on fumigant effectiveness and the rate of volatile emission from fumigant treated wood. The data from these tests will be used to improve our understanding of fumigant movement through the development of fumigant movement models.

The efforts to identify potential replacements for pentachlorophenol for the treatment of sapwood on western redcedar poles and the protection of field-drilled bolt holes are continuing. A series of laboratory and field trials have been established to evaluate the performance of the most promising chemicals. Several chemicals applied to prevent decay of field-drilled bolt holes appear promising 7 years after application, including Boracol 40 and ammonium bifluoride. The remaining trials will be assessed in the coming year.

The efforts to identify more reliable methods for detecting decay and assessing residual strength are also continuing, with an emphasis on developing reliable estimates of strength effects associated with colonization by the

various fungi isolated during the air-seasoning study. These tests have shown that colonization of Douglas-fir sapwood by Stereum sanguinolentum is associated with a gradual decline in work to maximum load and modulus of rupture, while colonization of Douglas-fir heartwood by Postia placenta was associated with less substantial strength effects. These differences may reflect the difficulty of colonizing heartwood. The relationship between colony size and strength is less clearcut. Both S. sanguinolentum and P. placenta rapidly colonized the beams, but caused strength effects more slowly. Further tests are underway using Peniophora spp. and A. carbonica.

The field portion of the air-seasoning study was completed 2 years ago; however, we are continuing to study the various trends shown by the data. This past year, we evaluate the effects of pole orientation and core position on the frequency of the four most commonly isolated fungi, P. placenta, A. carbonica, Peniophora spp., and S. sanguinolentum. In addition to the apparent preference for sapwood or heartwood, the heartwood colonizing fungi (P. placenta and A. carbonica) appear to colonize the upper surface of the pole sections, reflecting an apparent preference for checks in the wood. The remaining two fungi exhibited no preference and were found uniformly distributed in the sapwood around the pole. Further studies are underway to relate weather patterns with the various colonization patterns.

The final objective under the Cooperative is an evaluation of groundline wrap systems. These formulations formerly contained pentachlorophenol along with creosote and a mixture of water-soluble pastes. Recently, the formulations have been changed, with copper naphthenate replacing pentachlorophenol. Since the revised formulations may perform quite differently, we have established a test of 5 new formulations on Douglas-fir pole sections and are comparing the

performance of these compounds with a pentachlorophenol containing standard. Performance will be assessed by sampling for chemical movement into the wood and microbial colonization of the poles with time.

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- \*Empire State Electric Energy Research Corporation  
New York State Electric and Gas Corporation
- \*Portland General Electric Company
- \*Pacific Gas and Electric Company

**\*Western Wood Preservers Institute**

- J. H. Baxter & Company
- Koppers Company, Inc.
- McFarland-Cascade Company
- Niedermeyer-Martin Company
- J. A. Taylor Lumber Company

**\*Pole Supplier**

- Crown Zellerbach Corporation

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\*Asterisk denotes funding. All supplied poles, hardware, or other assistance.

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**OBJECTIVE I  
DEVELOP SAFE, ENVIRONMENTALLY ACCEPTABLE CHEMICALS TO CONTROL  
INTERNAL DECAY OF DOUGLAS-FIR POLES**

**A. EVALUATE PREVIOUSLY ESTABLISHED TESTS OF FUMIGANT PERFORMANCE OF DOUGLAS-FIR**

Over the course of the initial Bonneville Power Administration support and continuing through the current cooperative, a number of field tests have been established to evaluate various fumigant formulations (Table I-1). As these tests mature, annual sampling provides valuable information on the rates of chemical depletion and microbial recolonization.

1. Douglas-fir poles treated with Vapam, Vorlex, or Chloropicrin: The test line established in 1969 to evaluate the performance of Douglas-fir treated with the wood fumigants Vapam, Vorlex, or chloropicrin was not sampled this past year. It will, however, be sampled this year to determine treatment effectiveness 20 years after initial chemical application.

Table I-1. Characteristics of fumigants currently registered by the Environmental Protection Agency for application to wood.

Trade Name(s)	Active Ingredient	Concentration %	Toxicity (LD <sub>50</sub> )	Source
Timber Fume (Chloropicrin)	Trichloronitromethane "	96%	205 mg/kg	Osiose Wood Preserving, Inc. Great Lakes Chemical Company
Wood Fume	Sodium n-methyldithio-carbamate	32.1	1700-1800 mg/kg	Osiose Wood Preserving, Inc.
Pole Fume (Vapam)	" "			Kop-Coat, Inc.
Vorlex	20% methylisothiocyanate 80% chlorinated C <sub>3</sub> hydrocarbons	99%	538 mg/kg	NorAm Chemical Company
MITC-FUME	methylisothiocyanate	96%	305 mg/kg	Osiose Wood Preserving, Inc.

2. Douglas-fir poles treated in 1977 with allyl alcohol, methylisothiocyanate, or Vorlex: The ability of methylisothiocyanate (MITC), a solid at room

temperature, and allyl alcohol to arrest decay was evaluated by treating Douglas-fir poles with 1 liter of allyl alcohol, 20% MITC in diesel oil, or 100% MITC ('86 Ann. Rept., pg. 7). The poles have been sampled annually by removing increment cores from selected zones around the pole. These cores were either cultured on a nutrient media for the presence of decay fungi, or the outer and inner core segments were used in a closed-tube bioassay to detect levels of residual fumigant in the wood.

The allyl alcohol had little or no influence on fungal survival in the wood, and poles treated with this chemical were retreated with Vapam last year. These poles will no longer be sampled. The remaining treatments continue to provide relatively good protection, although 40 and 20 percent of the remaining poles treated with 20 or 100% MITC, respectively, contained at least one fungal infested increment core (Table I-2). Cores from the Vorlex-treated poles were free of decay fungi, despite the presence of decay fungi the previous year. This variation reflects the difficulty of culturing decay fungi from wood and emphasizes the importance of repeated annual sampling to establish colonization trends. In addition, it is important to determine the relative levels of colonization in the treatment groups. For example, only 3 and 1 percent of the cores removed from the 20 and 100% MITC-treated poles contained viable decay fungi (Fig. I-1). These levels represent extremely low rates of reinfestation, perhaps reflecting sampling in zones which initially experienced low levels of chemical treatment.

The poles were not sampled this past year for residual fumigant content, but previous samplings suggest that the fumigant (with the exception of allyl alcohol) continue to be present at low but detectable levels in the poles (Table I-3).

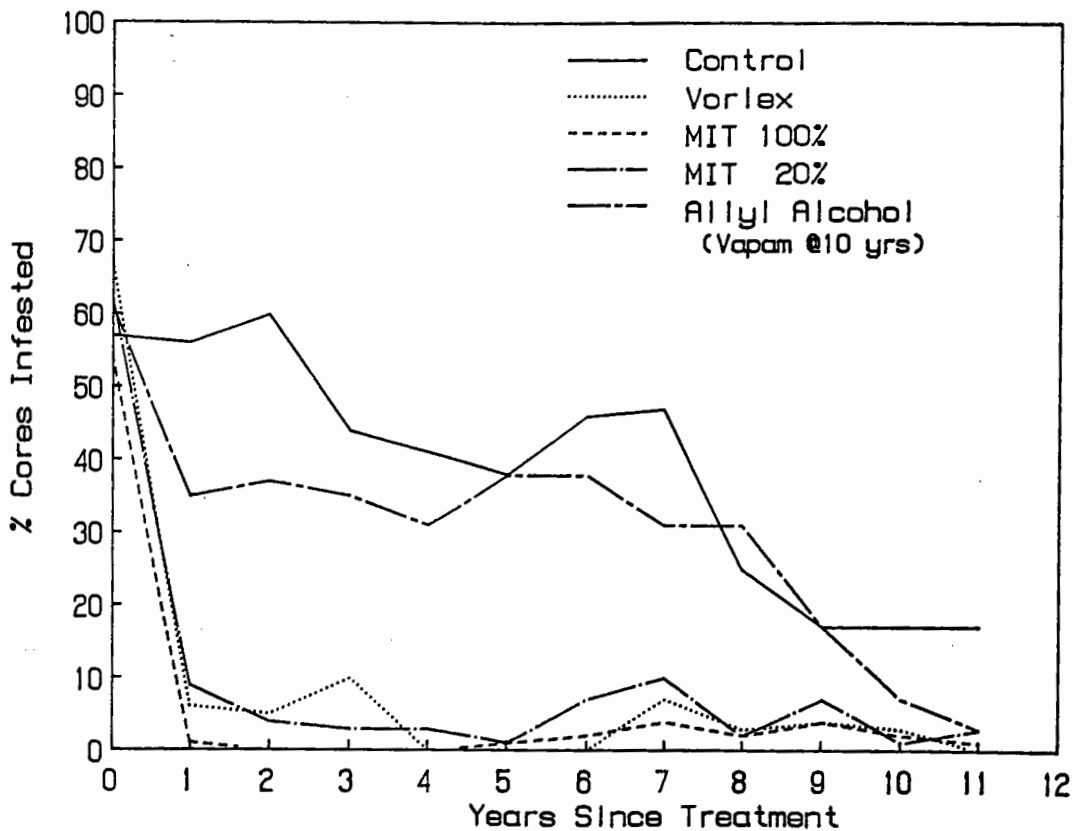


Figure I-1. Percent of cores removed from various sites on Douglas-fir transmission poles treated with Vorlex, 20% methylisothiocyanate in diesel oil, 100% methylisothiocyanate, or allyl alcohol/Vapam which contain Basidiomycetes, a class of fungi containing many important wood decayers.

**3. New York field test of encapsulated MITC:** In 1981, twenty-four 9-year-old CCA-treated Douglas-fir poles were remedially treated with 475 or 950 ml of gelatin-encapsulated MITC or 950 ml of Vapam. A fourth group of poles were left untreated to serve as controls. This latter group was subsequently treated with 950 ml of Vorlex in 1985. These poles contained high levels of decay fungi as a result of inadequate sterilization during the treatment process.

The poles have been sampled on an annual basis since fumigant treatment by removing increment cores from sites around and above the initial treatment sites (see '86 Ann. Rept., pgs. 25-28 for sampling scheme). These cores were cultured for the presence of decay fungi or used in a closed-tube bioassay for the presence of residual fungitoxic vapors.

Table I-2. 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.<sup>a</sup>

Year	Untreated	Number of poles containing decay fungi			
		Allyl Alcohol/Vapam	Vorlex	Methylisothiocyanate 20% <sup>b</sup>	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 <sup>5</sup>	6 <sup>6</sup>	0 <sup>4</sup>	1 <sup>5</sup>	0 <sup>5</sup>
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
1987	3	3	2	1	2
1988	3	1 <sup>c</sup>	0	2	1

<sup>a</sup> 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.

<sup>b</sup> Diluted in diesel oil.

<sup>c</sup> The allyl alcohol poles were re-treated with Vapam in 1987.

Table I-3. Residual fumigant vapors in Douglas-fir poles nine years after fumigant treatment as measured using a closed-tube bioassay.<sup>a</sup>

Meters above ground	Segment location from surface (cm)	Growth of the assay fungus as % of control				
		No fumigant	Allyl Alcohol	Vorlex	Methylisothiocyanate 20% <sup>b</sup>	100%
2.4	0-2.5	100	79	82	72	51
	12.5-15	100	74	97	79	72
1.8	0-2.5	97	87	49	79	64
	12.5-15	95	92	82	97	51
1.2	0-2.5	97	82	87	85	77
	12.5-15	100	92	85	77	77
0	0-2.5	100	92	85	77	77
	12.5-15	82	100	92	85	90
Control	(no wood)	39 mm <sup>c</sup>				

<sup>a</sup> For the closed-tube bioassay, a core was removed at each height from four to six poles. A 2.5-cm-long core segment was sealed in a test tube below an agar slant inoculated with *Postia 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.

<sup>b</sup> In diesel oil.

<sup>c</sup> Average growth in 8 tubes.

After 7 years, the poles continue to remain relatively free of decay fungi (Fig. I-2, Table I-4). Both the Vorlex and MITC (950 ml) treatments were free of decay fungi, while poles treated with Vapam or 475 ml of MITC contained low levels of fungal colonization. Vorlex was applied to the control poles to determine if this highly effective nematocide might also affect infestations by carpenter ants. Observations of the treated poles indicated that Vorlex had little effect on colonies infesting the poles. It is possible that the colonies were established at sites beyond the zone of chemical diffusion around the initial treatment site, or that the ants were able to move away from the zone of chemical protection. Carpenter ants pose unique control problems since they are highly mobile and do not ingest wood. It is unlikely that, unless fumigants are applied directly to or immediately adjacent to a nest, that these chemicals will have any effect on these insects.

Closed-tube bioassays also continue to show residual fumigant protection in both MITC and Vorlex treatments (Table I-5), while cores removed from the Vapam-treated poles exhibited little fungitoxicity. The lower MITC dosage appears to be slowly losing its protective effect, particularly in the outer sampling zone. While these levels suggest that the poles will eventually be reinvaded, previous tests using Vorlex and chloropicrin suggest that even the lower inhibition levels present in the outer shell are adequate for protection and this reinvasion process will take many years.

The continued protection provided by MITC indicates that gelatin encapsulation has little or no negative impact on chemical performance. Gelatin encapsulation provides an excellent means for protecting the applicator from this highly caustic solid prior to treatment. Although the higher cost of gelatin has hindered the use of this approach, increased safety coupled with a minimal

impact on chemical performance continue to make gelatin encapsulation a highly attractive method for safely delivering fumigants to wood.

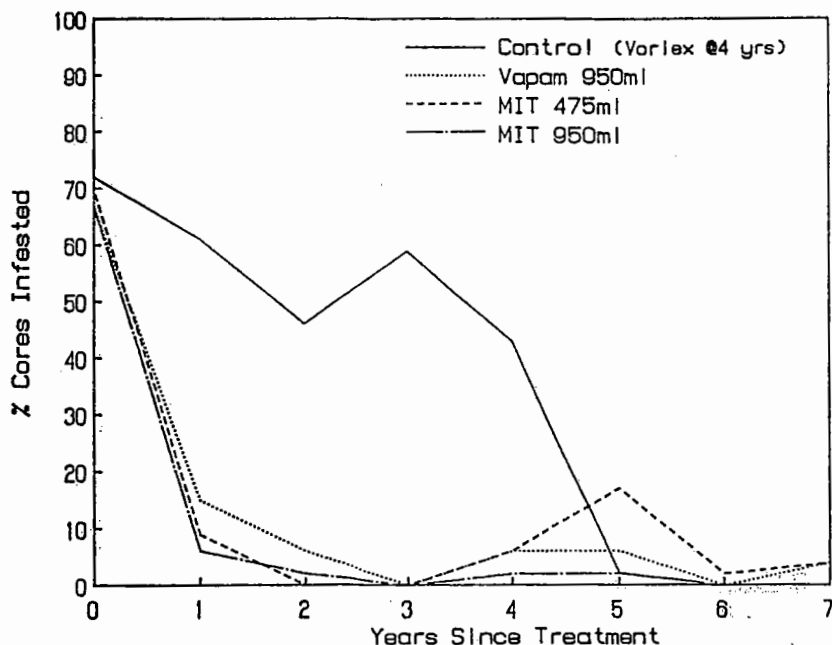


Figure I-2. Percent of cores removed from CCA-treated Douglas-fir poles remedially treated with 950 ml Vapam, 475 ml methylisothiocyanate (MITC), or 950 ml of MITC which contained Basidiomycetes as determined by culturing on nutrient media. The MITC was encapsulated with gelatin prior to application.

**4. Treatment of Douglas-fir poles with encapsulated MITC--effect of moisture content on chemical release:** In 1983, a study was initiated to evaluate the effect of moisture on the release rate and performance of gelatin encapsulated MITC ('86 Ann. Rept., pg. 30-32). The poles were treated by drilling a series of 2.2 cm diameter by 43 cm long holes in a spiral pattern, offset by 90 degrees from 0 to 5 meters from the groundline at 1 meter intervals. Each treatment hole received 88 ml of MITC in 4 gelatin capsules along with 0, (dry), 40 (moist) or 70 ml (wet) of water. The poles have been sampled on an annual basis by removing increment cores from sites within and above the

treatment zone for closed tube bioassays and culturing. Five poles were treated at each moisture content.

Table I-4. Incidence of decay fungi in Douglas-fir poles in New York prior to and after treatment with Vapam or gelatin-encapsulated methylisothiocyanate (MITC).<sup>a</sup>

Sampling Date	Meters above Groundline	Cores with decay fungi (%)			
		No Fumigant <sup>c</sup> (Vorlex) 950 ml	Vapam 950 ml	Encapsulated MITC <sup>b</sup>	
				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	0	0	0
July 1985 <sup>c</sup>	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
July 1987	0	0	0	0	0
	0.6	0	0	6	0
	1.2	0	0	0	0
July 1988	0	0	0	0	0
	0.6	0	6	6	0
	1.2	0	6	6	0

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

<sup>b</sup> About 450 ml of water per pole was added along with the capsules for the 475 ml MITC treatments, and about 900 ml of water was added with capsules for the 950 ml treatments.

<sup>c</sup> Control poles were retreated with gelatin-encapsulated Vorlex after the 1985 sampling.

Five years after treatment, the poles continue to remain relatively free of decay fungi, although low levels of colonization have been detected in the upper levels of the dry treatments and the lower zone of the wet treatment (Table I-6). Last year's sampling revealed the presence of decay fungi in the upper



reaches of the wet treatment poles, suggesting that low levels of fungal colonization are occurring away from the initial treatment zone.

Table I-5. Closed-tube bioassays of cores removed from New York poles after treatment with Vapam, gelatin-encapsulated MITC, or Vorlex.<sup>a</sup>

Chemical	Dosage (ml)	Years Since Treatment	Sampling Height (m)	Average growth of <i>P. placenta</i> (as a % of control)			
				Core Zone <sup>b</sup>			
				Outer		Inner	
			1987	1988	1987	1988	
MITC	475	6	0	24	33	14	8
			0.6	5	61	17	16
			1.2	7	30	0	16
MITC	950	6	0	0	17	0	0
			0.6	0	34	0	0
			1.2	0	5	0	1
Vapam	950	6	0	57	78	77	47
			0.6	77	93	54	96
			1.2	70	86	69	85
Vorlex	950	2	0	18	0	0	0
			0.6	13	23	0	0
			1.2	22	35	0	0

Control tubes (no wood): Avg. = 8.3 mm<sup>c</sup> (1987)/26 mm (1988).

<sup>a</sup> The closed-tube bioassay used a 2.5 cm wood segment removed from the pole. These segments are placed in agar tubes preinoculated with an assay fungus, *Postia placenta*. Fumigant effectiveness is then evaluated as the ability of a wood sample to inhibit radial growth of the fungus and cores with lower numbers have higher fumigant levels.

<sup>b</sup> Increment cores were divided into three segments: 0-2.5 cm, 2.5-12.5, and 12.5-15 cm. The middle segment was used for culturing, and the outer (0-2.5 cm) and inner (12.5-15 cm) segments were used for closed-tube assays.

<sup>c</sup> Control tubes showed poor growth in 1987, ranging from only 5 mm to 20 mm after 7 day's growth.

While the presence of decay fungi may be cause for concern, closed tube bioassays continue to show that relatively high levels of fungitoxic compounds remain in the wood (Table I-7). It is unlikely that decay fungus could cause significant wood damage in the presence of these high residual fumigant levels. The levels in the upper zones of the dry treatments do appear to be declining and should be more closely monitored over the next few years to insure that the fumigant remains at protective levels.

Table I-6. Frequency of decay fungi isolated from Douglas-fir poles treated with gelatin encapsulated methylisothiocyanate (MITC).

Sampling Date	Meters above Groundline	Cores with decay fungi (%) <sup>a</sup>		
		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	20	0	40
	0.9	0	0	0
	1.8	0	0	0
	2.8	0	0	0
	3.7	0	0	0
	4.6	0	0	0
Sept. 1986	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. 1987	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	0	0	0
Sept. 1988	0	0	0	10
	0.9	0	0	0
	1.8	0	0	0
	2.8	0	0	0
	3.7	0	0	0
	4.6	0	0	0
	5.5	10	0	0

<sup>a</sup> The initial fungal estimates were based on culturing of shavings collected during treatment hole drilling. Subsequent data has been based on culturing increment cores removed from sites opposite from the treatment holes. Either 0 ml (dry), 40 ml (moist), or 70 ml (wet) of water was added to each treatment hole to aid in fumigant release from the gelatin.

The poles evaluated in this trial contained advanced internal decay which, in some cases, extended over 6 m up the poles. Since decayed wood tends to retain less chemical than sound wood, the relative period of protection may be somewhat reduced in these treatments. At present, the moist treatments appear to provide the highest levels of residual fungitoxic protection, while the higher and lower moisture treatments appear to be slightly less effective. Nevertheless, all of the treatments continue to prevent reinvasion by decay fungi and are performing as well as previous, non-encapsulated MITC trials.

Table I-7. Residual fumigant effectiveness in Douglas-fir utility poles following application of gelatin encapsulated methylisothiocyanate as measured by a closed-tube bioassay.

Meters above ground	Core location inside treated shell (cm)	Growth of assay fungus (as % of control) <sup>a</sup>					
		Dry		Moist		Wet	
		1987	1988	1987	1988	1987	1988
0	0-2.5	-	4	-	28	-	19
	12.5-15	-	40	-	18	-	22
0.9	0-2.5	8	4	8	25	24	32
	12.5-2.5	10	24	16	55	28	83
1.8	0-2.5	4	27	0	18	16	42
	12.5-15	3	20	17	33	16	58
2.8	0-2.5	18	17	0	0	8	0
	12.5-15	0	0	8	0	16	20
3.7	0-2.5	3	12	0	8	8	0
	12.5-15	4	36	0	11	8	7
4.6	0-2.5	24	24	0	11	10	23
	12.5-15	20	31	11	0	8	11
5.5	0-2.5	11	61	8	7	12	22
	12.5-15	13	67	4	0	0	0
Control	(no wood)	27 mm					

<sup>a</sup> 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. 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, *Postia placenta*. Fumigant effectiveness is then evaluated as the ability to inhibit radial growth of the fungus. Cores with lower numbers have higher fumigant levels.

## B. EVALUATE NEW CHEMICALS FOR CONTROLLING INTERNAL WOOD DECAY

1. Ability of solid fumigants to control decay fungi in Douglas-fir heartwood: Last year, we reported on the performance of pelletized sodium n-methyldithiocarbamate (NaMDC) and Mylone, alone or in combination with various additives to control the decomposition of these fumigants and effect fungal control ('88 Ann. Rept., pg. 9-21). The results suggested that the decomposition of both NaMDC and Mylone could be enhanced and controlled by the addition of various additives; however, results were somewhat variable due to problems with the test method. Over the past year, we have improved the test procedure by changing the sterilization method and the incubation conditions after treatment. Formerly, we sterilized the blocks by steaming blocks at their equilibrium moisture contents and soaking them in sterile distilled water to raise the moisture content to a level sufficient for fungal growth. This procedure resulted in somewhat low moisture levels and also produced a high amount of moisture variability. In addition, the procedure introduced the possibility of contamination during the soaking process. To overcome this limitation, we now pressure soak the blocks (4 to 6 hours at 125 psi) to raise the moisture content to 100 to 150 %, then steam sterilize and inoculate in the usual manner. This process produces a block with an average moisture content of 80 percent of the time of fumigant treatment.

The other procedural modification involved aeration following chemical application. Because fumigants produce fungitoxic volatiles, it is important to provide adequate ventilation in the incubation chambers after treatment. Failure to aerate produces extremely high chemical levels in a treatment chamber, leading to artificially high degrees of fungal control. Formerly, we provided aeration by incubated the blocks in plastic chambers with the lids partially

opened. The chambers were placed under a fume hood to eliminate any volatiles from the laboratory. Unfortunately, the passage of air over the blocks produced rapid drying, with wood moisture contents declining to 25% and sometimes as low as 12% over a one-week incubation period. Fungal growth at these low moisture contents is extremely limited, and the degree of movement and interaction of the chemical with the wood may be substantially altered. While declining moisture content had less of an effect over a one-week incubation period, it produced dramatic reductions in fungal survival when untreated control blocks were incubated for periods of four or more weeks. The chemicals currently under investigation are slow release formulations which require longer incubation periods. To overcome this problem, blocks were incubated in sealed plastic chambers which were attached to an aeration system which passed humidified, filtered air over the blocks, making a complete air exchange of air every 20 minutes. The combination of wetter blocks at the start of fumigant treatment and humidified air during incubation have stabilized treatment conditions, making results more consistent and comparable.

This past year we evaluated the effects a number of additives on the performance of solid NaMDC, including the presence of 1% copper sulfate at pH 4, 7, 10, or 12 and the effect of surface area on release rate.

Blocks which were pressure soaked prior to inoculation to increase moisture content generally contained higher levels of MITC at the conclusion of the tests. This effect conflicts with previous studies in which MITC has been shown to sorb at higher levels in dry wood. Moisture enhances the decomposition of NaMDC and the increased moisture levels in the soaked blocks appear to have markedly improved NaMDC decomposition (Figure I-3). These results indicate that additional water may be necessary when pellets are applied to dry wood, although

the addition of 1.2 ml to the treatment hole at the time of treatment did not appear to enhance chemical release in the drier blocks. Dry wood is less likely to decay, and it is likely that pellets added to dry wood will slowly release low levels of chemical which can provide long term protection to the wood. As wood moisture content increased, decomposition of NaMDC to produce MITC should exhibit a corresponding rise.

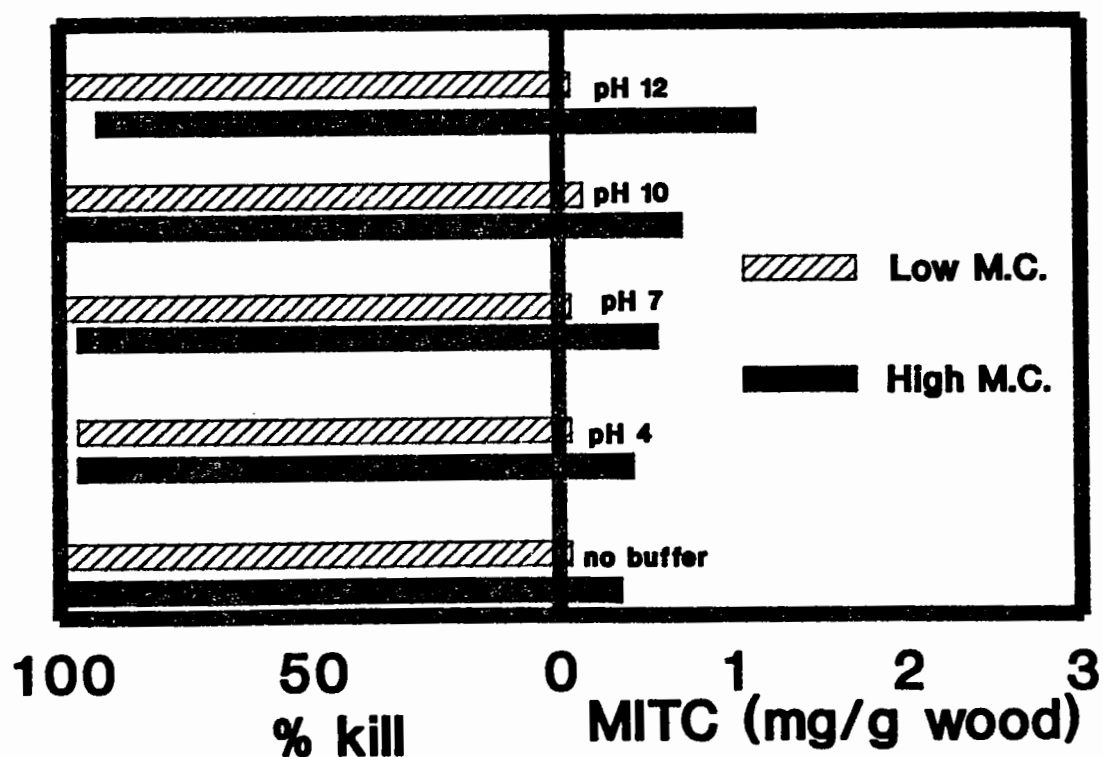


Figure I-3. MITC content and percent fungal survival in Douglas-fir heartwood blocks treated with 5, 0.15-mg pellets of NaMDC with or without pH 4, 7, 10, or 12 buffer. "Wet" blocks were pressure soaked while "dry" blocks were soaked without pressure for 30 minutes prior to fungal colonization and treatment.

The addition of various buffer salts produced no consistent effect on decomposition of NaMDC to MITC (Figure I-4). All of the treatments produced

virtually 100% kill of the test fungus (Antrodia carbonica) within four weeks after treatment, but none of the treatments controlled the fungal infestation after 1 week (Figure I-4). Application of NaMDC with pH 12 buffer appeared to produce a slightly higher degree of control one week after application; however, the relative differences between the various treatments were minimal. Similarly, chemical levels associated with the various treatments varied widely one week after treatment, then uniformly declined well below 1 mg per oven dry gram of wood four weeks after treatment. Chemical depletion of MITC from the small blocks appears to be consistently rapid, with little residual chemical content four weeks after treatment. The chemical appears to move as an initial highly concentrated wave. In a large wood structure, this chemical would continue to move through the wood, controlling established decay fungi at greater distances from the initial treatment site, but the large surface to volume ratio in the test blocks accentuates chemical loss. Treatment with pH 7 buffer appeared to result in slightly higher levels of MITC four weeks after treatment, although the relative chemical levels necessary for long term protection against fungal invasion remain poorly defined. These results confirm our previous findings, but differ from those found in soil using liquid formulations. Dehydration and pelletizing may alter the response to pH. Furthermore, soil is a highly reactive medium which actively mineralizes chemicals and has a highly active microbial flora which can interact in chemical decomposition. The results indicate that addition of buffer does not markedly enhance fungal control, although it might have more subtle effects on the rate and characteristics of NaMDC decomposition.

In earlier tests, the effects of various additives on NaMDC decomposition was investigated using powdered formulations which maximized the surface area

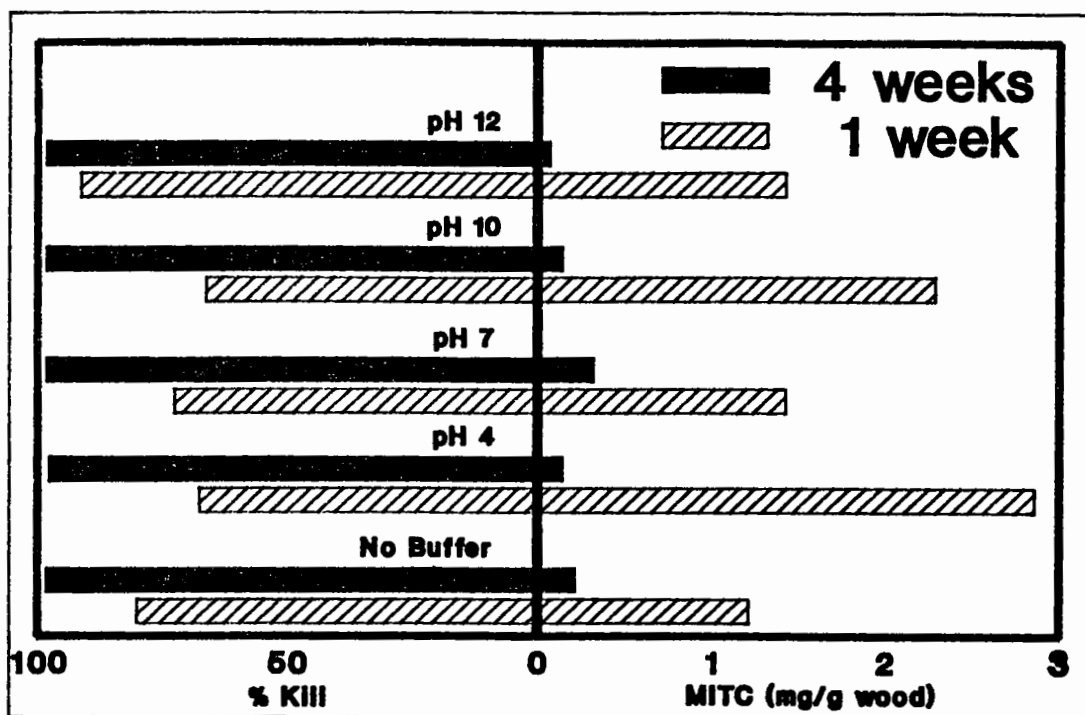


Figure I-4. Effect of addition 5, 0.15-mg pellets of NaMDC in combination with pH 4, 7, 10, or 12 buffer on survival of *Antrodia carbonica* and decomposition of NaMDC to MITC in Douglas-fir heartwood blocks as measured by culturing and gas chromatographic analysis, respectively, one or four weeks after treatment.

exposed to chemical interaction. Pelletized formulations severely restrict the surface area exposed to interaction and may alter chemical performance. In addition, these compounds have low water solubilities and compression into pellet further restricts the potential for chemical/water interactions. The effect of surface area on chemical performance was assessed by making a series of 0.15 g pellets. Some of these pellets also contained pH 4, 7, 10, or 12 buffer. One, two or three of these pellets were applied to individual test blocks. Last year ('88 Ann. Rept., pg. 14), our tests showed that pellet dosages appeared to produce little or no effect on fungal control or MITC content. Our recent tests, using more uniform test blocks, indicate that increasing the number of pellets resulted in both decreased fungal survival and increased MITC content with all five pH treatments (Figure I-5). This effect was most dramatic between one and



three pellets, with five pellets producing 100 percent fungal control in all treatments. While the results contradict previous studies, the most recent tests were performed using more consistently colonized blocks at more uniform moisture contents.

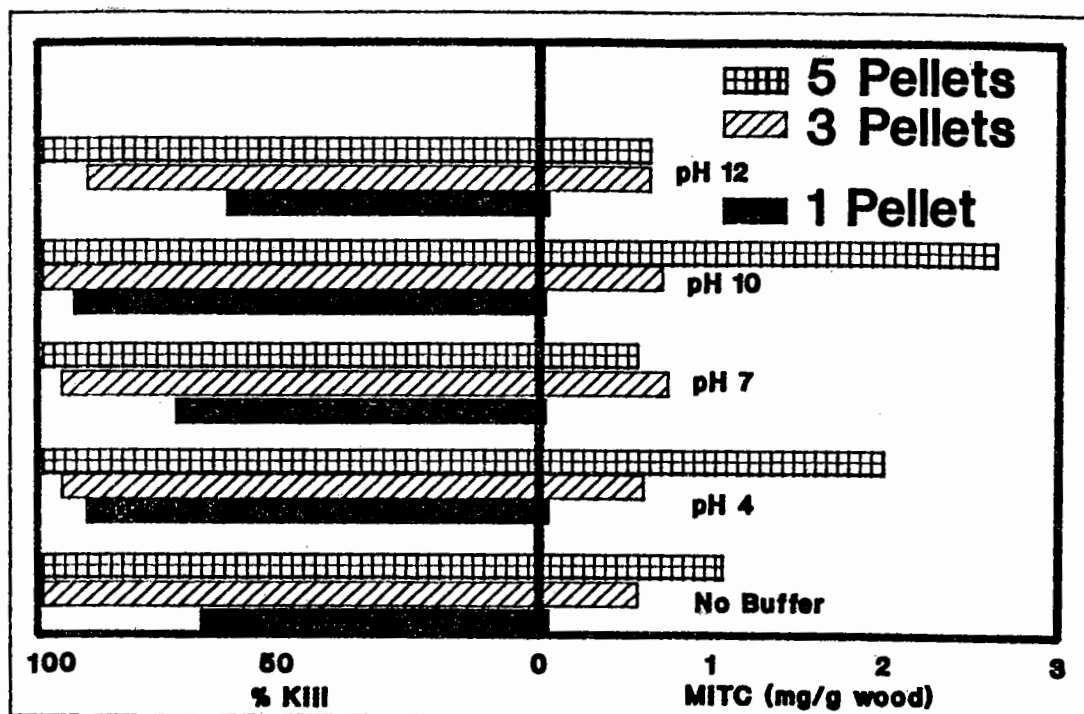


Figure I-5. Effect of pellet dosage of NaMDC on fungal survival of *A. carbonica* and MITC content in Douglas-fir heartwood blocks as measured by culturing and gas chromatographic analysis, respectively.

The addition of 1% copper sulfate to the NaMDC pellets appeared to have little influence on MITC release or fungal survival. While there were slight differences between individual treatments, there was no consistent effect of copper on NaMDC decomposition. Copper and zinc have been shown to enhance Vapam decomposition in soil; however, these effects appear to be minimal in wood. Soil contains a wide variety of more accessible elements which can interact during

the decomposition process, while wood is a relatively barren medium. Higher levels of copper sulfate may have produced an effect in this environment, but these levels would also reduce the maximum amount of active ingredient which could be applied to the wood. The results indicate that the presence of low levels of metals will not markedly enhance the performance of NaMDC as a wood fumigant.

The most recent results clearly indicate that solid Vapam (NaMDC) is an effective wood fumigant under a variety of conditions. While some additives appear to affect the decomposition rate, these effects are variable and require further study. However, the laboratory results indicate that solid NaMDC is now ready for field testing and efforts will be made to develop sufficient quantities of this formulation for such a test.

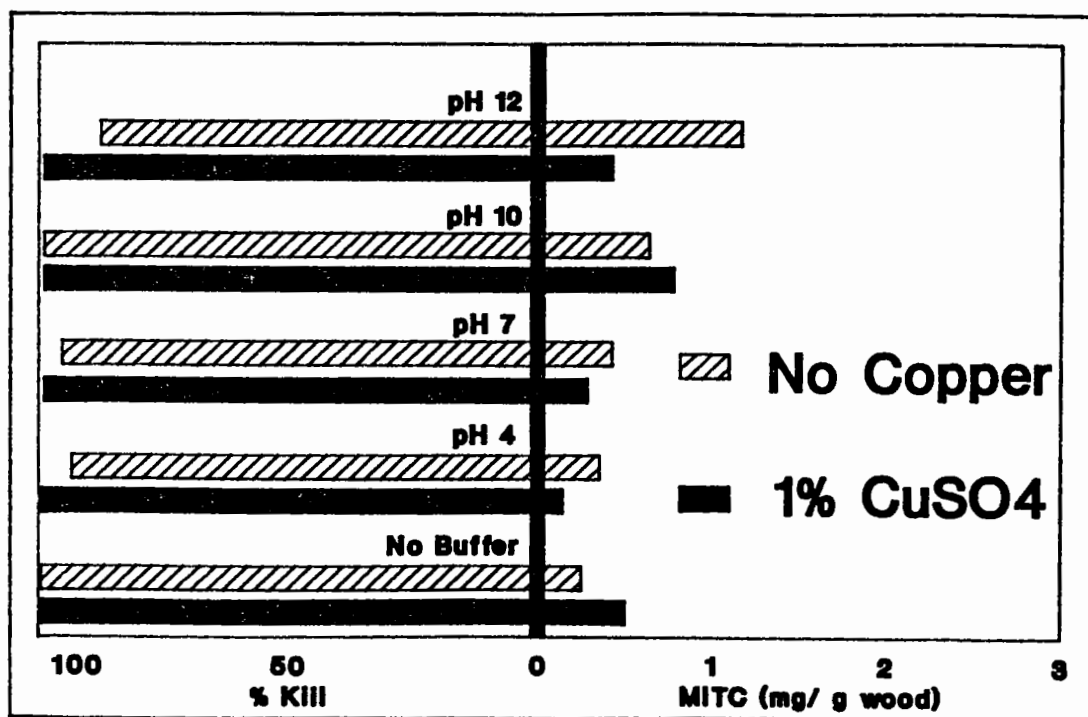


Figure I-6. Effect of copper sulfate on decomposition of 3, 15-mg NaMDC pellets to produce MITC or control a decay fungus, *Antrodia carbonica*, in Douglas-fir heartwood blocks as measured by gas chromatographic analysis and culturing, respectively.

2. Ability of fused borate rods to migrate through Douglas-fir heartwood and control Basidiomycetes: Last year ('88 Ann. Rept., pg 22-23) we provided preliminary results of tests evaluating the efficacy of fused borate rods in Douglas-fir heartwood. Boron is an extremely effective low mammalian toxicity fungicide and insecticide which has the ability to diffuse through moist wood and can be delivered in concentrated form in a fused, glass-like rod containing 100 percent sodium octaborate tetrahydrate. Fused borates have been used for controlling decay fungi in buildings, railroad ties, and utility poles in Europe, but have seen limited application in the United States.

The ability of fused borate rods to eliminate Antrodia carbonica and Postia placenta from Douglas-fir heartwood was evaluated using our small block test. The blocks were inoculated with the test fungus following a pressure soak which helped to insure that sufficient moisture was present. In addition, several sets of blocks were soaked without pressure to evaluate chemical movement and fungal survival in slightly drier wood.

Once the blocks were thoroughly colonized by the test fungus, a 1.2 cm diameter hole was drilled at the center of 2.5 by 2.5 by 10 cm long test blocks, a small piece of fused borate rod was added to the hole, and the hole was capped with a rubber serum cap. Borate rod was added at the rate of 50, 125, 250, 500, 750, or 1000 mg per block. These dosages correspond to 0.8, 2.0, 4.0, 8.0, 12.0, and 16.0 kg/m<sup>3</sup> of fused borate rod. The blocks were incubated at room temperature for 2, 4, 6, or 8 weeks after treatment. A series of 0.5 cm thick cross sections were cut from the ends of each block. The outer sections were discarded, while the next inner section was plated on potato dextrose agar to determine if the fungus survived the chemical exposure. Fungal survival was used

as the measure of treatment effectiveness. The next 5 sections were retained for staining for the presence of boron and for chemical analysis.

Table I-8. Ability of fused boron rods to eliminate Postia placenta or Antrodia carbonica from Douglas-fir heartwood blocks as measured by culturing samples removed from the blocks 2, 4, 6, or 8 weeks after chemical application.

Dosage (mg)	A. carbonica				P. placenta	
	Soaked		Dry		Soaked	
	2 wks.	6 wks.	2 wks.	8 wks.	4 wks.	8 wks.
50	100	25	100	25	53	0
125	100	25	94	-	3	0
250	62	25	91	13	0	0
500	53	0	94	16	0	0
750	-	-	-	-	0	0
1000	28	0	-	0	0	0
Control	94	100	100	91	97	100

As reported last year, the borate rod eliminated A. carbonica at dosages of 500 mg per block or greater in blocks at the higher moisture level after a 6 week incubation period. Fungal survival in the drier blocks was somewhat higher, reflecting the decreased moisture for breakdown of the rod and subsequent diffusion of the boron (Table I-8). In general, complete elimination of A. carbonica required 6 weeks, a considerably longer period than that found for many commonly used wood fumigants.

While A. carbonica appeared to exhibit some tolerance to boron, P. placenta was eliminated from blocks treated with 50 mg or more of borate in only 4 weeks, and an additional 4 weeks of incubation resulted in complete elimination of the fungus from the 50 mg treatment. This fungus is commonly used as a soil block test organism for evaluating potential wood preservatives, but it apparently has only minimal tolerance to boron. Postia placenta is one of the two most common inhabitants of Douglas-fir transmission poles and the ability of boron to control

this fungus as well as A. carbonica suggest that remedial application of boron may prove useful.

At present, borate rods do not appear to be capable of significant upward diffusion, particularly in Douglas-fir. The inability to migrate upward would limit the application of the chemical for groundline zones, unless additional treatment holes were drilled some distance above the groundline to allow for downward migration. However, fused borate rods would seem ideal for application above ground in areas where the initial protective shell has been broken during installation or use. Similarly, application of a borate rod to a field drilled bolt hole which will no longer be used to support pole hardware would provide additional protection in this zone.

The preliminary laboratory studies have led to the installation of a field trials at three widely spaced geographic regions. These procedures are described elsewhere in the report.

**3. Effect of moisture content of Douglas-fir heartwood on diffusion of boron from fused borate rods:** Public awareness of the potential hazards associated with chemicals used to protect wood against deterioration have renewed interest in identifying safer methods of protection. One chemical identified for this purpose is boron, which has extremely low mammalian toxicity yet is highly effective against insects and basidiomycetous decay fungi. Borates are capable of migrating long distances through wet wood and can diffuse through many woods generally considered impermeable to conventional wood preservatives. Also, borates can be formulated into fused rods that can be inserted in wood to prevent and control internal wood decay. Borate rods have been evaluated extensively outside the United States and have been tested in window joinery within the

United States. Preliminary trials indicate that the rods can effectively arrest colonization of Postia placenta in Douglas-fir poles.

While fumigants are most often used in the United States for controlling internal decay of Douglas-fir poles and timbers, borate rods may be useful where fumigant application is impractical. However, moisture content (MC) in the pole environment is characterized by wide seasonal and positional variation, and MC has been reported to affect diffusion strongly in freshly sawn lumber dipped in liquid boron solutions. For this reason, we evaluated the effect of various wood MC on diffusion of boron from fused borate rods through Douglas-fir heartwood.

Douglas-fir heartwood blocks measuring 2.5 by 2.5 by 10 cm were oven dried at 54°C to stable weight and weighed to the nearest 0.001 g. The blocks were then submerged in water and subjected to a 30-minute vacuum (27 in Hg), followed by a 1-hour pressure period (125 psi). Each soaked block was blotted dry, weighed, and aerated until the wood MC decreased to one of five levels: 20, 40, 60, 80, or 100 percent. When a block reached the desired moisture level, it was dipped in molten wax to prevent further moisture loss. Blocks having the same target MC were placed together into plastic bags and stored at 0°C for 2 weeks to allow wood more complete equilibration.

A hole 0.9 cm in diameter was then drilled 2.0 cm into each block approximately 1.0 cm from one end to receive a small section of borate rod (0.5 cm diameter). Each block received 125, 250, 500, or 1000 mg of borate [100% anhydrous disodium octaborate (Impel), CSI, Inc., Charlotte, NC]. The hole was immediately sealed with a tight-fitting rubber septum, and the blocks were placed in plastic bags to retard moisture loss. Blocks were incubated at room temperature (23° to 25°C). At 1 week, 4 weeks, 8 weeks, and 12 weeks, blocks with each combination of moisture content and chemical dosage were removed, and

0.5-cm-thick sections were cut adjacent to and at distances of 1.0, 3.0, 5.0, and 7.0 cm from the treatment hole. The sections were immediately placed in an oven (104°C) to retard further diffusion of the boron. After drying, all sections were stained with a cumin/salicylic acid indicator for the presence of boron.

The first, third, and fifth sample sections were then ground, and 0.4 g of the meal was extracted for 30 minutes with 25 ml of 0.5 M sulfuric acid in an ultrasonic water bath. The wood meal was filtered off and an aliquot of the solution extract analyzed for residual boron content by inductively coupled ion plasma spectroscopy. The results were converted to percentages of boric acid equivalent for reporting.

One week after treatment, staining of the cut cross sections indicated boron penetration adjacent to the treatment hole in all blocks except those with 20 percent MC. Complete penetration was achieved in blocks with 100 percent MC, while penetration increased gradually at 40, 60, and 80 percent MC. Higher chemical dosages produced a slight improvement in diffusion, although no movement was detected in the blocks with 20 percent MC.

After 4 weeks of incubation, staining indicated that boron had diffused along the length of blocks in all treatments. While chemical dosage appeared to have only a slight effect on the degree of migration, the lack of effect most probably reflects the high sensitivity of the indicator; higher chemical concentrations associated with higher dosages are not detectable with the cumin indicator.

Staining after incubation of the blocks for 8 weeks showed more complete protection of the cross-section, and differences between blocks with the various moisture levels were slight.

These results indicate that borate rods break down, and the chemical migrates at relatively rapid rates under moisture conditions commonly found in wood in service. Although diffusion in the wood will be slower with lower moisture levels, the risk of fungal colonization will also be decreased.

Chemical analysis of the sections indicated that chemical concentrations in the wood were extremely low 1 week after treatment. As expected, the concentrations were highest near the treatment site and declined with distance (Fig. I-7). Higher MC was associated with higher concentrations, although this effect appeared to level off above 60 percent MC.

After 4 weeks of incubation, chemical concentrations immediately next to the treatment hole and 5 cm away in blocks with 60% or greater MC were well above the levels required for fungal and insect control. Concentrations in blocks with lower MC remained below threshold levels, while those in blocks with higher MC increased with increasing MC (Fig. I-8). As expected, higher dosages resulted in higher chemical concentrations in the wood. Concentrations in the blocks with 20 percent MC were barely detectable, which suggests that visual examination with the curcumin indicator produced inaccurate readings. This variation between indicator results and chemical analysis may reflect contamination from the bandsaw blade. Care was taken to avoid contaminating blocks of different treatment groups; however, the results suggest that extreme care is needed if boron movement is to be evaluated only by means of indicators. Incubation of treated blocks for 8 and 12 weeks confirmed this finding, showing that the boron diffused at all other MC levels (Figs. I-9, 10). Although boron diffusion through wood at 20 percent MC was slight, blocks with this MC are at little risk of decay. If their MC should increase, the boron would be ideally



placed to migrate through and protect the wood against subsequently fungal attack.

A previous study showed that boron diffusion through wood at 24% MC was lower than that found at higher MC; however, the Sitka spruce used in that study was freshly sawn and was treated by dipping in borate solution as it dried. Since the samples were not equilibrated to a selected MC, it is possible that moisture levels varied within individual samples. Slightly higher moisture levels in a given location would help to explain the limited diffusion at lower MC. Furthermore, dipping of samples would introduce moisture that may have further improved the prospects for diffusion.

Our results indicate that boron from fused boron rods diffused through Douglas-fir heartwood with MC at or above 40 percent. Preliminary trials indicate that dosages of 250 to 500 mg per test block are sufficient to control an established decay fungus 4 weeks after treatment. Fused borate rods may therefore have excellent prospects for controlling fungi in Douglas-fir poles. While boron lacks the mobility of the fumigants more commonly used for the purpose, their better safety and handling characteristics make them attractive for special uses such as the treatment of zones around field-drilled bolt holes above the ground. Application of borate rods above the field-drilled site would reduce the risk that fungi will colonize wood exposed during the drilling process.

**C. EVALUATE THE MOST PROMISING INTERNAL DECAY CONTROL CHEMICALS UNDER FIELD CONDITIONS**

1. Evaluation of Mylone (Basamid) in Douglas-fir pole sections: Extensive laboratory studies have shown that Mylone can effectively control decay fungi in Douglas-fir heartwood; however, the time required for complete control in the field is generally too slow for commercial application. Mylone is a crystalline

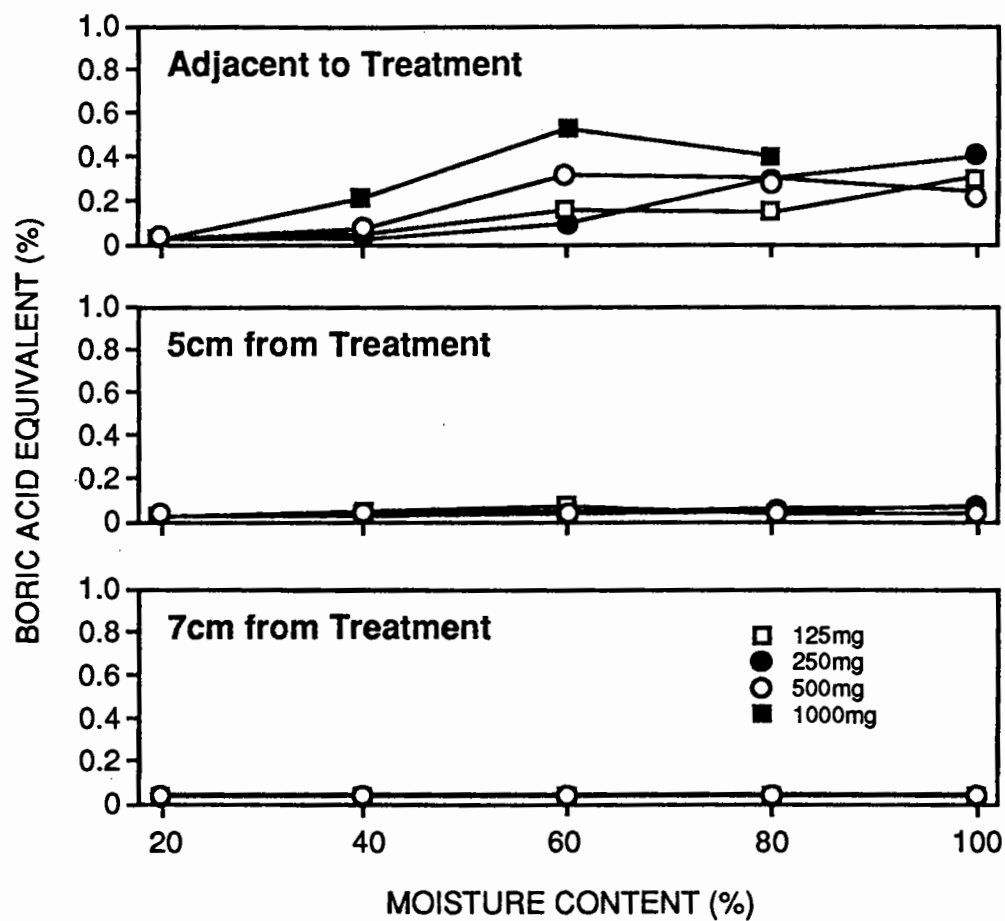


Figure I-7. Boron content of sections cut from Douglas-fir heartwood blocks 1 week after treatment with 125, 250, or 500 mg of fused borate rod, as determined by ICP spectroscopic analysis.

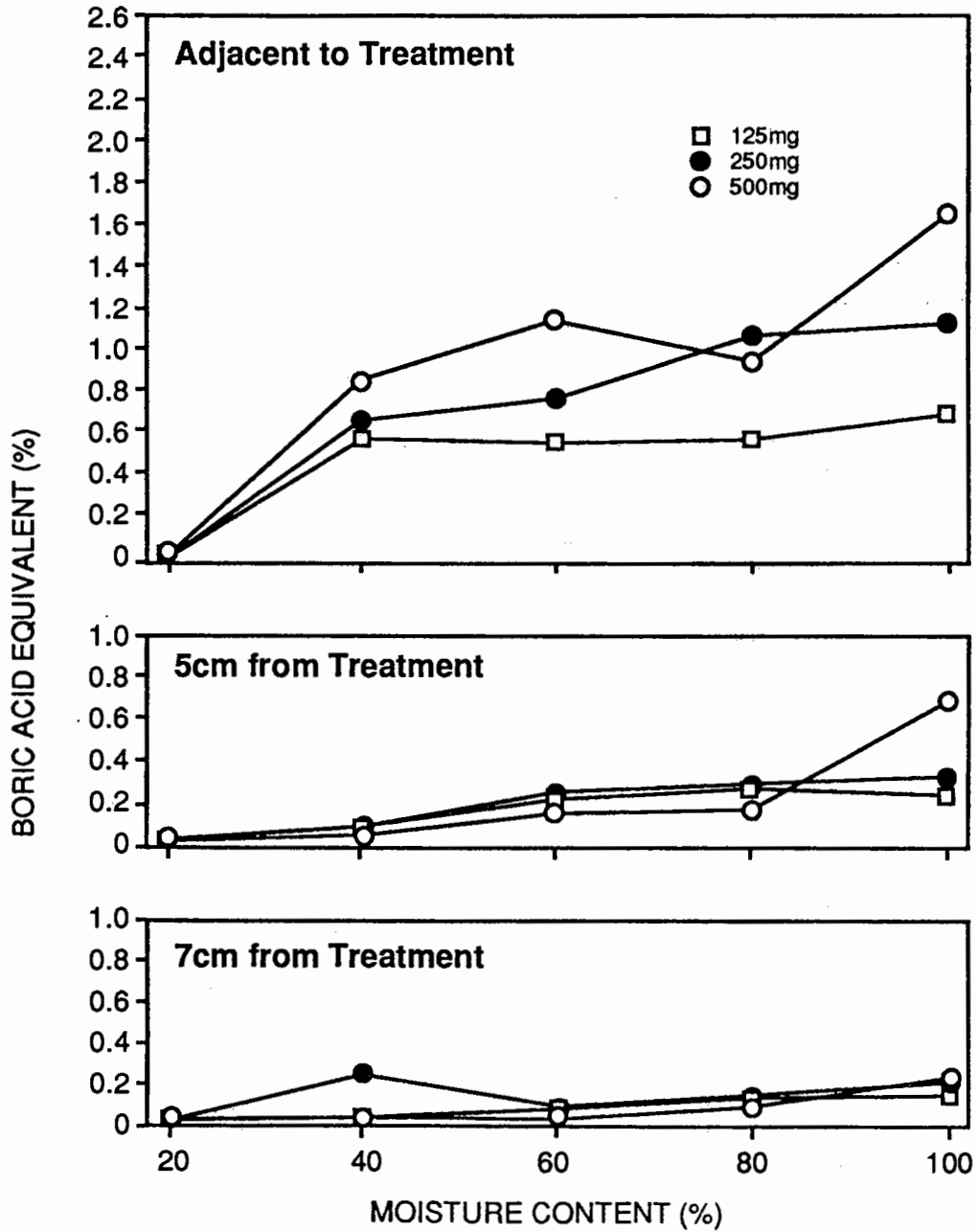


Figure I-8. Boron content of sections cut from Douglas-fir heartwood blocks 4 weeks after treatment with 125, 250, or 500 mg of fused borate rod, as determined by ICP spectroscopic analysis.

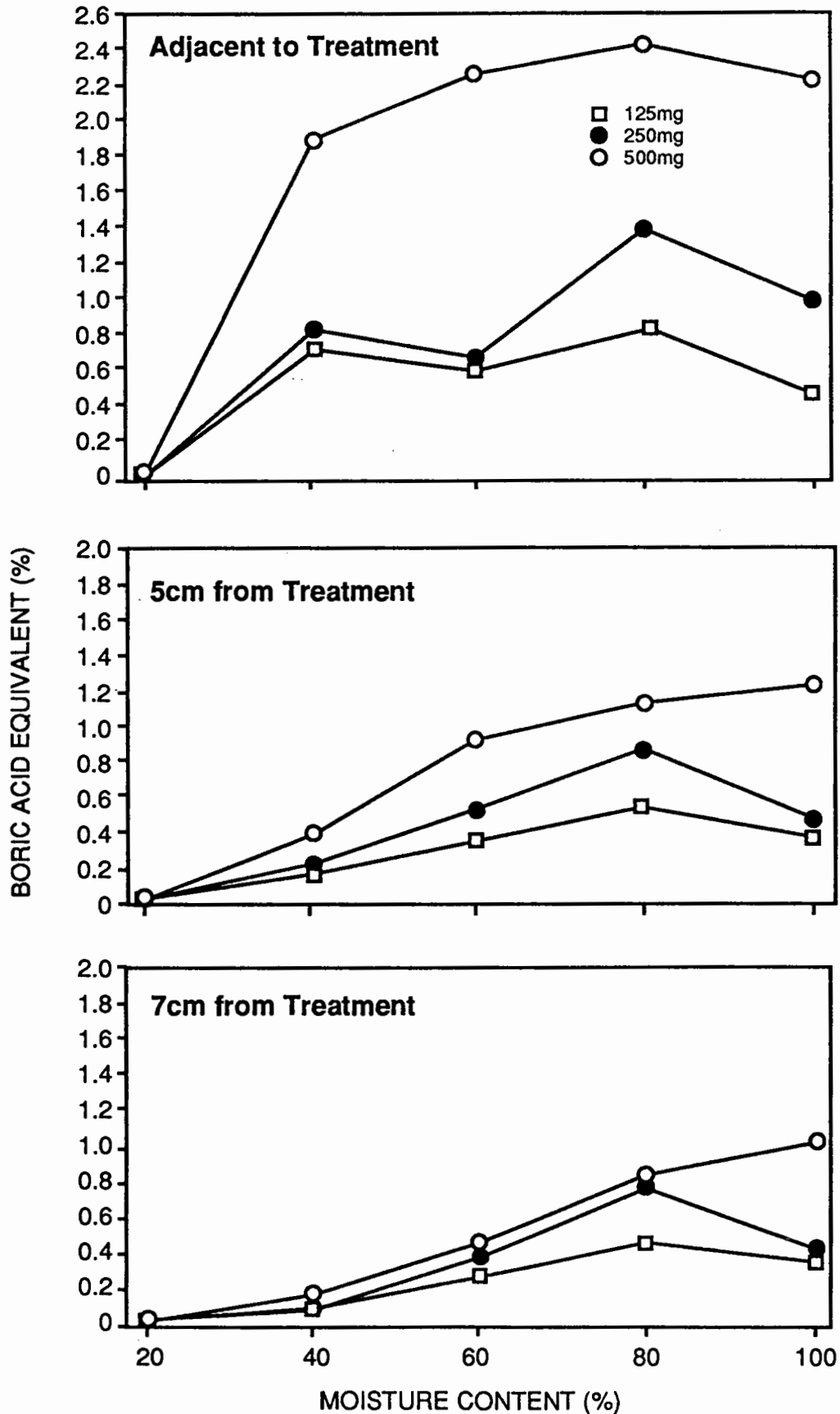


Figure I-9. Boron content of sections cut from Douglas-fir heartwood blocks 8 weeks after treatment with 125, 250, or 500 mg of fused borate rod, as determined by ICP spectroscopic analysis.

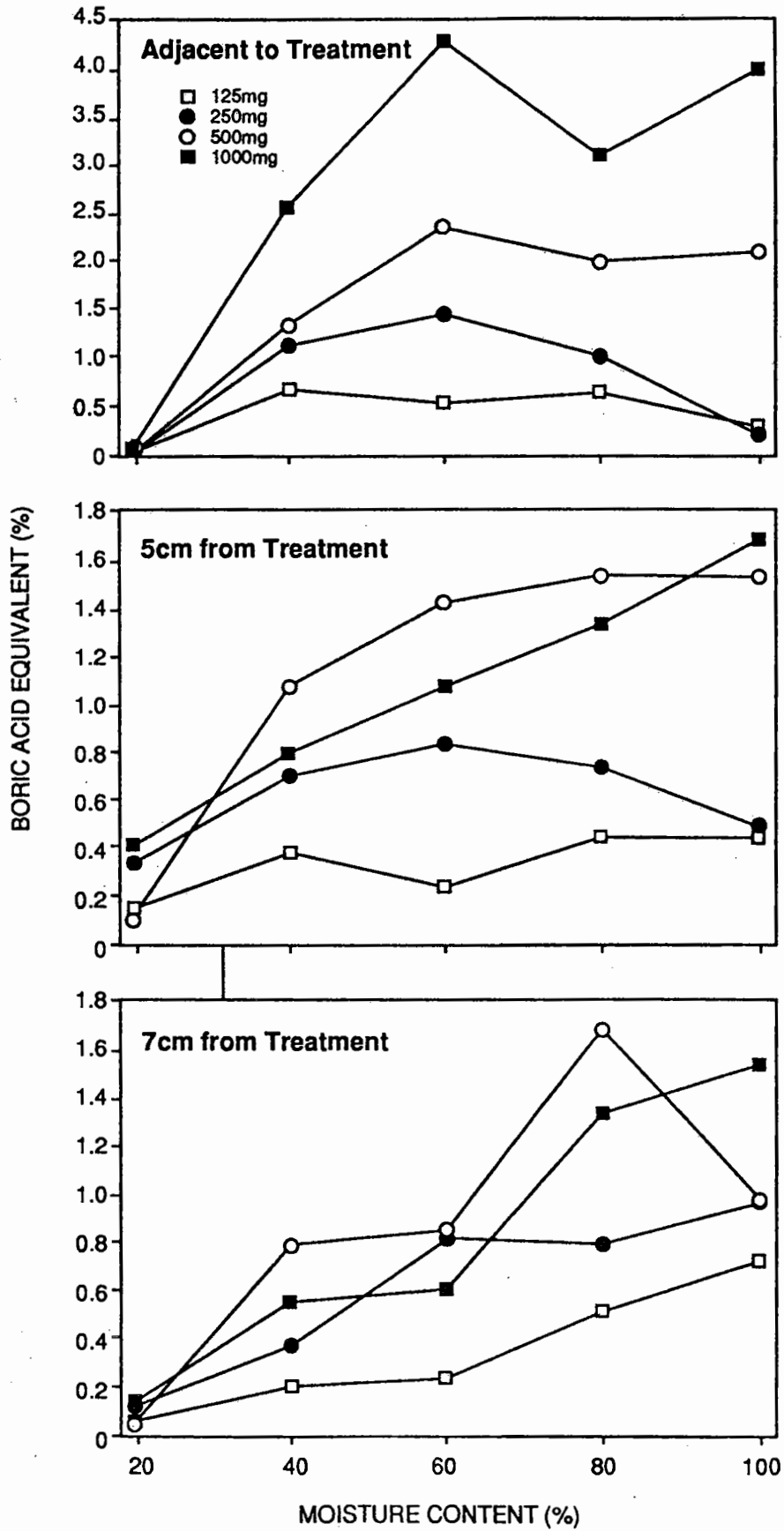


Figure 1-10. Boron content of sections cut from Douglas-fir heartwood blocks 12 weeks after treatment with 125, 250, or 500 mg of fused borate rod, as determined by ICP spectroscopic analysis.

cyclic compound which has relatively low fungicidal efficacy and must decompose to produce fungicidal products. In soil, Mylone can decompose to produce approximately 14 different compounds, but the primary products appear to be formaldehyde, methylamine, hydrogen sulfide, and MITC. The decomposition process in wood is poorly understood, although MITC, carbonyl sulfide, and carbon disulfide are detectable in wood following treatment. Before Mylone can be used commercially, techniques must be developed to improve the decomposition rate and to assure that a majority of the decomposition products are fungitoxic. Recent studies suggest that pH has a marked effect on Mylone decomposition, with more basic conditions enhancing both MITC production and fungal control. More acidic conditions appear to inhibit decomposition. Douglas-fir heartwood is acidic (3.5) and some modifications must be made to either the chemical or the wood to make pH conditions more conducive to Mylone decomposition. In addition to pH, earlier soil studies suggest that the presence of certain metals, organic compounds, and alcohols can all enhance Mylone decomposition.

While preliminary laboratory studies in small blocks have shown that the degree and rate of Mylone decomposition can be carefully controlled, larger scale tests must be performed to insure that the chemicals will decompose in an effective manner to protect poles against fungal attack.

In exploratory trials, nine posts were treated with 75 of Mylone powder alone (dry) or in combination with 100 ml of either a pH 10 or pH 12 buffer. These poles were stored under cover for 2 years and then sampled by removing increment cores from sites 0.3 m above or below the original treatment site. These cores were extracted in ethyl acetate and analyzed for residual MITC content using the gas chromatograph.

The results showed relatively little difference between the three treatments (Table I-9). In laboratory trials, Mylone produced substantially more MITC when applied in combination with a pH 12 buffer; however, the moisture contents of the poles in the field test were low and the buffer may have had little influence at these lower moisture levels. The results do indicate that Mylone is decomposing at a slow rate and that the volatile decomposition products are diffusing away from the application point in the wood, but it could not be determined if these levels would be sufficient to arrest or inhibit fungal attack. This test was only intended to provide guidance on establishing dosages and treatments for a larger trial.

Table I-9. Residual MITC content at selected heights above or below the treatment site in Douglas-fir pole sections treated with 75 g of Mylone alone or in combination with pH 10 or 12 buffer as measured by gas chromatographic analysis of wood extracts.

Treatment	Dosage (g)	Total MITC (ug/oven dry g of wood)	
		0.3m above	0.3m below
Mylone (dry)	75	3.24	3.98
Mylone (pH 10)	75	5.15	7.52
Mylone (pH 12)	75	9.41	4.71

In the larger study, 75 untreated Douglas-fir posts (25-30 cm in diameter by 1.5 m long) will be obtained from cooperating wood treaters. These sections will be coated on each end with an elastomeric seal to retard chemical loss. A series of three 1.8-cm-diameter by 15-cm-long holes will be drilled downward

at a steep angle near the center of each post. The shavings from each hole will be collected and cultured on nutrient media for the presence of decay fungi.

The posts will then be treated with one of the following chemical/additive combinations:

1. Control (no chemical)
2. Mylone
3. Mylone plus 1% copper sulfate
4. Mylone plus 10% glucose
5. Mylone plus 10% lignin
6. Mylone plus 5% boric acid
7. Mylone plus 50 ml acetone
8. Mylone plus 50 ml methanol
9. Mylone plus 50 ml ethanol
10. Mylone plus 50 ml water
11. Vapam

Each of the dry additives (2-6) will be tested on 5 posts with or without 5 percent powdered pH 12 buffer. Seventy five grams of dry chemical will be applied to each of the three treatment holes per pole. Following treatment, the holes will be plugged with tight fitting wood dowels and the pole sections will be placed on racks out of ground contact at the OSU Peavy Arboretum Test Site.

Six, 12 and 24 months after treatment, the posts will be examined by removing cores from 3 equally spaced sites around the posts 0.3 or 0.6 m above and below the initial treatment site. These cores will be used for chemical and biological assays. In the chemical assays, the outer (0 to 2.5 cm) and inner (12.5 to 15.0 cm) segments of each core will be extracted for 48 hours in ethyl acetate. The ethyl acetate extract will be analyzed for residual MITC content using gas chromatography. Cores from adjacent locations will be evaluated in a closed tube bioassay to determine if volatile fungitoxic compounds are present in the wood. The middle segments from both the chemical and bioassays will be cultured for the presence of decay fungi.



At the conclusion of the test, the specimens will be extensively cored to provide a more complete picture of chemical distribution. In addition to G.C. analysis, cores will be extracted in solvent combinations of various polarities and analyzed by high performance liquid chromatography to determine the levels of various non-volatile decomposition products in the wood.

**2. Ability of fused borate rods to prevent fungal infestation in Douglas-fir poles:** Last year, we reported on the effectiveness of fused borate rods for controlling Antrodia carbonica in Douglas-fir blocks ('88 Ann. Rept., pg. 22-23). The complete details of this work are described elsewhere in this report. The performance of this chemical in the small block test has encouraged the establishment of field tests in Douglas-fir pole sections.

Douglas-fir pole sections (25 to 30 cm in diameter by 1.5 m long) treated with pentachlorophenol in heavy oil were obtained from a local cooperator. A series of steep sloping holes were drilled near the groundline of each pole. Three or five holes were drilled per pole, with one-half of the poles in each group having the holes spaced at 90 or 120 degrees apart. Poles with three holes were treated with 240 g of fused borate rod (sodium octaborate tetrahydrate), while the five hole treatments received 400 g. Twenty ml of water was added to each hole to help release the boron, and the holes were plugged with a tight-fitting wooden dowel. Fifteen poles were treated with each treatment pattern/dosage combination:

- Three holes (240 g) 90 degree spacing
- Three holes (240 g) 120 degree spacing
- Five holes (400 g) 90 degree spacing
- Five holes (400 g) 120 degree spacing
- Control (no treatment)

Following treatment, a series of small diameter holes (1.2 cm diameter by 10 cm long) were drilled at 0.3 m intervals above the groundline, and wooden dowels which had previously been colonized by a test fungus (Postia placenta) were placed in the holes, which were then sealed with rubber stops. At one-year intervals, these dowels will be removed and cultured to determine if boron diffusion affected fungal survival.

One-third of the poles from each treatment group were then set at the OSU Peavy Arboretum, while the remainder were sent to Hilo, Hawaii, and Charlotte, North Carolina, for installation under more severe conditions.

These pole sections will be sampled on an annual basis by removing increment cores from sites above and below the treatment sites. Cores will be removed from three equidistant points around the pole -15, +15, 30, 45, and 60 cm away from the treatment zone. These cores will be examined for the presence of boron using the curium extract/salicylic acid indicator. The cores will then be returned to the laboratory and cultured for the presence of decay fungi, which will be used as the measure of treatment effectiveness.

If high degrees of boron diffusion are noted, additional cores will be removed for chemical analysis.

**3. Treatment of New York State Electric and Gas Douglas-fir poles with fused borate rods:** While fumigants have provided excellent protection against internal decay fungi in Douglas-fir poles, their high toxicity and liquid nature have limited application to the groundline zone where the risk of accidental spills is reduced. There is increasing evidence that a large percentage of poles experience some decay above the groundline, particularly in areas where field drilling is necessary to attach pole hardware. Ideally, this damage would be protected by application of a preservative spray shortly after the damage

occurred, but this is rarely the case. There are presently no commonly accepted methods for remedially treating decay in above ground portions of utility poles.

One method for effecting such control is application of fused borate rods. These glass-like rods contain 100 percent sodium octaborate tetrahydrate and are applied to sites above the damaged zone. This chemical readily diffuses with moisture through the wood, eliminating established decay fungi and preventing reinvasion. Borate rods are increasingly used in Europe to protect utility poles, railroad ties and building timbers; however, they have seen little application in the United States. Borate rods may also be useful for controlling internal decay at the groundline in poles located in environmentally sensitive areas where application of conventional wood fumigants may be restricted. Before extensive use of borate rods occurs, it is important to determine precise dosages and retreatment schedules for this formulation.

Twenty-four poles which were previously sampled for the presence of decay fungi by removing increment cores at the groundline and culturing these cores, will be used in this test.

Three 1.8 cm diameter by 25 cm long holes will be drilled at equidistant sites around the groundline moving up 15 cm and around 120 degrees for each hole in the pole. Shavings from these holes will be collected for later culturing to more precisely define the degree of fungal colonization prior to treatment.

Each hole will receive one or two fused borate rods along with 0 or 50 ml of water to accelerate breakdown of the rod. Each treatment combination will be replicated 6 times. The holes will then be plugged with tight fitting dowels. The treatment groups will be as follows:

- 3 rods per pole, no water
- 3 rods per pole, 150 ml water

- 6 rods per pole, no water
- 6 rods per pole, 150 ml water

The poles will be sampled 1, 2, 3, and 5 years after treatment by removing increment cores from sites above and below the treatment sites (-15, +15, and +45 cm from the groundline). The inner and outer 2.5 cm segments of each core will be retained and sprayed with a cumin/salicylic acid indicator for the presence of boron. The inner segment will be cultured on nutrient media for the presence of decay fungi to determine the effectiveness of the treatment.

#### 4. Evaluation of MITC-fume in Douglas-fir and southern yellow pine pole:

Methylisothiocyanate was recently registered with the Environmental Protection Agency for application to wood poles. The registered formulation is encapsulated in glass tubes (~30 g per tube) which are sealed with a combination of a plastic plug and an aluminum cap. The formulation is activated by removing this cap with pharmaceutical pliers and inserting the tubes, open end down, into the treatment hole.

While MITC has provided excellent protection to Douglas-fir poles in field tests, previous tests evaluated formulations which were in intimate contact with the wood surrounding the treatment hole. The MITC-FUME formulation depends upon migration from a single point source at the end of the tube. The effects of this reduced area for volatilization on chemical distribution and fungal control are unknown. For this reason, the following laboratory and field trials were established.

Laboratory: Initial laboratory trials were established to evaluate the volatilization rate of MITC from the opened tubes. The tubes were punched open at the top and stored under a fume hood. At selected intervals, the tubes were weighed to determine weight lost. The fume hood rapidly draws vapors across the

tubes and should optimize MITC volatilization. These initial trials indicated that it would take approximately 800 days for all of the chemical to volatilize from the tubes. This time period differed from previous trials using gelatin encapsulated MITC; however, the gelatin permitted diffusion all along the capsule, while the glass restricted movement to the small hole at the end of the tube.

In the second trial, the safety of glass-encapsulated MITC was examined by placing an open tube of MITC-FUME in a 4 L desiccator and withdrawing air samples from the chamber at regular intervals over a 24-hour period. These samples were examined for MITC content by gas chromatography. An additional set of tubes was crushed prior to being placed in the desiccator to simulate dropping of a tube during application. The latter tubes were sampled over a 30-minute period.

MITC movement through the hole at the top of the tube was relatively slow, with chemical levels slowly rising to nearly 15 ppm after 24 hours (Figure I-11). This low chemical level agrees with the initial release studies and suggests that the small tube opening severely restricts chemical movement. This slow release rate may have negative consequences when rapid control of fungi is necessary, but it minimizes chemical exposure during application.

As expected, shattering the tubes resulted in more rapid MITC release, with levels rising to nearly 44 ppm within 30 minutes (Figure I-12). However, chemical levels were relatively low for the first 5 to 10 minutes of sampling. This test was conducted to evaluate the risk to the applicator in the event a tube broke. Ideally, the applicator would rapidly evacuate the area following tube breakage, but our tests indicate that the rate of release from severely cracked tubes provides a margin of safety for clean-up and containment of the

chemical. These tests were performed in closed chambers with a limited air volume. In field applications, a much higher volume of air is present for dilution and currents can help to dissipate any volatiles released from the tubes. Thus, field application of the tubes should pose minimal danger of chemical inhalation.

Field Trials: While understanding MITC release rate from the tubes provides some useful information on the safety of application, it does little to help understand the movement of this chemical in wood. To better evaluate this parameter, 75-cm-long x 30-cm-diameter Douglas-fir pole sections were obtained from a local cooperator. One-half of the sections were cut from freshly peeled poles, with moisture contents exceeding 30 percent, while the remainder were partially seasoned (<25% moisture content). The moisture content of each section was determined by removing an increment core, which was weighed, oven dried and reweighed.

Each section was end coated to retard changes in moisture content, and a 2.1 cm diameter hole was drilled at a 45 degree angle 25 cm into the wood. One glass vial of MITC-FUME was inserted into the hole, and each hole was plugged with a tight fitting rubber stopper. Sections were incubated outdoors at ambient temperature, in a 32°C/90% relative humidity room, and in a 5°C cold room. The vials were removed from the pole sections at selected time points and weighed to determine the rate of chemical release from the tubes. A total of 3 poles were tested under each temperature/moisture regime.

The results indicate that release rates from the poles were, once again, relatively slow. Initially, movement was more rapid from tubes in wood at higher moisture content--under hot, wet conditions--but these differences eventually disappeared and the sections at each temperature were combined for further

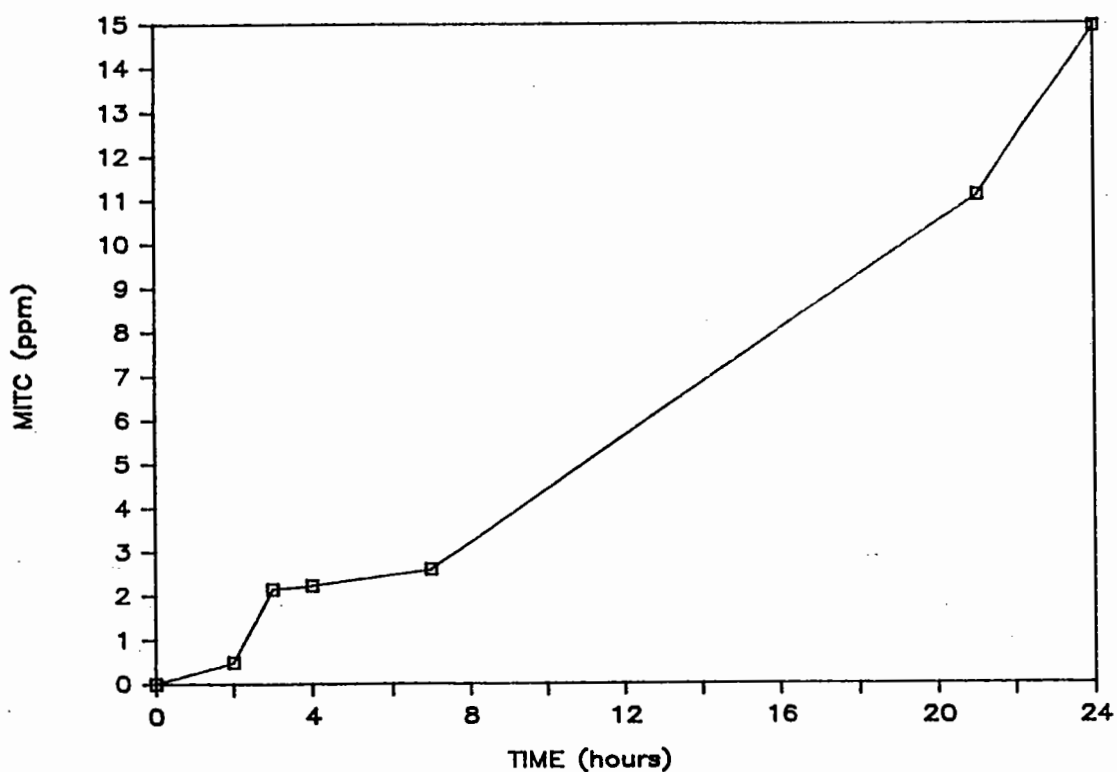


Figure I-11. MITC levels in a 4 L glass desiccator containing 30 g of MITC in a borosilicate tube opened at one end as measured by gas chromatography of air samples over a 24-hour period.

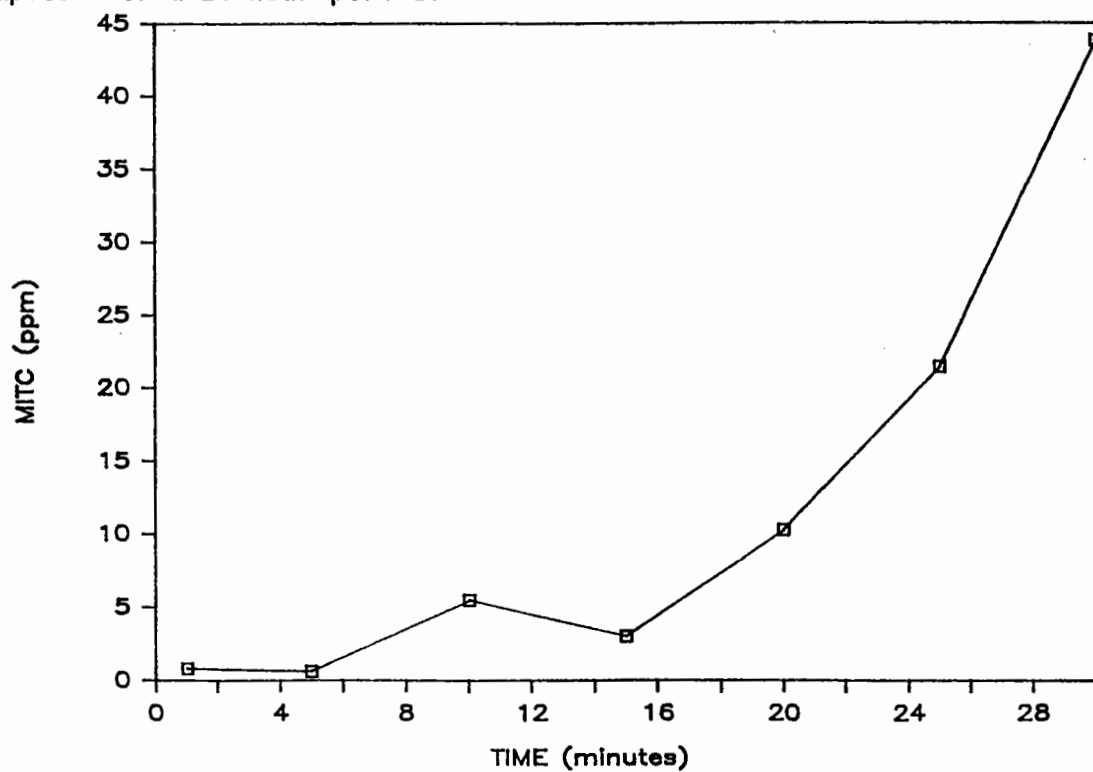


Figure I-12. MITC levels in a 4 L glass desiccator containing 30 g of MITC in a borosilicate tube opened at one end and shattered, as measured by gas chromatography of air samples removed over a 30-minute period.

analysis (Table I-10). It is likely that the sections equilibrated to ambient moisture levels at the selected regimes, negating the initial moisture differences. Previous reports have shown that MITC moves more rapidly through moist wood, where it is ideally poised to control the fungi which are more active at these same moisture levels. Conversely, higher levels of MITC are sorbed to dry wood, provided a reservoir for long-term fungal control.

Long-term examination of the pole sections indicated that virtually all of the MITC was released from the tubes in sections incubated at 32°C, while virtually no chemical was released from sections incubated at 5°C (Figure I-13). Release rates from the sections exposed at ambient temperature were initially slow over the winter, but increased dramatically over the warmer summer months. At present, approximately one third of the chemical has been released from tubes under ambient conditions. These results indicate that release rate may vary substantially with environmental conditions. While similar changes in chemical release rate with temperature probably occur with the other fumigants, the small area through which the chemical must diffuse in the MITC-FUME tubes appears to magnify these effects. This variation may affect both the rate of fungal control in standing poles as well as the ultimate duration of treatment. At present, the results indicate that complete MITC release from tubes in poles at ambient temperature may take up to 2 years, while release in the poles stored at 5°C will take several years before release is complete. Although few poles are continuously exposed at such low temperatures, many poles in northern climates are exposed to these temperatures for 6 months or more each year. In these cases, care must be taken to insure that linemen removing poles treated with MITC-FUME examine the tubes and remove them from the pole prior to disposing of the wood if there is residual chemical in the tube.



Table I-10. Release rate of MITC from MITC-FUME tubes placed in Douglas-fir heartwood pole sections which were then incubated at ambient temperature, 5°C, or 32°C. Release rate was determined by weight loss from the tubes.

Test Conditions	MITC loss (g) at 35 days	
	Dry Wood	Wet Wood
Ambient	0.91	0.37
5°C	1.70	0.96
32°C	7.39	8.64

<sup>a</sup> Dry wood had a moisture content (MC) below 25 percent, while wet wood had an MC greater than 30 percent. Each tube of MITC-FUME initially contained 30 g of active ingredient.

In a second test of chemical release from the MITC-FUME tubes, two Douglas-fir pole sections were each treated with one tube of MITC-FUME. But one treatment hole also received 10 ml of water to evaluate the effects of additional moisture on release rate. The tubes were removed at regular intervals and weighed to determine the rate of chemical release. These release rates were compared with that of a single MITC-FUME tube exposed under a fume hood.

MITC release was initially stimulated by the addition of moisture, releasing three times the amount of chemical released from the tube in the dry treatment hole (Table I-11). After 20 days, however, the rate of release declined to a level which was similar to that found in the dry pole. This trend suggests that addition of water may be useful for accelerating MITC release to control existing fungal attack, but the effect on long-term performance will be minimal.

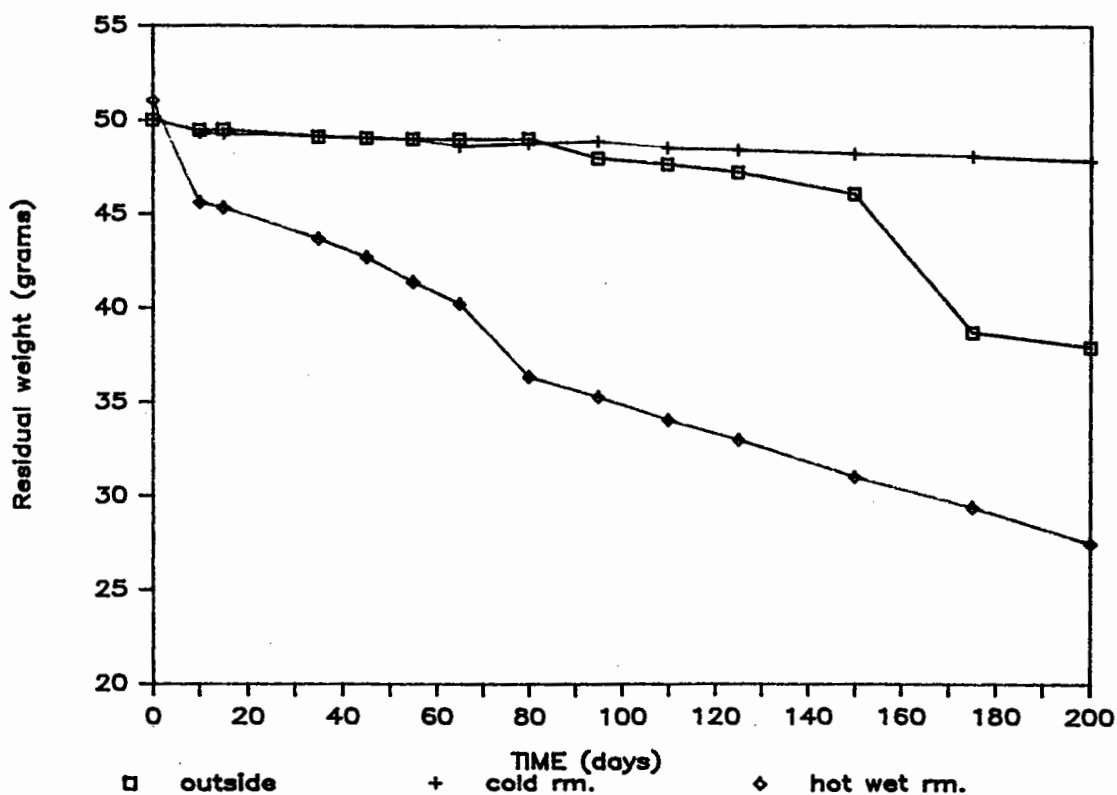


Figure I-13. Rate of release of MITC from Douglas-fir pole sections treated with 30 g of MITC-FUME and incubated outdoors, at 32°C or at 5°C for 200 days.

Table I-11. Release rate of MITC from MITC-FUME tubes exposed to the atmosphere or placed into Douglas-fir poles with or without 10 ml of water.

Elapsed time (days)	MITC Release Rate (mg/day)		
	Open Tube	Dry Wood	Wet Wood
0 to 10	63	62	119
11 to 20	62	197	99
21 to 30	57	52	93
31 to 50	25	49	51
51 to 80	32	44	43
81 to 100	36	3	12

While the rates of release and the effects of various environmental parameters on the performance of MITC-FUME are all important, it is essential that this formulation perform in a manner similar to the currently registered fumigants in the two important pole species, Douglas-fir and southern pine.

Pole sections of each species (25 to 30 cm diameter by 3.6 m long) were treated with chromated copper arsenate (for southern pine) or ammoniacal copper arsenate (for the Douglas-fir) to a nominal retention of 4.0 kg/m<sup>3</sup>. This treatment was designed to provide a barrier to external fungal attack but not interfere with MITC detection. The poles were set to a depth of 0.9 m in the Oregon State University Peavy Arboretum test site located near Corvallis, Oregon. A series of 2.3-cm-diameter by 30-cm-long holes were then drilled in each pole in a spiral pattern beginning at the groundline and moving upward at 120 degree by 15 cm intervals. Individual tubes of MITC-FUME were opened and inserted, open end down, in the treatment holes which were then sealed with tight fitting wood dowels. Poles received 60, 120, 180, or 240 g of MITC or 500 ml of Wood-FUME (Vapam). Each dosage was applied to 6 poles per wood species.

The treated poles were then painted from the groundline to 1.2 m above the groundline with an elastomeric film to simulate an oil-treated shell which retards fumigant loss.

Fumigant performance in the poles was assessed using a combination of bioassays and chemical tests. In the bioassays, a series of three 0.6 cm diameter holes were drilled to a depth of 15 cm at 120 degree intervals around the pole 15 cm below the groundline, as well as 30, 90 and 150 cm above the highest treatment hole. A wooden dowel infested with a test fungus, Postia placenta, was placed in each hole. These dowels were then removed at 6-month intervals and cultured on a nutrient media to determine if the fungus survived

the exposure. Death of the test fungus would suggest that the chemical was moving through the wood at concentrations required for controlling established decay fungi.

A series of increment cores were removed from sites adjacent to the bioassay locations. These cores were divided into 4 equal segments. The outer and inner sections were individually placed into 5 ml of ethyl acetate and extracted for a minimum of 48 hours at room temperature. A sample of this extract was then analyzed for residual MITC content by gas chromatography as previously described. The two middle cores were used in a closed tube bioassay with P. placenta as the test fungus to detect volatile fungitoxic products.

The six-month samples have been analyzed, while the one-year samples are currently being collected. Bioassays of dowels removed 6 months after treatment indicated that there were some difficulties with the bioassay procedures. Initial plans called for watering the poles daily to maintain a humid environment for fungal growth. Unfortunately, watering was not possible and the dowels were exposed to an extremely hot dry period. As a result, survival was low in dowels from both the untreated and treated poles. There were, however, some trends in fungal survival in the wood species. In general, fungal survival was lower 0.3 m above the treatment site in the Douglas-fir poles, while survival in the southern pine poles was more variable (Table I-12). Previous studies indicate that fumigant movement is considerably faster in southern pine and the reasons for delayed fungal control in the test poles remain unclear. These tests were primarily designed to rapidly assess chemical movement without performing chemical analyses. While the bioassays may provide a long-term guide to fumigant performance, the accuracy of short-term results should be carefully judged.

Chemical analysis of extract from cores removed from the treated poles again revealed that MITC levels were higher in Douglas-fir poles (Table I-13). There was little evidence of MITC movement beyond the first sampling site (0.3 m). As expected, there was a gradual increase in MITC content at the first sampling site with increased dosage, although there appeared to be little difference between the 180 and 240 g treatments. Chemical levels were generally highest in the inner core segment, reflecting a treatment pattern which directs the chemical towards the center of the pole. MITC levels in the Wood-Fume treatment were generally lower than the MITC treatments, reflecting the low efficiency of chemical decomposition of the dithiocarbamate salt to produce MITC. These low rates of chemical conversion generally support the use of lower dosages of pure MITC in place of Wood-Fume, although further sampling will be required to more precisely define appropriate MITC-FUME dosages.

The slow rate of MITC movement in the southern pine poles is perplexing, since previous reports show that fumigant movement is more rapid through this species. While it is possible that the chemical has already diffused from the wood, this is highly unlikely since wood/chemical interactions with MITC are quite strong. These test results are somewhat preliminary, and further evaluations of chemical movement and fungal survival will be necessary before definite conclusions can be drawn on the efficacy of MITC-FUME at the various treatment levels.

#### **D. EVALUATE BASIC PROPERTIES OF FUMIGANTS IN WOOD**

1. Effects of voids on fumigant movement and performance: Many poles in service are treated with fumigants despite the presence of large voids near the groundline. The effects of these voids on fumigant movement and effectiveness

Table I-12. Survival of *Postia placenta* in hem-fir dowels exposed for 6 months in Douglas-fir and southern pine poles treated with MITC-FUME or Wood-Fume as determined by culturing the dowels following exposure.

Chemical Treatment	Dosage (g)	<i>P. placenta</i> survival (%) <sup>a</sup>		
		1.0 m	3.0 m	5.0 m
SOUTHERN PINE				
MITC-FUME	60	27 (100)	33 ( 75)	50 (100)
	120	27 (100)	33 ( 75)	44 ( 88)
	180	5 ( 18)	33 ( 75)	62 (124)
	240	16 ( 59)	39 ( 88)	83 (166)
Wood-FUME	500	13 ( 48)	67 (152)	67 (134)
Control	-	27	44	50
DOUGLAS-FIR				
MITC-FUME	60	5 ( 15)	5 ( 13)	22 ( 56)
	120	5 ( 15)	14 ( 36)	38 ( 97)
	180	0 ( 0)	5 ( 13)	56 (143)
	180 <sup>b</sup>	8 ( 24)	8 ( 20)	8 ( 20)
	240	0 ( 0)	11 ( 28)	50 (128)
Wood-FUME	500	0 ( 0)	13 ( 33)	20 ( 51)
Control	-	33	39	39

<sup>a</sup> Values represent percent survival of 18 dowels at each location above the uppermost treatment hole. Values in parentheses represent percentage of control survival value for that wood species at the sampling height.

<sup>b</sup> The treatment holes in this group received 250 ml of water equally distributed among the holes.

are unclear; however, decay voids are invariably associated with checks which lead to the pole exterior and could increase the loss of fumigant from the wood. In 1987, a series of tests were established to compare fumigant movement in poles with and without artificial voids. Voids were produced at the center of 2.4 m

Table I-13. Residual MITC content in increment cores removed from selected sites above the treatment holes of Douglas-fir or southern pine poles treated with varying dosages of MITC-FUME or Wood-Fume as measured by gas chromatographic analysis of ethyl acetate extracts of the wood.

Chemical Treatment	Dosage (g)	MITC Content (ug/oven dried g of wood)					
		0.3 m		0.9 m		1.5 m	
		outer	inner	outer	inner	outer	inner
SOUTHERN PINE							
MITC-FUME	60	0.0	0.8	0.0	0.0	0.0	0.0
	120	1.1	14.1	0.0	0.0	0.0	0.0
	180	2.7	11.8	0.0	0.0	0.0	0.0
	240	1.9	6.4	0.0	0.0	0.0	0.0
Wood-FUME	500	0.0	2.1	0.0	0.0	0.0	0.0
DOUGLAS-FIR							
MITC-FUME	60	5.3	131.7	0.0	1.6	0.0	0.0
	120	84.3	296.2	1.5	114.8	0.0	0.0
	180	132.1	534.1	0.0	4.0	0.0	0.0
	180 <sup>b</sup>	2.5	303.6	0.0	0.0	0.0	0.0
	240	132.0	624.1	0.0	2.1	0.0	0.0
Wood-FUME	500	4.1	352.2	0.0	2.0	0.0	0.0

<sup>a</sup> Values represent the mean of 18 samples per site above the upper treatment hole. Outer values correspond to the outer 2.5 cm segment of increment cores removed from the selected sites, while the inner zone corresponds to the inner 12.5 to 15.0 cm zone on the same core.

<sup>b</sup> These poles received 250 ml of water equally distributed among the treatment holes.

long pole sections prior to treatment with chloropicrin or Vapam at locations above the void. These poles were then placed in an outdoor exposure site and monitored annually by removing increment cores for chemical analysis and closed tube bioassays. Last year, ('88 Ann. Rept., pg. 53) closed tube bioassays indicated that fungitoxic levels of Vapam or chloropicrin were present in all

pole sections regardless of the presence of voids. Closed tube bioassays of cores removed two years after treatment indicate that chloropicrin continues to be well distributed above and below the void, although chemical distribution appears to be less uniform 0.9 m above the treatment sites in poles with and without voids. These results suggest that the void has had little influence on chloropicrin movement. Rather than act as a sink for chemical which then exited the wood, the void appears to be a passive space for fumigant movement through the pole. Since air exchange within a void would be expected to be quite small, it is possible that lack of air exchange minimizes the potential for loss of fumigant outside the pole.

The Vapam treated poles exhibited little evidence of residual fungitoxicity. This lack of effect is not surprising since Vapam appears to be a relatively short-lived treatment with less residual time in the wood.

**2. The methylcarbamodithioate anion from Vapam and its derivatives:** As we examine Vapam treated poles, we are continually impressed with the long-term performance of the chemical in the apparent absence of any volatile fungitoxic products within two years of treatment. This effect has led to the theory that deposition of non-volatile Vapam decomposition products may provide long-term protection against fungal invasion. To better evaluate these effects, a series of studies were initiated to identify Vapam decomposition products in wood.

There are 14 theoretical breakdown products from Vapam. This report describes the chemistry of the anion of sodium methyldithiocarbamate. The methylcarbamodithioate anion (Figure I-15, #1), generated by the base-promoted reaction of carbon disulfide and methylamine, is a simple species with a diverse chemistry. Depending on conditions, air contact or other oxidation of anion (1) gives methylisothiocyanate (2), diamide (3), dithione (5), dimethylthiourea (7),



Table I-14. Residual fungitoxic protection in wood removed from Douglas-fir pole sections with and without voids following treatment with chloropicrin or Vapam as measured using a closed tube bioassay with Postia placenta as the test fungus.

Chemical Treatment	Dosage (ml)	Void (+/-)	Avg. growth (% of control) <sup>a</sup>							
			- 0.9 m		- 0.3 m		0.3 m		0.9 m	
			a	b	a	b	a	b	a	b
Vapam	80	+	77	83	77	68	71	74	74	71
	160	+	97	97	97	77	88	86	94	91
Vapam	80	-	74	88	54	77	68	71	65	88
	160	-	77	80	51	48	74	51	100	77
Chloropicrin	80	+	68	57	0	0	20	33	82	77
	160	+	34	77	25	0	25	0	88	34
Chloropicrin	80	-	57	0	0	0	28	0	82	20
	160	-	74	45	0	0	28	22	68	51
Controls	-	-	-	-	100	99	97	99	-	-
Control tubes (no wood) X= 35 mm										

<sup>a</sup> Values represent the mean of 9 tubes per treatment as a percentage of fungal growth in tubes containing no wood. Low numbers reflect fungal inhibition.

<sup>b</sup> a = outer zone (0 to 2.5 cm) of increment cores, while inner represents the 12.5 to 15.0 cm section of the same core.

sulfur, thiosulfate, and sulfate. The unstable thioacid of anion (1) reverts to carbon disulfide and methylamine, but acidifying a mixture of anion (1) and compound (2) gives diamide (6), also unstable (Figure I-15). This report presents additional chemistry of the anion (1) and its derivatives.

HPLC analysis was performed on a  $\gamma$  RP-1 pH-stable column (5- $\mu$ m particles, 200 mm x 4.6 mm; E.S. Industries); a Rheodyne 7125 injector (20  $\mu$ l) and the following Shimadzu components were used: LC 6A pumps, SPD 6A UV detector (250 nm), SCL 6A controller, and CR 3A data processor. Mobile phases (and compounds determined) for HPLC analyses, unless otherwise specified, were 100% MeOH (sulfur); 16% MeCN, 36% MeOH, 48% water (3,4,5); 100% water (7). A flow rate of 1 ml/min gave retention times of 2-10 min. Spectral analyses were conducted with Shimadzu UV-265 FW UV-visible spectrophotometer and a Nicolet 5DXB FT-IR spectrophotometer. X-ray diffraction patterns were obtained with a Scintag PAD-V x-ray diffractometer (Cu source). Melting points are uncorrected.

The sodium salt of 1, obtained as a 33% solution (Vapam<sup>R</sup>, (1a)), and authentic samples of compounds (4) and (5) were used as received from Stauffer Chemical Co. (Richmond, CA).

N,N<sup>1</sup>-dimethylthioperoxy dicarbonic diamide (3) from anion (1) and acid:

In a typical experiment, anion 1a (5 ml, 15 mmol), water (5 ml) and MeOH (10 ml) were treated with 11 N H<sub>3</sub>PO<sub>4</sub> (5 ml) at room temperature. Within a few seconds the mixture became milky; a granular solid gradually separated. Filtration after 1 h gave colorless diamide 3 (0.49 g, 2.3 mmol, 31%, mp 96-98°C dec., lit 103-104°). IR (KBr pellet) of this compound was identical to IR of authentic diamide (3) prepared from (1a) and iodine. The melt comprised 2 phases, compound (7) and sulfur (HPLC). During cooling, and sometimes without cooling, the melt partially crystallized, remelting at 110-115°C. Yields of diamide (3) as conditions varied were 31% at 5°C, 30% at 50°C, 31% with air sparging, 28% with nitrogen sparging, 28% in a nitrogen-flushed closed 60-ml container. As the volume of 11 N H<sub>3</sub>PO<sub>4</sub> changed, the yields (ml acid, yield) were 3 ml, 30%; 2.5 ml, 25%; 2 ml, 20%; 1.5 ml, 14%; 1 ml, 7%; 0.5 ml, trace. When the volume of water in the reaction mixture was changed to 300 ml, the yield was 18%. Sulfuric and acetic acids were as effective as H<sub>3</sub>PO<sub>4</sub> in converting 1 to 3, but CO<sub>2</sub> caused no reaction.

Solid diamide (3) was stable, but its solutions were somewhat unstable and very sensitive to base. This compound could be recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-HOAc (minimum heating), but it decomposed rapidly in methanol or ethanol if not acidified. UV (λ max) ε: cyclohexane (249 nm) 21600; 95% EtOH acidified with HOAc or H<sub>3</sub>PO<sub>4</sub> (244 nm) 25900; H<sub>2</sub>O acidified with H<sub>3</sub>PO<sub>4</sub> (237 nm) (insufficiently soluble to measure ε); x-ray diffraction (2θ, decreasing intensity): 12.83; 26.02; 24.46; 13.29; 27.63.

Thermal (base-catalyzed) equilibration of 4-methyl-5-(methylimino)-1,2,4,-dithiazolidine-3-thione (4) and 2,4-dimethyl-1,2,4-thiadiazolidine-3,5-dithione (5): Separate solutions of compounds 4 and 5 in 2-propanol (3 ml aliquots, ca. 50 mg/l) were either untreated, treated with 3 ml ammonium hydroxide vapor, or treated with 0.3 ml acetic acid, and left at room temperature. Solutions were analyzed (HPLC) for compounds 4 and 5 after 2 days and then after longer intervals.

Photointerconversion of 4 and 5: Dilute solutions of compounds (4) and (5) (ca. 40 mg/l in 15% MeOH, 85% water, acidified with  $H_3PO_4$ ), 6 mm deep, were placed in separate open vials 6 cm below a Mineralight<sup>R</sup> mercury vapor lamp (model UVG-11, 254 nm). Samples were analyzed for compounds (5) and (4) at the intervals shown on Figure I-16 (HPLC eluent was 30% MeCN, 70% water).

Anion 10: When exposed to air, dilute aqueous anion (1) ( $10^{-4}M$ ) very slowly gave an unidentified product, anion (10) ( $\lambda$  max 320).  $Cu II$  ( $10^{-6} M$ ) greatly accelerated the transformation ( $t_{\frac{1}{2}}$  about 30 min). After 4 days, a solution of anion (10) contained at least 90% of the initial anion (1) to compound (11) ( $\lambda$  max 275 nm,  $\epsilon = 0.78$  of the  $\epsilon$  of anion (10)). Immediate basification of compound (11) regenerated anion (10) nearly quantitatively; basification after 1 hr. regenerated about 75% anion (10) (UV).

Conversion of anion (1) to diamide (3), an oxidative coupling of sulfur moieties, has been effected by iodine, thionyl chloride and sulfuryl chloride. It was surprising to find that acidifying anion (1) gave diamide (3) (30% yield) without added oxidant. The yield was not significantly changed when the reaction mixture was sparged with nitrogen or air or when the reaction was conducted in a closed, nitrogen-flushed container. Oxygen is thus not the likely oxidant,

but the nature of the reaction was not established. Because of the simplicity of the method and the high purity of the product, this reaction provides an excellent method for preparing diamide (3), despite the modest yield.

The base-catalyzed isomerization of methyliminothione (4) to dithione (5) entails a rearrangement in which a sulfur-sulfur bond is broken and a sulfur-nitrogen bond is formed. The previous publication did not report the presence of compound (4) after treatment with base. Reaction of compound (5) with HBr reverses the rearrangement, since neutralization of the of the HBr salt gives compound (4). In the present study, compounds (5) and (4) both underwent base-catalyzed rearrangement and isomerization. After 2 days the ratios of compounds (4) and (5) in untreated (2-propanol) solutions had changed only slightly, but ammonia-treated solutions contained 79% compound (5) and 21% compound (4) (HPLC). After 16 days the ratio of the products in untreated solutions was also 79% compound (5) to 21% compound (4), but no isomerization of 4 and 5 was detectable in solutions treated with acetic acid.

Compounds (5) and (4) were also found to interconvert photochemically. When acidified solutions of either isomer were irradiated at 254 nm, a photo-stationary mixture of compound (4) (84%) and compound (5) (16%) was obtained (Fig. I-16). Photoisomerization was accompanied by gradual loss of both isomers. This loss was more rapid in the solution that was initially compound (4), suggesting that compound (4) is more easily photodegraded.

A chance observation revealed that dilute anion (1) underwent a copper-catalyzed conversion to anion (10) ( $\lambda_{\max}$  275), was not established. Copper catalysis was also observed in conversion of methylisothiocyanate to anion (1) and dithione (5).

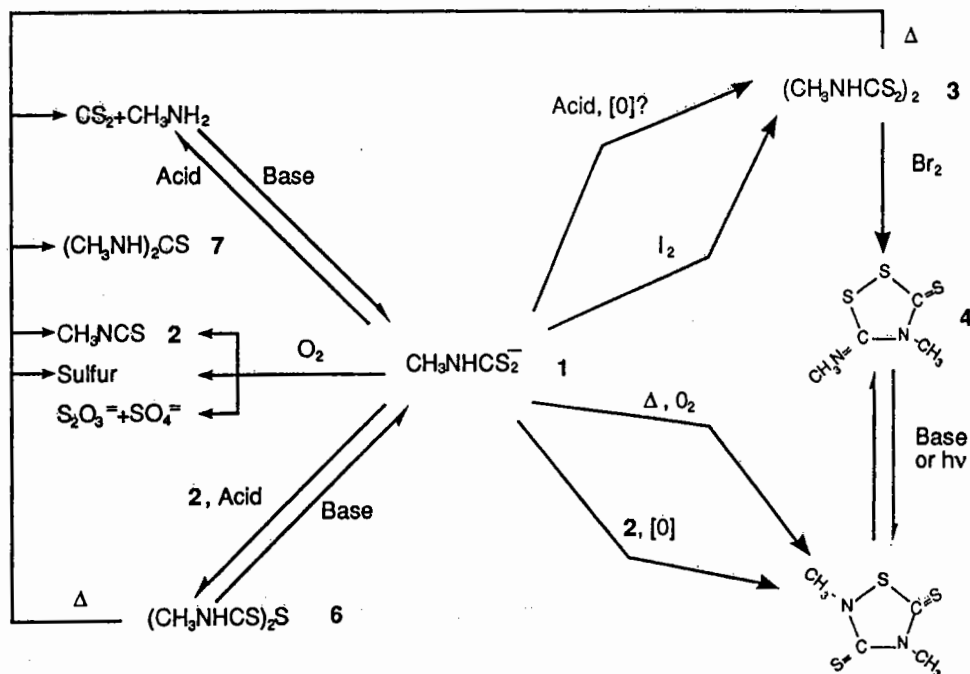


Figure I-15. Summary of methylcarbamodithioate chemistry.

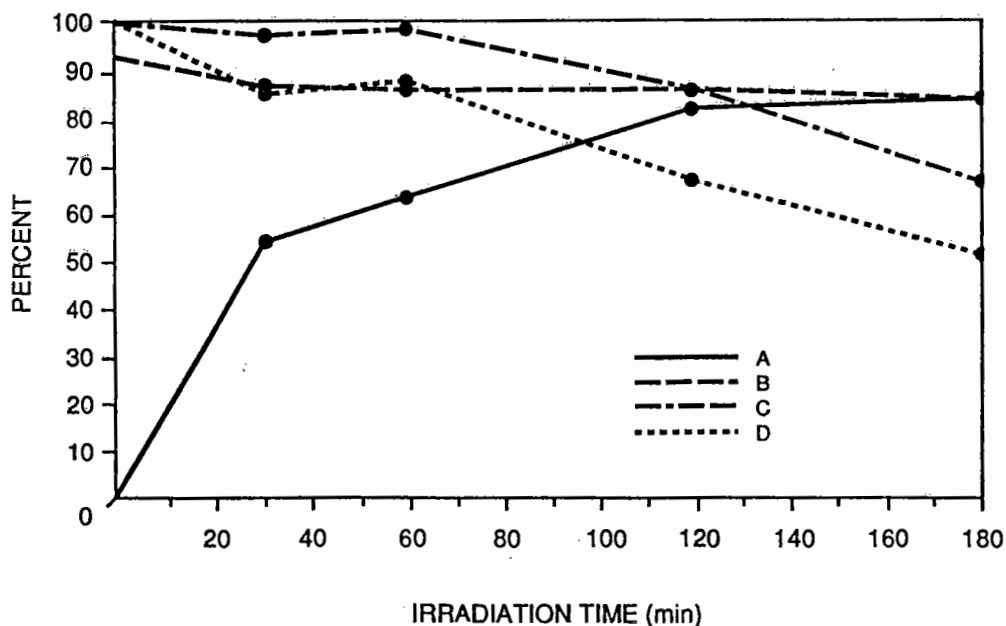


Figure I-16. (A) Percent of compound (4) in irradiated compound (5), relative to total amount of compounds (4) + (5). (B) Percent of compound (4) in irradiated compound (4), relative to total amount of compounds (4) + (5). (C) Total of compounds (4) + (5) in irradiated compound (5), relative to initial amount of compound (4) + compound (5). (D) Total of compounds (4) + (5) in irradiated compound (4), relative to initial amounts of compounds (4) + (5). (See Figure I-15 for key to chemicals.)

3. Emission of MITC, carbonyl sulfide, and carbon disulfide from Vapam or MITC treated Douglas-fir heartwood: Fumigants continue to be applied to building timbers through which they could diffuse into the inhabited interior. While the tendency of fumigants to sorb to wood limits the prospects for high levels of emission, we established experiments to determine the long-term emission rate of volatiles from Vapam or MITC treated wood.

The results of these tests have been described in detail previously ('88 Ann. Rept., pg. 45-52), but briefly Douglas-fir (9 by 14 by 20 cm long) heartwood blocks were treated with 40 ml of Vapam or 20 ml of MITC. The blocks were stored in sealed chambers and a constant airflow was passed over the wood surface. At selected time points, air samples were withdrawn and injected into the gas chromatograph. Peaks for MITC, carbonyl sulfide, and carbon disulfide were identified and quantified by comparison with prepared standards.

After almost 1,000 days, emission rates of all three compounds have declined to the level of detection (Figure I-16-18). At an earlier point in the study, emission levels of both CS<sub>2</sub> and COS exceeded OSHA safety levels, but those test were performed under extremely limited aeration conditions which maximized accumulation of volatile compounds in the chambers. Under normal conditions, the small quantity of fumigated wood and the circulation of air through a building would minimize chemical levels. One area of concern; however, would be treatment of many beams outside a building which was tightly weatherized. Emission levels of all three components from wood treated with either fumigant have now declined to the level of detection, suggesting that the wood will continue to release small quantities of chemical which earlier health studies suggest will pose no major health hazard.

In general, emissions from MITC-treated wood remained higher than those from Vapam treated wood for longer periods of time, but even these levels have declined. At one point, emission levels from the MITC treated blocks were 20 times those found in the Vapam treated samples. These differences would suggest that Vapam should be applied where there is concern for some potential emission into a building; however, caution must still be exercised to insure that the treatment is applied as far from the building as possible (i.e., at the end of the beam).

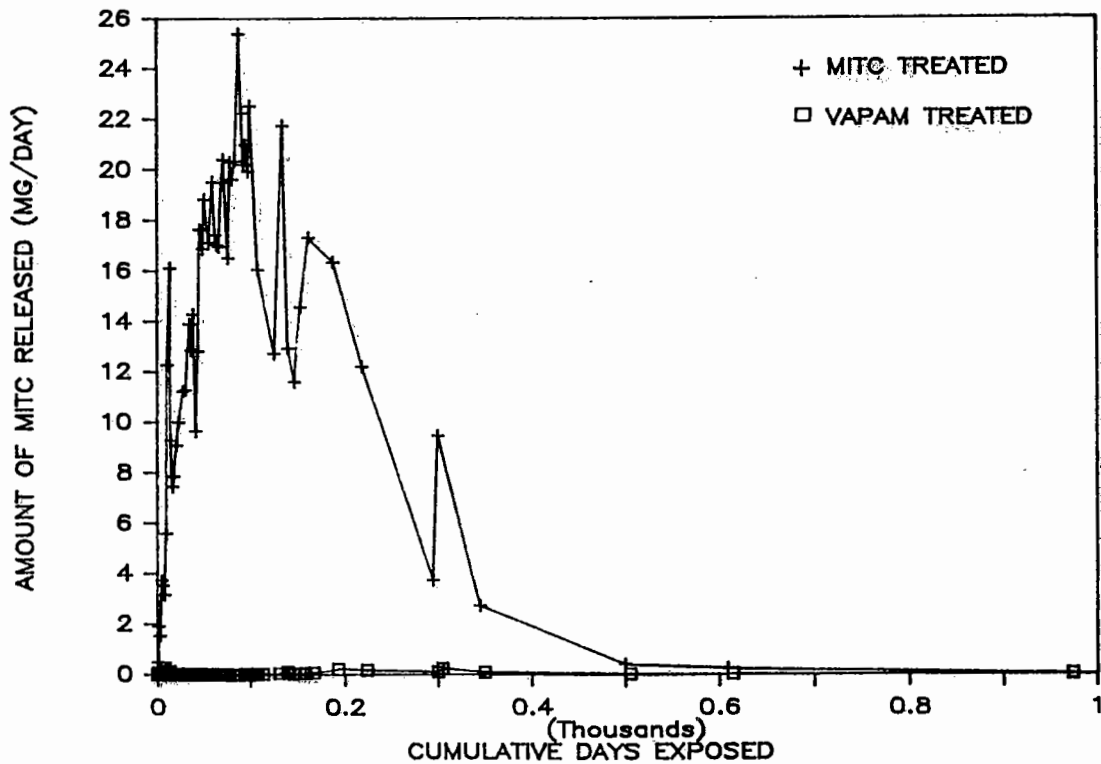


Figure I-16. MITC content of air samples removed from tanks containing Douglas-fir heartwood blocks which were treated with 40 ml of Vapam or 20 ml of MITC, as measured by gas chromatographic analysis.

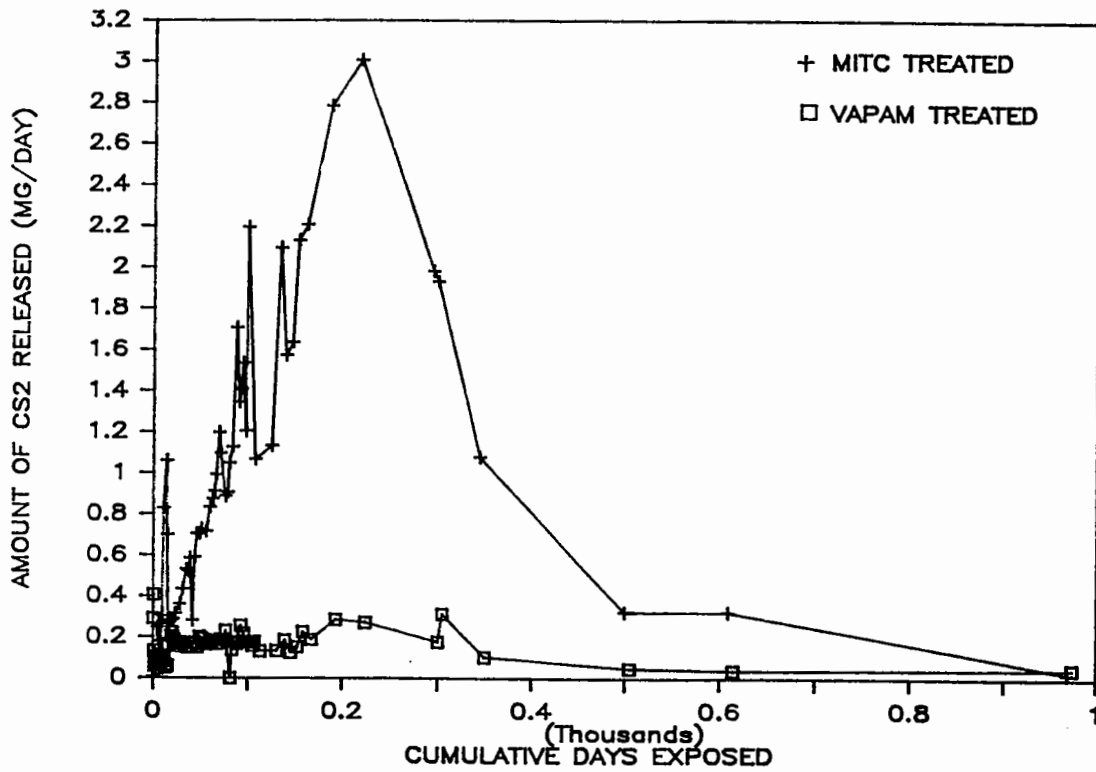


Figure I-17. CS<sub>2</sub> content of air-samples removed from tanks containing Douglas-fir heartwood blocks which were treated with 40 ml of Vapam or 20 ml of MITC, as measured by gas chromatographic analysis.

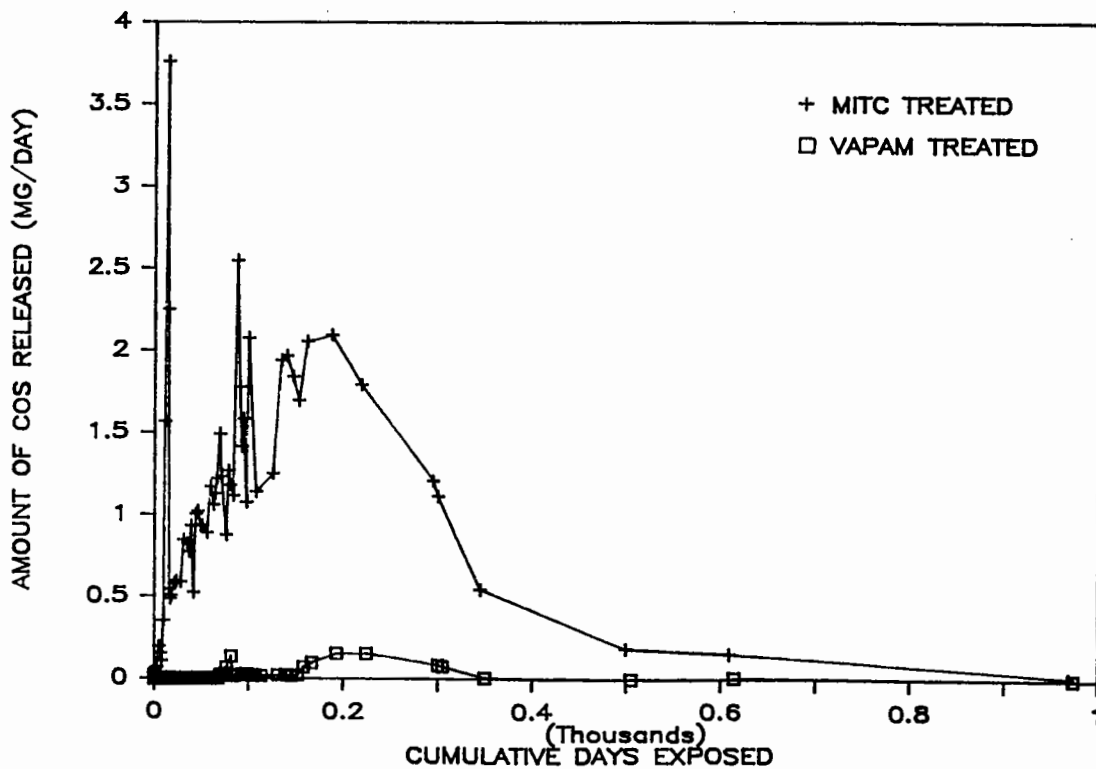


Figure I-18. COS content of air-samples removed from tanks containing Douglas-fir heartwood blocks which were treated with 40 ml of Vapam or 20 ml of MITC, as measured by gas chromatographic analysis.



## OBJECTIVE II

### IDENTIFY ENVIRONMENTALLY ACCEPTABLE CHEMICALS FOR PROTECTING WESTERN REDCEDAR SAPWOOD AND FIELD-DRILLED BOLT HOLES

#### A. FIELD EVALUATION OF CHEMICALS ON CEDAR TEST POLES

While western redcedar has a naturally durable heartwood, the sapwood of this species has little durability. For many years, utilities purchased butt-treated western redcedar poles. As the sapwood decayed above ground, it posed a major hazard to linemen whose spikes cut out as they climbed the pole to perform routine maintenance. Until recently, the problem of sapwood decay of western redcedar was controlled by spray application of pentachlorophenol in diesel oil at 10 to 15 year intervals. Unfortunately, the use of pentachlorophenol has come under increasing scrutiny and this research project was established to identify safer chemicals for this application.

In 1981 and 1985, chemicals which had previously performed well in laboratory trials were applied to a series of 2.4-m-long western redcedar pole stubs. The poles were placed in the Peavy Arboretum test site and subjected to regular watering to improve conditions for decay and accelerate preservative leaching. The effectiveness of the chemical applications as evaluated after 2 years by removing increment cores for testing using the Aspergillus bioassay and small plugs for use in a modified soil block test. The results indicated that several of the treatments were providing some protection to the outer sapwood, although this level of protection was not comparable to that provided by the standard 10 percent pentachlorophenol solution.

These same poles were resampled this past year. Aspergillus bioassays of increment cores removed from the test poles suggest that residual levels of some

test chemicals remain in the pole sections (Table II-1). For example, the 10% penta treatments in both oil and water continued to exhibit a bioassay response in the outer sampling zone (0 to 0.6 cm). Of the other treatments, only ammonium bifluoride produced any zone of effect, and the size of this zone was small, suggesting the possibility that some heartwood was inadvertently included in the sample. The absence of a zone of effect does not necessarily mean that the chemical is no longer effective, since chemicals which are strongly bound to the wood perform poorly in the bioassay. However, for chemicals with some water solubility, the bioassay is a highly sensitive method for assessing residual protection.

Table II-1. Average *Aspergillus niger* zone of effect (mm) from increment cores removed from poles sprayed with selected decay control chemicals eight years prior to sampling.

Chemical	Conc. (%)	Carrier	Zone of effect	
			0-0.6 cm	0.6-1.2 cm
Ammonium bifluoride	20	water	2 (0)	0 (0)
Copper-8-quinolinolate	0.12	oil	0 (0)	0 (1)
Copper-8-quinolinolate	0.9	water	0 (0)	0 (0)
3-iodopropynyl butyl carbamate	2.0	water	0 (0)	0 (0)
Pentachlorophenol	10	oil	10 (11)	7 (8)
Pentachlorophenol	10	water	7 (6)	0 (3)
Pentachlorophenol	2.5	water	0 (0)	0 (0)
Control	-	-	0 (0)	0 (0)

<sup>a</sup> Each value represents the mean of 18 samples. Figures in parenthesis reflect results from the same poles after 2 years.

Soil block tests of wafers removed from the same test poles produced extremely variable results. Most of the pole surfaces were badly decayed and plugs removed from these surfaces were extremely fragile. Wood weight losses

from these plugs varied widely, probably reflecting the fact that a majority of the carbohydrate fraction was already removed during the field exposure. Thus, wood weight losses may provide a misleading interpretation of chemical efficacy, with badly decayed poles producing low wood weight losses and thus good chemical performance. The exception to this finding was the pentachlorophenol treatments, which remained sound and experienced minimal weight losses. The pole sections will be reexamined in the coming weeks and rated for degree of fungal attack to provide a more accurate measure of chemical performance.

The pole sections treated in 1985 with copper naphthenate or zinc naphthenate were also examined this past year. Aspergillus bioassays of increment cores from these poles revealed only minimal zones of effect in the one copper naphthenate treatment (Table II-2). Copper and zinc naphthenate normally both produce only minimal zones of effect in the bioassay.

Table II-2. Average Aspergillus niger zone of effect (mm) from increment cores removed from poles sprayed with selected decay control chemicals 4 years prior to sampling.

Chemical	Conc. <sup>a</sup> (%)	Carrier	Zone of effect (mm) <sup>b</sup>	
			0-0.6 cm	0.6-1.2 cm
Copper naphthenate (S-520)	2.0	oil	0.7	0.9
Copper naphthenate (S-522)	2.0	oil	0.0	0.0
Zinc naphthenate (W-552)	2.0	water	0.0	0.0

<sup>a</sup> Concentrations expressed as percent metal (copper or zinc).

<sup>b</sup> Values represent means of 5 pole sections per treatment. Increment cores were divided into outer (0-0.6 cm) and inner (0.6-1.2 cm) zones, which were used in the A. niger bioassay.

Soil block tests on the same three chemicals revealed that all three all providing some degree of protection against fungal degradation (Table II-3). The effects were most noticeable with the copper naphthenate formulations, which are experiencing weight losses approximately one half those found in the untreated controls. These weight losses are still more than twice those found with similar penta-chlorophenol treatments. The zinc naphthenate treatments are experiencing weight losses which are only slightly lower than those found in the controls, suggesting that this chemical may not be appropriate for this application.

Copper naphthenate has now replaced pentachlorophenol for spraying western redcedar poles in service. The results suggest that copper naphthenate is providing some protection to the western redcedar pole stubs; however, the degree of protection is somewhat diminished from that provided by pentachlorophenol. This decreased level of protection will likely require the use of either stronger treatment solutions or more frequent retreatments to provide the same level of performance.

**B. ACCELERATED LABORATORY TESTING OF POTENTIAL PENTACHLOROPHENOL REPLACEMENTS FOR WESTERN REDCEDAR SAPWOOD DECAY CONTROL**

The smaller western redcedar sapwood blocks which were treated with the chemicals which had performed well in laboratory tests have now been exposed for 2 years (Table II-4). These blocks are now being sampled for Aspergillus bioassays and for soil block testing. The results of these tests will be presented in the next report.

**C. EVALUATE TREATMENTS FOR PREVENTING DECAY IN FIELD DRILLED BOLT HOLES**

The field trials to evaluate the ability of initial treatment of field-drilled bolt holes with Polybor, ammonium bifluoride, Patox washers, Boracol 40

or 10% pentachlorophenol to prevent fungal colonization and decay are now in their eighth year. Culturing of increment cores removed from sites above and

Table II-3. Wood weight losses of sapwood plugs removed from western redcedar poles four years after treatment with selected wood preservatives as measured using a modified soil block test.<sup>a</sup>

Chemical	Conc. (%)	Carrier	Weight loss (%) at depth (mm)			
			0-3	4-7	8-11	12-15
Copper naphthenate (S-520)	2.0	oil	19.5	16.5	23.0	29.0
Copper naphthenate (S-522)	2.0	oil	17.5	15.0	16.0	17.0
Zinc naphthenate (W-552)	2.0	water	22.0	28.0	35.0	29.0
Control	-	-	31.0	38.0	42.0	46.0

<sup>a</sup> Values represent means of 15 samples per treatment. Chemical concentration are expressed as percent active metal basis.

below the hardware on each bolt hole indicate that a number of poles are now beginning to experience increased levels of fungal colonization. At present, only 17% of cores removed from untreated bolt holes contain decay fungi (Table II-5). While the low levels of fungal colonization appear to reflect a minor problem, few utilities would willingly accept nearly one fifth of their poles experiencing internal decay above the groundline in the critical crossarm area. The potential for bolt hole associated decay places added importance on the need to identify safe, easily applied treatments to prevent this attack.

Of the treatments evaluated in this test, the three diffusible compounds (Polybor, Boracol, and ammonium bifluoride) all appear to be providing some

protection to the bolt hole, while the pentachlorophenol and Patox washer treatments are providing a slightly lower degree of protection (Table II-5). Diffusible compounds can migrate with any moisture which enters the bolt hole

Table II-4. Chemicals tested as potential pentachlorophenol replacements in western redcedar.

Chemical	Source	Carrier	Concentration
Azaconazole	Janssen Pharm.	water	0.30
			0.15
ACAR 86013		water	1.0
86032		water	1.0
Copper-8-quinolinolate	Chapman Chem. Co.	oil	0.12 (Cu)
Copper-8-quinolinolate	Nuodex	water	0.3 (Cu)
Copper naphthenate	Tenino Wood Presv.	oil	2.0 (Cu)
CWP 44	Chapman Chem. Co.	water	10.0
Diiodomethyl-paratolyl sulfone	Akzo Chemie	oil	1.0
Dodecyl dimethyl ammonium salt	Nuodex	oil	8.0
		water	8.0
3-iodo 2-propynyl butyl carbamate (IPBC)	Troy	water	2.0
	Beecham (DAP)	oil	0.5
Isothiazolone	Rohm and Haas	oil	1.0
Methylene bithiocyanate (MBT) plus Thiocyanomethylthio benzothiazole (TCMTB)	Buckman Laboratories	water	4.0
TCMTB	Buckman Laboratories		2.0
Trimethylcocammonium chloride (TMCAC)	Akzo Chemie	water	4.0
Zinc naphthenate (a)	Mooney Chemical	water	5.0
			4.0
Zinc naphthenate (b)	Mooney Chemical	water	4.0
Pentachlorophenol	Chapman Chem. Co.	oil	10.0
Tributyltin oxide		oil	5.0
IPBC/Busperse 47 (B-47)	Troy-Buckman	oil	1.0/5.0
Isothiazolone/B-47	Rohm & Haas/Buckman	oil	1.0/5.0
TMCAC/IPBC	Akzo Chemie/Troy	oil	4.0/2.5
TCMTB/B-47	Buckman	water	4.0/5.0
			2.0/2.5
(MBT/TCMTB)/B-47	Buckman	water	4.0/5.0
			2.0/2.5
Isothiazolone/TMCAC	Rohm & Haas/Akzo Chemie	oil	3.5/6.0
Control	-	-	-

and thus will be ideally placed to prevent decay where conditions are most favorable for fungal development. However, continued moisture movement could decrease chemical concentrations below the threshold for fungal growth. Further sampling will be required to determine if chemical depletion occurs with the diffusible treatments.

The remaining two treatments both provided some protection, with degrees of colonization that were one half that of the control. The pentachlorophenol treatment lacks the ability to migrate from the point of application. Any checks which open beyond the shallow band of penta protection will be susceptible to fungal invasion. It is likely that other oilborne fungicides which lack the ability to migrate would perform in a similar manner. This limitation might be overcome by the use of stronger chemical solutions or by use of one of the pressure type devices formerly advocated for the treatment of field drilled bolt holes in marine piling. The Patox washer treatments were presumed to protect the bolt hole by migrating from the washer into the hole; however, the degree of protection afforded by these treatments was less than expected.

The results indicate that diffusible compounds are providing the highest degree of protection. While these chemicals may eventually be depleted by continued moisture movement, they have restricted fungal colonization and thus wood decay for the longest period. The results also indicate that application of any of the fungicides tested reduces the degree of fungal colonization around the bolt hole.

#### **D. RAPID EVALUATION OF REMEDIAL TREATMENTS FOR PROTECTING FIELD-DRILLED BOLT HOLES**

While field tests produce the most useful data for determining the efficacy of a particular chemical, the bolt hole tests have demonstrated the difficulty

Table II-5. Percentage of increment cores removed from sites around field drilled bolt holes in Douglas-fir poles which contain decay and non-decay fungi as determined by culturing on nutrient media.

Treatment	Cores containing decay <sup>nondecay</sup> fungi (%)			
	5 yr.	6 yr.	7 yr.	8 yr.
Patox Washer	11 <sup>41</sup>	5 <sup>12</sup>	5 <sup>22</sup>	8 <sup>31</sup>
Polybor	16 <sup>28</sup>	0 <sup>11</sup>	0 <sup>25</sup>	0 <sup>25</sup>
Ammonium bifluoroide	3 <sup>17</sup>	0 <sup>5</sup>	2 <sup>16</sup>	0 <sup>14</sup>
Boracol 40	3 <sup>44</sup>	0 <sup>18</sup>	2 <sup>27</sup>	0 <sup>33</sup>
Pentachlorophenol	6 <sup>55</sup>	2 <sup>25</sup>	2 <sup>17</sup>	8 <sup>30</sup>
Control	10 <sup>55</sup>	3 <sup>30</sup>	9 <sup>26</sup>	17 <sup>46</sup>

of assessing certain treatments under field conditions. In the eight years that the field test of potential bolt hole decay control chemicals has been underway, a variety of new chemicals have been identified and regulatory environment for wood preservatives has changed dramatically.

To better evaluate new chemicals in this changing environment, we sought an accelerated laboratory test which could reliably predict field performance. The method for preparing blocks for this test has been previously described ('88 Ann. Rept., pg. 62-65).

The blocks treated by this method have been weathered and are now undergoing decay resistance testing. In this procedure, blocks were oven-dried (54°C) for 5 days and weighed. The blocks were then water soaked under pressure (125 psi) for 15 hours to raise the moisture content prior to autoclaving for 30 minutes at 100°C in autoclavable plastic bags. The decay chambers consisted of autoclavable bags containing 1 liter of vermiculite and 500 ml of 1.0% malt



extract. A 0.6-cm-diameter by 7.5-cm-long dowel infested with Postia placenta was inserted in the bolt hole in the test block, which was placed in and the bag. The bags were sealed and incubated at room temperature (23-25°C) for 6 months. At that time point, 2 controls were removed, oven-dried, and weighed to determine wood weight loss. The results showed only minimal weight loss in the untreated control blocks. The lack of weight loss appears to reflect the relatively large size of the test specimens coupled with the use of moderately durable Douglas-fir heartwood in a test with relatively low hazard decay conditions. Efforts are underway to repeat this procedure under conditions more conducive to biological attack.

**E. FUNGAL COLONIZATION OF FIELD-DRILLED BOLT HOLES IN DOUGLAS-FIR POLES EXPOSED IN EASTERN WASHINGTON**

Above ground decay of Douglas-fir poles represents a major consideration in electric transmission lines west of the Cascade Mountains, but is considered insignificant east of this range due to the low rainfall in this region. Internal decay extending upwards of 20 feet above the groundline has been reported in numerous Douglas-fir poles, possibly as a result of the high incidence of wind-driven rain and long periods of wet weather. Recently, a single pole structure failed in eastern Washington and a pocket of internal decay was located near a field-drilled bolt hole. This decay, tentatively identified as Postia placenta, raised concerns that other poles might also be experiencing similar above ground decay, particularly in areas where irrigation inadvertently splashed on the poles. Under these conditions, the high summer temperatures--coupled with the added moisture--would provide ideal conditions for fungal growth and decay.

To address this problem, a series of increment cores were collected from selected sites above the groundline of 25 poles by Bonneville Power Administration personnel. The cores were placed in plastic drinking straws which were sealed and shipped to the Oregon State University Forest Research Laboratory. The cores were then flamed briefly to remove any surface contaminants and placed on the surface of malt extract agar in petri dishes. The plates were observed for the presence of fungal growth from the cores over a one-month period, and any fungi were subcultured for later identification. These fungi were then examined for evidence of characteristics typical of Basidiomycetes, a class of fungi which contains many important wood decayers.

The results indicate that 6 of the 28 cores contained fungi; however, only one of these fungi was considered to be a possible Basidiomycete (Table II-6). This fungus, which was isolated from a site below the insulator of Pole Number 2/6, had multiple clamps and was not the same species previously identified from the failed pole. The ability of this fungus to cause wood decay is currently under study.

The low incidence of fungi above the groundline of the poles suggests that the initial pole failure which precipitated this investigation was an isolated incident which may reflect a failure to achieve adequate sterilization during the initial pressure treatment process. This, in itself, is of interest owing to the normally long Boulton seasoning period required in the BPA specifications. It is possible that a single, green pole included in a charge of drier poles may have received a shorter Boulton-seasoning cycle. Any fungi established in this pole prior to treatment might have survived the shorter treatment process. Alternatively, specific conditions in the pole which failed may have created an ideal site for colonization by the Basidiomycete, which slowly colonized and

decayed the wood. It is difficult to determine whether either of these permitted the colonization to occur; however, it is apparent the the incidence of decay fungi in poles in the eastern part of Washington are sparsely colonized above the groundline and should not pose a future hazard.

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Table II-6. Increment cores removed from the Sacajewea-Sun Harbor Line (Pasco, Washington) from which microfungi or Basidiomycetes were cultured.

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Pole number	Microfungus	Basidiomycete
2/2	X	X
2/6	X	
2/10 (Q1)	X	
2/10 (Q3)	X	
2/11	X	
2/13	X	

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**OBJECTIVE III****DETECT EARLY DECAY AND ESTIMATE RESIDUAL  
STRENGTH OF POLES IN SERVICE****A. DETECT INCIPIENT DECAY USING EXTRACTS OR OTHER INDICATORS OF FUNGAL DEGRADATION**

In previous years, we have evaluated the use of fluorescent-coupled lectins for detecting decay fungi in wood and the use of warm water extracts from decaying wood for detecting the products of wood decay fungi.

No new work was undertaken under this task, however, efforts to better understand the results obtained using Fourier Transformed Infrared Spectroscopy (FTIR) continue. We have nearly 1000 Douglas-fir, ponderosa pine, or alder samples decayed to varying weight losses by soft, white and brown rot fungi which will be examined to determine if FTIR has any ability to reliably detect incipient decay.

**B. EFFECT OF FUNGAL COLONY SIZE AND DENSITY ON RESIDUAL STRENGTH OF DOUGLAS-FIR SAPWOOD AND HEARTWOOD**

As we analyze the air-seasoning data collected over a four-year period from seasoning yards located throughout the Pacific Northwest, we are continually confronted with the difficulty of determining the relative importance of individual isolations of a given fungus from the wood. While culturing is a definitive indication that some viable propagable of a given fungus is present in the wood, it provides little information on the degree of infestation. For example, culturing one increment core containing a single spore and a second core containing an extremely active fungal colony which has produced substantial wood decomposition would produce the same result, a positive isolation. Both results reflect the potential for decay, but the latter colony obviously has a far greater potential for short-term wood degradation.

In order to develop a better understanding of the relationship between fungal colonization and wood properties, the four fungi most commonly isolated from the air-seasoning Douglas-fir were selected for further study. Peniophora spp. and Stereum sanguinolentum (formerly Haematostereum sanguinolentum) were studied in Douglas-fir sapwood, where they were most commonly isolated, while Postia placenta (formerly Poria placenta) and Antrodia carbonica (formerly Poria carbonica) were studied in Douglas-fir heartwood, the site where these two organisms were most commonly present.

The details of these tests as well as results for Peniophora sp. and A. carbonica were described previously ('88 Ann. Rept., pg 71-79). Briefly, sterile beams were inoculated with one of the test fungi by injecting a drop of spore/mycelial fragment suspension into a 2 mm diameter hole drilled perpendicular to the test face of each 1.25 by 1.25 by 20-cm-long beam. The beams were incubated at 28°C in plastic bags and selected beams were tested at monthly intervals. Beams were either tested in three point loading to determine modulus of rupture (MOR), work to maximum load (WORK), and modulus of elasticity (MOE), or 2.5 cm cubes were cut from selected locations along the length of each beam for longitudinal compression strength testing (LCS) on a Instron Universal testing machine at a head speed of 0.2 cm/minute. Following bending tests, 16 thin sections were cut from the middle 7.5 cm of each beam tested in bending. These sections were cut into 4 equal sized cubes which were placed on potato dextrose agar or malt agar and observed for growth of the test fungus. The LCS beams were sampled for fungal growth by cutting 120  $\mu$  thick sections from five cubes cut from the beam center, each end of the beam, and from sites halfway between the beam center and end. These sections were macerated in sterile distilled water and mixed with cooling molten agar, which was poured into petri dishes and

allowed to solidify. Fungal colonies appearing in the media were then counted to develop estimates of fungal density in each beam.

Last year, we reported on results using A. carbonica and Peniophora sp. ('88 Ann. Rept., pg 71-80); however, problems were experienced with contamination shortly after the test was begun, making it difficult to analyze the results. This past year, we have modified the inoculation and handling procedures to minimize the risk of microbial contamination and have evaluated Stereum sanguinolentum on Douglas-fir sapwood and Postia placenta on Douglas-fir heartwood.

For S. sanguinolentum, a white rotter which commonly invades the sapwood of downed timber, the results of bending tests showed declines in both MOR and WORK with increasing incubation period, but only a minor change in MOE (Figure III-1). After 12 months, average MOR had been reduced by 30% from 6,163 to 4,325 psi, while work had declined 45% to 6 in.-lbs. from an initial value of 11 in.-lbs. This effect was most rapid between 1 and 5 months, then became more gradual upon longer incubation. Colonization of the beam was rapid. The test fungus was isolated from the entire length of inoculated beams at every time point, reflecting complete colonization of the beams. The isolation studies do not reflect the degree of fungal attack, only the presence of viable decay fungi.

The combination of longitudinal compression strength testing and colony density measurement was designed to examine the importance of not only colony size, but also colony density on wood strength. LCS also showed a decline with increasing incubation period, dropping 21% from 414 kg to 325 kg between 1 and 12 months of incubation (Figure III-2). Although radial compression strength is a better indicator of incipient decay, LCS does appear to be useful for following the course of degradation and can be correlated with bending

properties. Examination of strength by position in the beam showed that after 5 months, LCS declined slightly more towards the beam center, the initial inoculation point (Figure III-3). These results suggest that fungal activity should be highest near the beam center; however, colony density measurements were poorly correlated with LCS measurements over the course of the study and were sometimes inversely related to LCS (Figure III-4). Colony counts tended to increase between 0 and 5 months as the fungus initially colonized the beam, then remained about the same over the next 5 months (Figure III-5). We had expected that colony density would be closely correlated with wood strength, but other factors may complicate this relationship. Many fungi produce large quantities of diffusible enzymes which migrate for long distances through the wood, causing substantial strength effects while the quantity of fungal biomass remains quite small. Other fungi cause more gradual strength losses as they slowly move through the wood. Conversely, some fungi produce large quantities of spores or other propagables which can artificially increase the number of isolations in a density procedure like that used here. Compounding these effects is a trend for mycelial density of many fungus to decline in a given area as readily available substrates are utilized. The colonization pattern in the S. sanguinolentum inoculated beams appears to be a rapid colonization of the wood with an increase in fungal density over the first 5 months after which the density stabilized. The colonization pattern coincides with rapid reduction in bending strength and LCS, which also becomes more gradual upon longer incubation periods. Stereum sanguinolentum is a common colonizer of fallen timber and must rapidly colonize the wood to compete with other pioneering colonizers. As the readily available nutrients present in the sapwood are exhausted, colony density declines, and the remaining biomass must utilize more structural components of the wood cell wall.

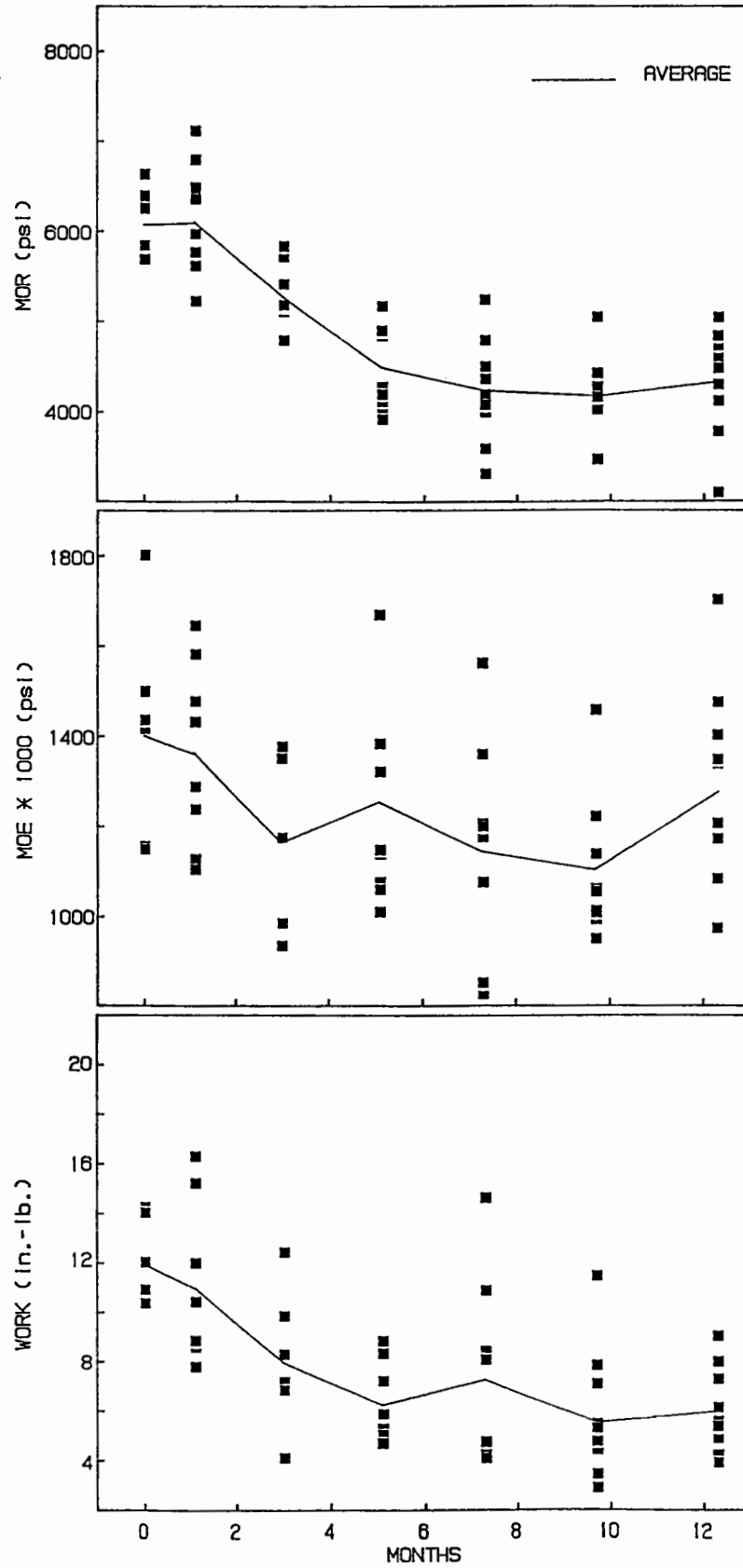


Figure III-1. Effect of colonization by *Stereum sanguinolentum* on modulus of rupture, work to maximum load, and modulus of elasticity of Douglas-fir sapwood beams following 0 to 12 months of incubation at 28°C.



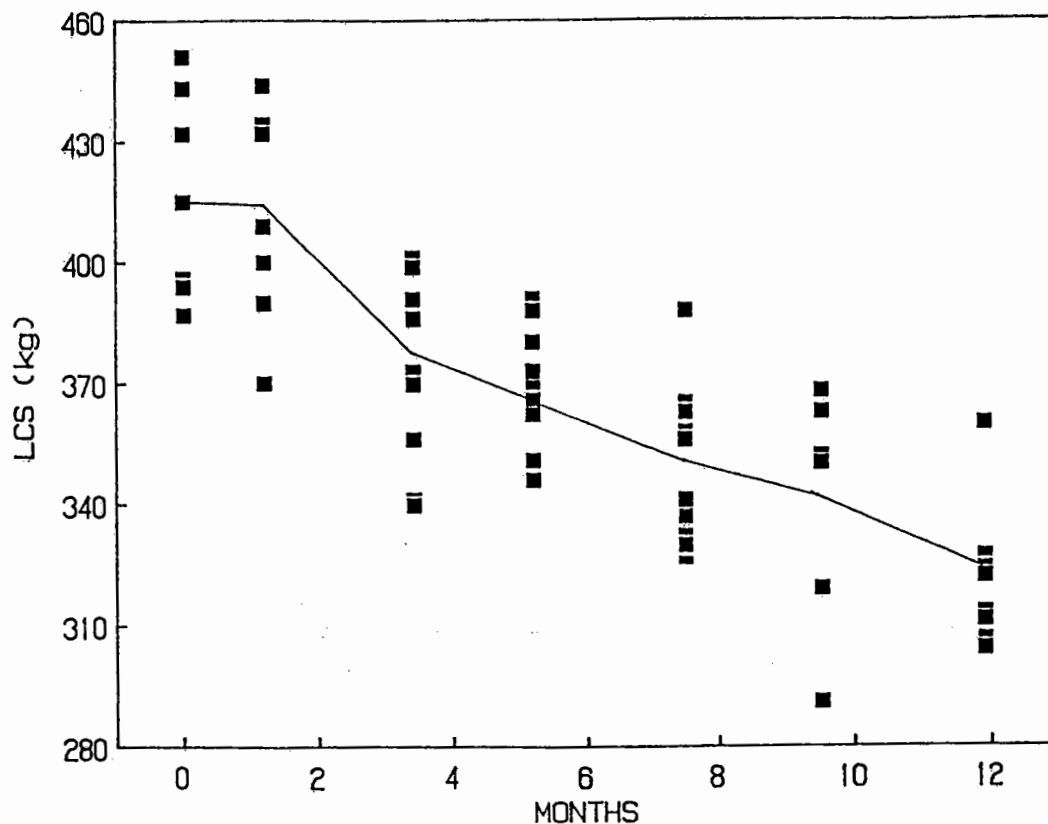


Figure III-2. Longitudinal compression strength of Douglas-fir sapwood beams inoculated with a mycelial suspension of Stereum sanguinolentum after 0 to 12 months of incubation at 28°C.

The Postia placenta colonized Douglas-fir heartwood beams were only evaluated over a 7-month period because the fungus failed to colonize many of the beams in the test. MOR and WORK declined more gradually than in S. sanguinolentum infested beams, while there was no consistent effect on MOE (Figure III-6). Unlike S. sanguinolentum, P. placenta colonized the beams more slowly, probably reflecting the presence of heartwood extractives which inhibited initial mycelial growth.

Longitudinal compression strength measurements showed only minimal change over the 7-month incubation period (Figure III-7), while colony density gradually increased for the first 5 months, then declined (Figure III-8). LCS measurements along the beams followed a trend similar to that found with the S. sanguinolentum beams, except that strength loss closer to the point of inoculation was evident

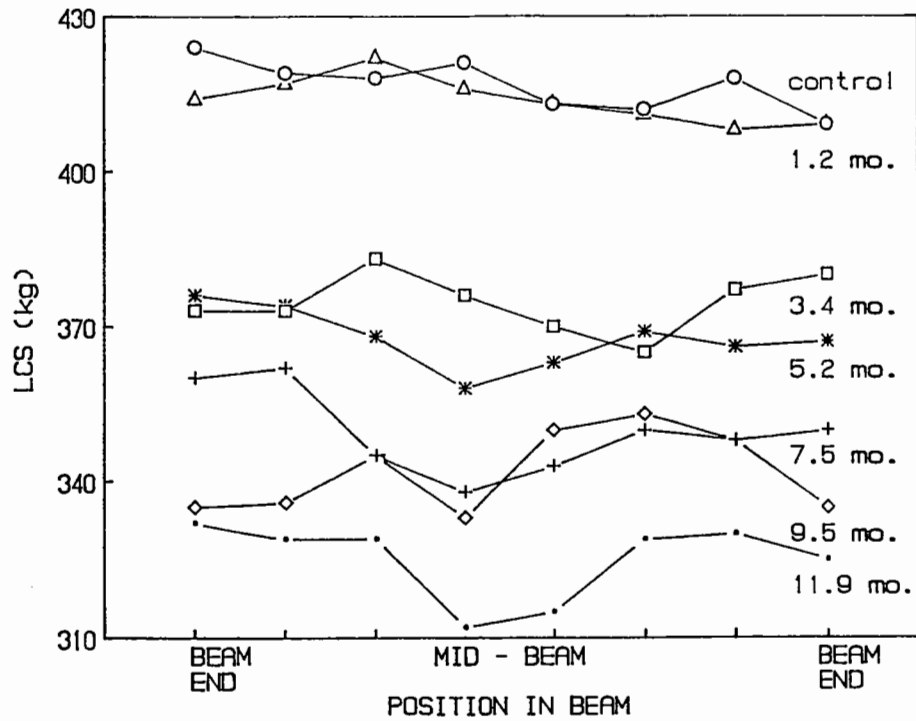


Figure III-3. Longitudinal compression strength at selected points along Douglas-fir sapwood beams inoculated with a mycelial suspension Stereum sanguinolentum after 0 to 12 months incubation at 28°C.

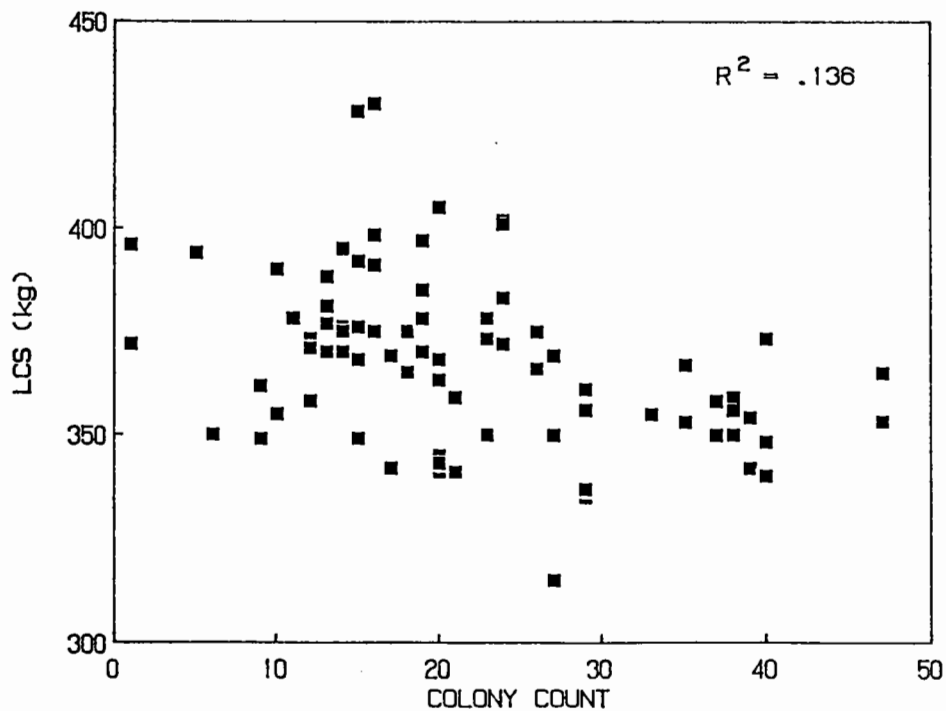


Figure III-4. Longitudinal compression strength versus the density of Stereum sanguinolentum in Douglas-fir sapwood beams 5 months after inoculation with a mycelial suspension of the test fungus.

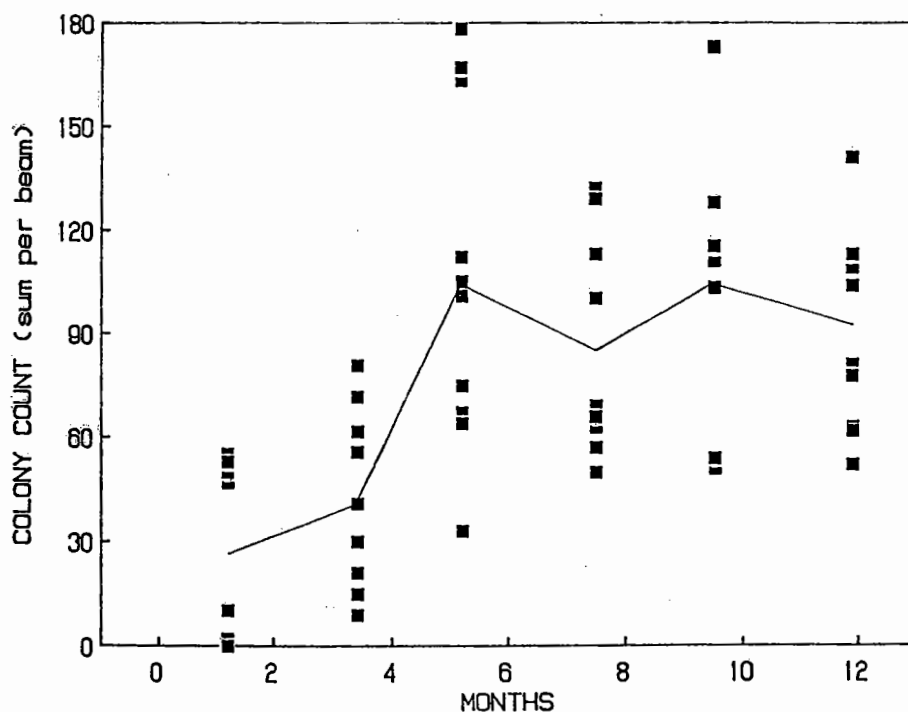


Figure III-5. Total colony counts of Stereum sanguinolentum in Douglas fir sapwood beams over a 12 month incubation at 28°C as measured by culturing macerated wood sections on nutrient media.

only after 7 months (Figure III-9). While colonies were detected in all sampling positions along the beam with S. sanguinolentum one month after inoculation, colonization of beams by P. placenta was much more variable. Isolation from the mid-point of P. placenta infested beams was always positive, but the fungus moved inconsistently toward beam ends as the test progressed. The wide range of strength values at each time point, with the exception of the control beams, indicate that degree of fungal attack was also very variable. Douglas-fir heartwood is classified as moderately durable in ground contact and durable in above ground exposures. Air-seasoning should be considered as an above ground exposure. While P. placenta is commonly isolated from Douglas-fir heartwood, it still must overcome the presence of heartwood extractives in the absence of readily available nutrients. Thus, it is likely that the initial effects of

colonization by this fungus are minimal. Conversely, the level of colonization of heartwood by competing microorganisms is far lower than sapwood, reducing the need for a fungus to rapidly occupy the substrate to exclude competition. Under prolonged exposure, this fungus develops a sufficient biomass to begin attacking the wood structure and exert considerable effects on strength as evidenced by its association with substantial internal decay of Douglas-fir heartwood in service. This delayed effect on strength properties is reflected in the finding that Douglas-fir pole sections, although heavily colonized by decay fungi after 2 years of air-seasoning, only begin to experience significant heartwood strength losses after the third year of seasoning. This delayed effect makes it difficult to accurately assess the significance of fungal isolation in relation to wood properties.

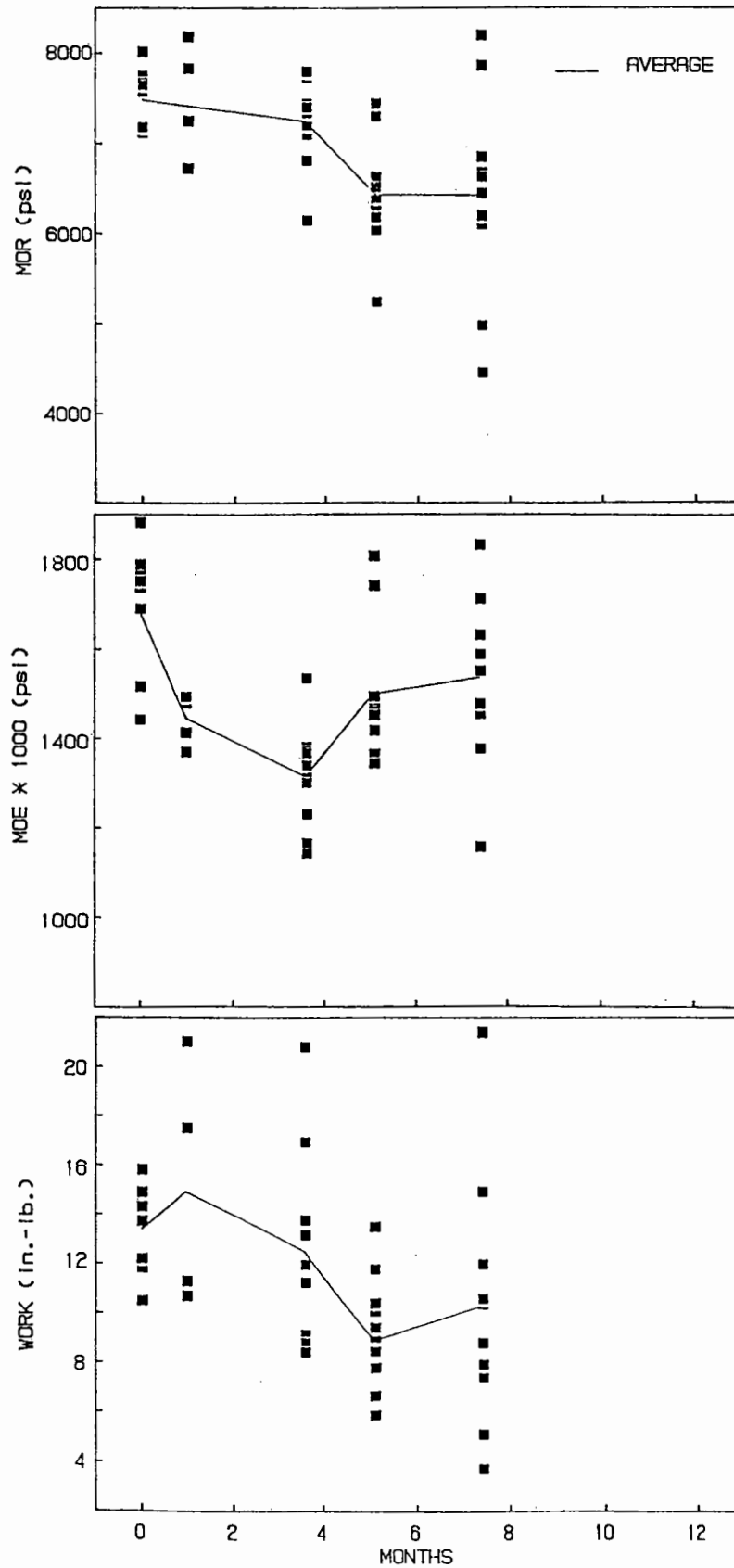


Figure III-6. Modulus of rupture, modulus of elasticity, and work to maximum load of Douglas-fir heartwood beams 0 to 7 months after inoculation with a mycelial suspension of *Postia placenta*.

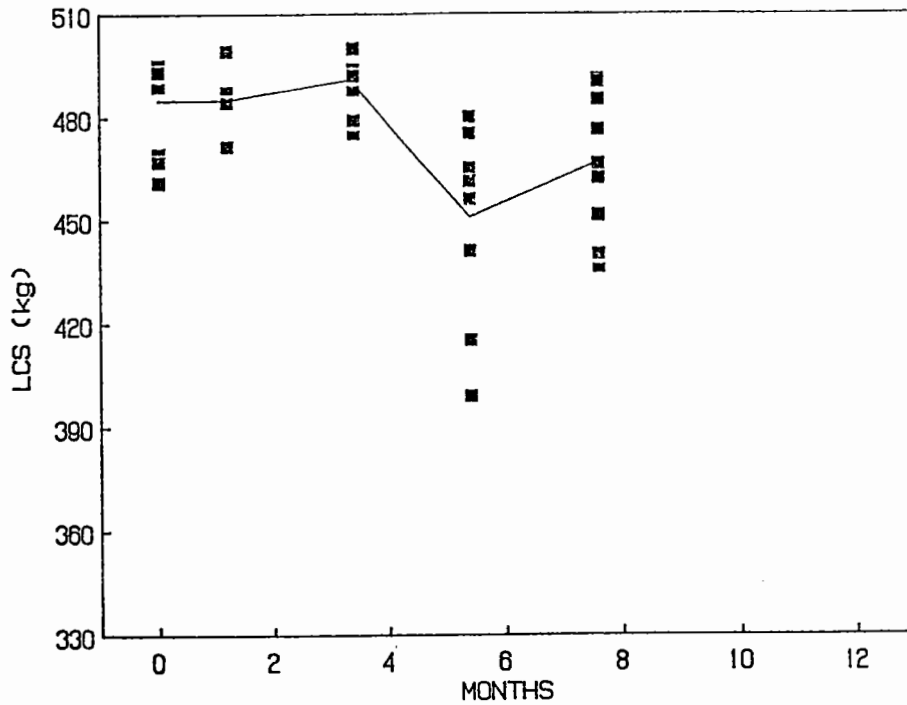


Figure III-7. Longitudinal compression strength of Douglas-fir heartwood beams 0 to 7 months after inoculation with a mycelial suspension of Postia placenta.

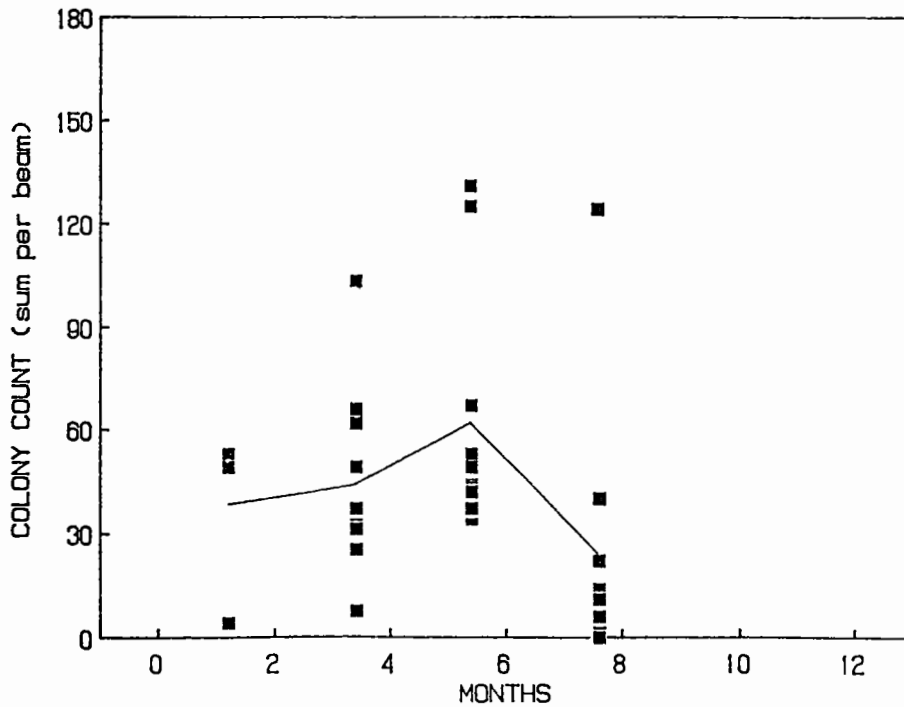


Figure III-8. Fungal colony density of thin sections cut from Douglas-fir heartwood beams 0 to 7 months after inoculation with a mycelial suspension of Postia placenta, as measured by culturing dilutions of macerated sections on a nutrient media.

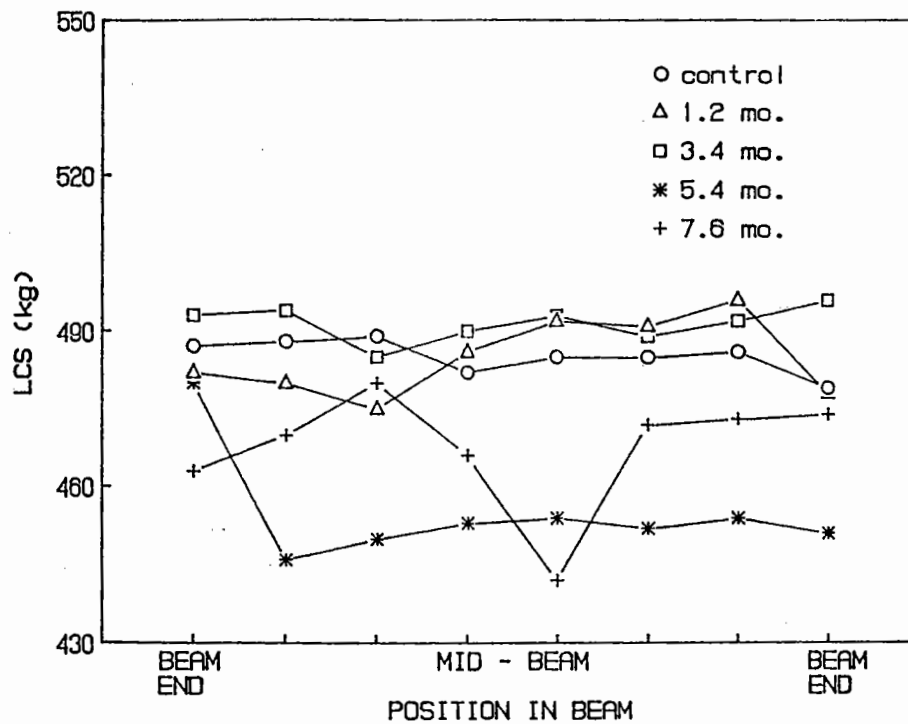


Figure III-9. Longitudinal compression strength at selected points along Douglas-fir heartwood beams 0 to 7 months after inoculation with a mycelial suspension of Postia placenta.

## OBJECTIVE IV

### EVALUATE THE POTENTIAL FOR INFECTION AND DECAY DEVELOPMENT IN AIR-SEASONING POLES

#### A. DECAY DEVELOPMENT STUDY

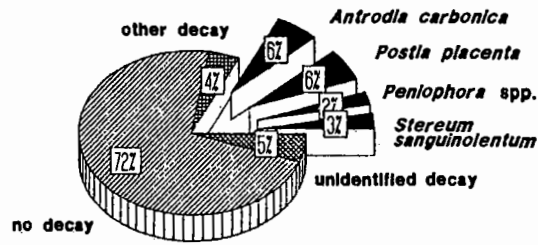
The field portion of the decay development study has been complete for two years; however, we are continuing to analyze the results to determine the significance of various colonization patterns in the poles. Data has been collected on the sequence of colonization in Douglas-fir pole sections, with and without an initial flood treatment of ammonium bifluoride, after 1 to 3 years of air-seasoning at four Pacific Northwest sites. The fungal species isolated from pole sections at the various sites have been previously reported ('88 Ann. Rept., pg. 81-83).

Over the past year, we have begun to evaluate the pattern of colonization for the four most commonly isolated Basidiomycetes, Peniophora spp., Stereum sanguinolentum, Antrodia carbonica, and Postia placenta. The increment cores removed from the poles were initially divided into 2.5-cm-long segments for culturing, allowing us to determine the relative depth of a given fungal infestation. Increment cores were removed every 10 cm around the pole and every 15 cm along the pole length. The pattern permitted some delineation in colony size within individual poles. For analysis, cores from a given position on the poles were combined for poles sampled at a given time at each exposure site. The combined data were plotted to determine if certain species were colonizing specific sites on the poles or were specific to a given exposure site.

As shown in previous years, the percentage of cores containing decay fungi rose gradually with seasoning time, with 28 percent of cores removed from poles air-seasoned for one year containing decay fungi (Figure IV-1). This figure rose to 62 and 96 percent after two and three years of air-seasoning, respectively.

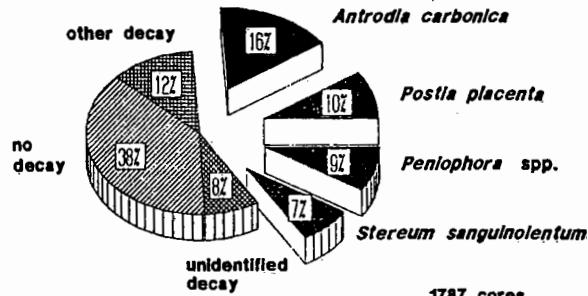


**1 YEAR**



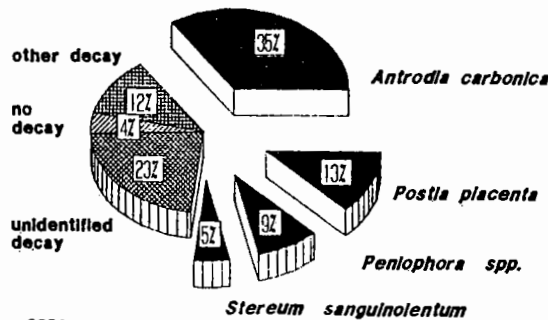
2233 cores

**2 YEARS**



1787 cores

**3 YEARS**



2031 cores

Figure IV-1. Percentage of cores removed from Douglas-fir poles air-seasoned for A.) one, B.) two, or C.) three years that were colonized by Basidiomycetes as determined by culturing on a nutrient media.

While isolation frequency of Peniophora spp. and S. sanguinolentum both rose slightly between one and two years of air-seasoning, the incidence of these fungi did not increase between two and three years. The incidence of both A. carbonica and P. placenta gradually increased over the air-seasoning period.

Wood moisture contents in the exposed pole sections generally declined with increased length of air-seasoning (Table IV-1). Moisture contents in the outer 2.5 to 3.75 cm were generally below 20 percent, while those at 5 cm varied more widely. Moisture contents at Oroville were lower than the three other sites. Moisture contents were also highest on the lower face after 1 year, reflecting potential moisture movement from the ground as well as protection from the sun. Higher moisture contents on the lower pole surface did not appear to favor colonization of the heartwood, which tended to occur on upper surface of the pole sections. The moisture meter did not permit moisture measurements at deeper points in the wood, although these moisture levels would be expected to rise higher than those at 5 cm.

Analysis of the position of isolation for the four most commonly isolated fungi showed two patterns of colonization. Both Peniophora spp. and S. sanguinolentum were primarily isolated from the outer shell corresponding to the sapwood zone (Figure IV-2). Although some isolations were made from zones deeper in the wood, the incidence of isolation did not increase between 2 and 3 years of seasoning. The lack of increased heartwood colonization suggests that these fungi do not normally continue to colonize the heartwood zone. Colonization by both of these fungi also appeared to be random along the length of the pole section and around the circumference. Many fungi penetrate end grain more easily than radial or tangential wood faces; however, there was no evidence of higher levels of colonization near the pole ends by either of the sapwood colonizing

Table IV-1. Wood moisture content at selected depths and locations along Douglas-fir pole sections air-seasoned for one, two, or three years at four Pacific Northwest air-seasoning sites.

Depth (cm)	Site	Year	Treatment	Top <-----		22.5		45.0		90.0		45.0		22.5		-----> Butt			
				U	L	U	L	U	L	U	L	U	L	U	L	U	L		
1.25	A	1	(-)	17	15	17	18	16	18	16	18	16	18	17	17	16	19		
2.50				18	17	19	20	18	19	19	19	18	20	18	20	18	20	16	18
5.00				21	22	23	24	23	24	23	24	23	24	23	24	23	24	18	17
1.25	A	1	(+) )	16	20	16	19	16	16	16	16	15	17	15	17	13	15		
2.50				16	20	19	20	18	18	18	17	17	18	17	18	17	17	14	15
5.00				13	14	21	20	21	20	22	20	22	20	23	20	22	20	17	17
1.25	S	1	(-)	15	15	18	17	18	16	18	16	16	17	17	16	12	11		
2.50				18	17	19	18	19	18	19	19	18	20	18	19	19	11	10	
5.00				21	20	23	22	23	23	23	22	23	22	23	23	22	22	12	10
1.25	S	1	(+) )	14	20	15	17	15	17	15	17	16	18	16	19	17	20		
2.50				14	18	17	17	17	16	17	17	18	17	18	17	18	18	17	
5.00				14	18	22	20	21	22	21	22	21	21	22	21	21	22	19	16
1.25	E	1	(-)	16	14	17	17	16	16	16	16	16	16	16	16	14	13		
2.50				17	16	18	18	17	18	17	18	17	18	17	18	17	18	15	14
5.00				21	19	23	23	23	22	24	23	24	23	22	23	23	24	15	20
1.25	E	1	(+) )	18	18	16	16	16	16	16	16	16	16	16	16	16	17		
2.50				18	17	17	19	18	19	18	18	18	17	19	18	18	18	17	
5.00				18	18	20	22	21	23	22	23	22	23	16	23	22	23	20	19
1.25	0	1	(-)	11	11	13	15	13	13	13	13	12	15	12	15	10	11		
2.50				11	12	12	15	14	15	15	15	15	14	16	14	15	11	12	
5.00				12	13	15	15	19	16	21	17	17	19	18	19	17	17	12	12
1.25	0	1	(+) )	16	15	12	13	13	12	14	13	13	13	14	13	12	13		
2.50				15	13	13	13	14	13	15	15	15	14	16	15	15	13	15	
5.00				14	13	17	18	18	17	19	18	18	19	18	19	19	18	14	18

Table IV-1. (continued)

Depth (cm)	Site	Year	Treatment	Top <		22.5		45.0		90.0		45.0		22.5		Butt	
				U	L	U	L	U	L	U	L	U	L	U	L	U	L
1.25	A	3	(-)	9	9	11	12	11	12	11	12	11	13	10	13	9	11
2.50				11	10	14	14	14	15	14	15	14	15	14	14	12	12
5.00				15	13	27	20	33	20	33	20	25	19	25	19	17	17
1.25	A	3	(+)	8	12	10	12	10	11	10	13	10	11	11	11	8	9
2.50				10	14	13	17	13	16	14	15	14	15	16	15	10	12
5.00				20	15	25	20	22	19	22	19	25	19	24	19	15	15
1.25	S	3	(-)	12	11	13	12	13	13	15	13	12	11	12	11	9	10
2.50				15	12	17	14	18	15	22	14	15	13	15	13	11	12
5.00				18	14	23	16	23	20	25	20	21	20	21	16	14	14
1.25	S	3	(+)	11	12	13	15	12	15	14	13	12	14	12	14	11	12
2.50				11	13	15	17	15	18	12	16	15	15	16	17	13	15
5.00				15	14	21	19	20	19	21	18	22	18	22	19	17	16
1.25	E	3	(-)	10	10	11	11	12	12	12	12	11	12	10	12	10	10
2.50				11	11	14	14	15	15	16	14	15	15	13	15	11	12
5.00				12	12	21	19	24	20	24	19	24	19	22	24	18	15
1.25	E	3	(+)	10	10	11	11	10	12	10	12	10	13	11	11	10	10
2.50				11	12	13	14	13	14	14	15	14	16	15	15	10	12
5.00				17	16	20	18	24	18	24	19	20	19	21	18	13	13
1.25	0	3	(-)	8	7	8	8	8	8	8	9	8	8	9	9	8	8
2.50				7	8	7	8	8	9	8	10	8	9	9	9	9	8
5.00				7	8	8	10	10	11	10	12	10	11	9	11	9	10
1.25	0	3	(+)	9	8	9	9	9	9	9	9	9	9	9	9	9	10
2.50				8	9	9	8	8	9	8	9	8	9	8	9	9	9
5.00				9	9	9	9	10	10	9	10	9	10	9	10	8	10

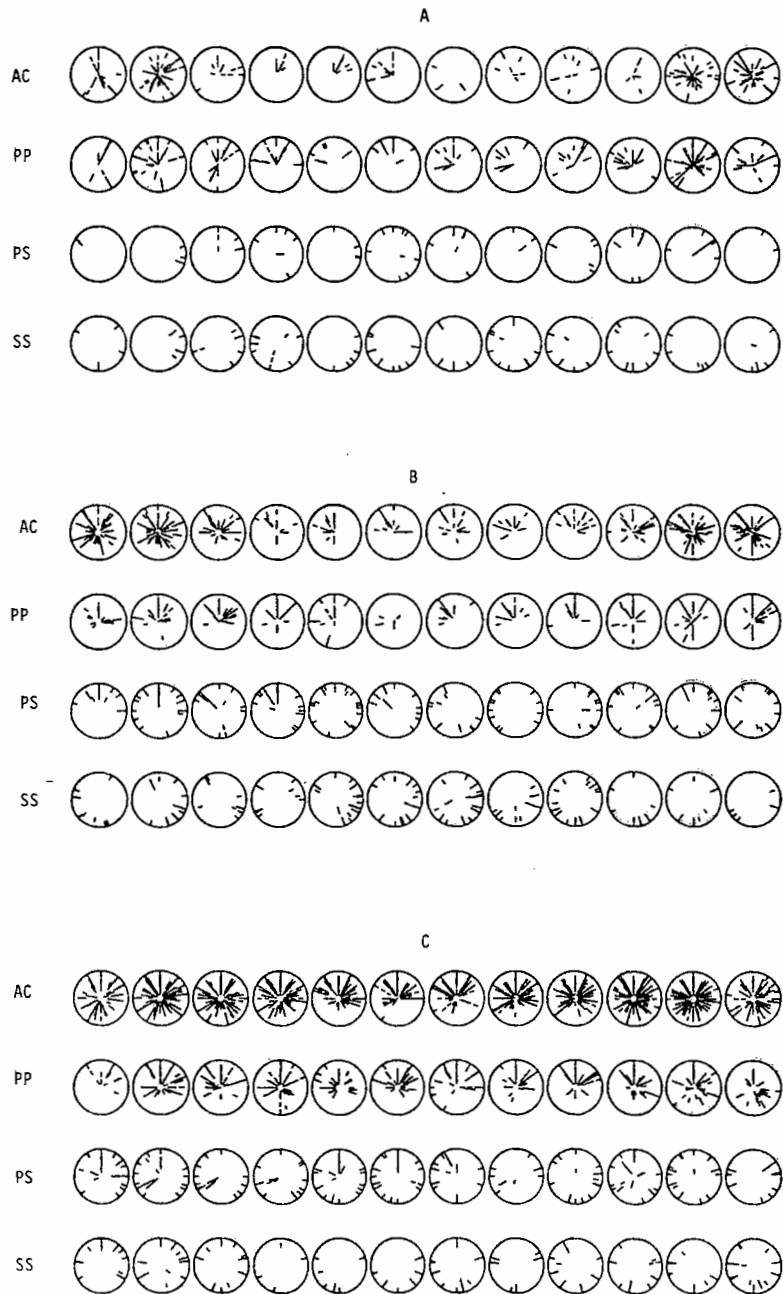


Figure IV-2. Colonization patterns of *Antrodia carbonica* (AC), *Postia placenta* (PP), *Peniophora* spp. (PS), and *Stereum sanguinolentum* (SS) in Douglas-fir pole sections exposed for A.) one, B.) two, or C.) three years at four Pacific Northwest air-seasoning sites. Each circle represents combined data for a 15 cm thick cross section of twenty 1.8 m long pole sections, with the butt of each pole on the left and the top at the right.

fungi. These fungi appear to be capable of direct penetration along the pole length, suggesting that they colonize the wood by germination of spores in small checks or directly on the wood surface. The absence of increased isolation between 2 and 3 years of air-seasoning suggests that either all of the available substrate has been occupied by these fungi, or that conditions on the wood surface are no longer conducive to germination and growth of fungal spores. Both Peniophora spp. and S. sanguinolentum are among the early colonizers of fallen Douglas-fir logs in the woods and must be capable of rapidly invading moist wood before other, competing organisms. Conditions in the air-seasoning pole reflect those in the fallen log for only a short time period, and, as the pole seasons, conditions may no longer be conducive to germination of spores of either fungal species. Fungi already present in the poles would continue to grow and colonize new substrate, accounting for the slight rise in degree of isolation frequency after 1 year of air-seasoning.

The remaining two fungi examined were primarily isolated from the inner zones corresponding to the heartwood, although sapwood colonization was also noted. Both of these species tended to be isolated more frequently from the upper face and from the exposed ends of the pole sections. Sealing the ends appeared to have little influence on the degree of colonization suggesting that the fungus colonized through checks which opened beyond the sapwood shell. These checks would be widest near the ends of the pole sections.

Isolation frequency of both P. placenta and A. carbonica increased with air-seasoning times, but the incidence of latter fungus increased substantially between two and three years. Antrodia carbonica is more frequently isolated from Douglas-fir poles in service than P. placenta, despite the fact that the latter fungus is far more aggressive in culture and can cause more severe strength and

wood weight losses. The higher isolation frequencies suggest that either the inoculum potential of A. carbonica is greater, or that this fungus is better adapted to growth on Douglas-fir heartwood. Additional tests are planned to determine the relative inoculum potential of these fungi.

In addition to comparisons between pole sections air-seasoned for 1 to 3 years, the effect of climate variation on reproducibility of colonization patterns was investigated by exposing 2 additional sets of pole sections at each site one year after the initial set was exposed. These poles were sampled after one and two years of exposure by removing cores for culturing. The results indicate that there were slight differences in the degree of colonization by the four most common fungi; however, the patterns of colonization by each fungus were remarkably similar (Figure IV-3). These comparisons suggest that, while there may be relative differences in inoculum potential from year to year, these differences do not appear to change the balance of fungi present in the system.

Selected pole sections exposed at each site were initially treated by flooding a 20 percent solution of ammonium bifluoride on the upper surface. These sections were also sampled on an annual basis by culturing of increment cores. The poles had substantial reductions in the degree of colonization by all four of the major fungal species after one year of air-seasoning, but the degree of fungal colonization in the sections gradually increased between two and three years (Figure IV-4). The delayed colonization should reduce the potential for wood strength effects during the air-seasoning period. In addition to an initial reduction in fungal colonization, the ABF treatment also altered the fungal flora colonizing the wood. The sapwood of untreated sections was heavily colonized by Peniophora spp. and S. sanguinolentum, while these fungi were virtually absent from the treated sections. Fluoride is a high mobile ion

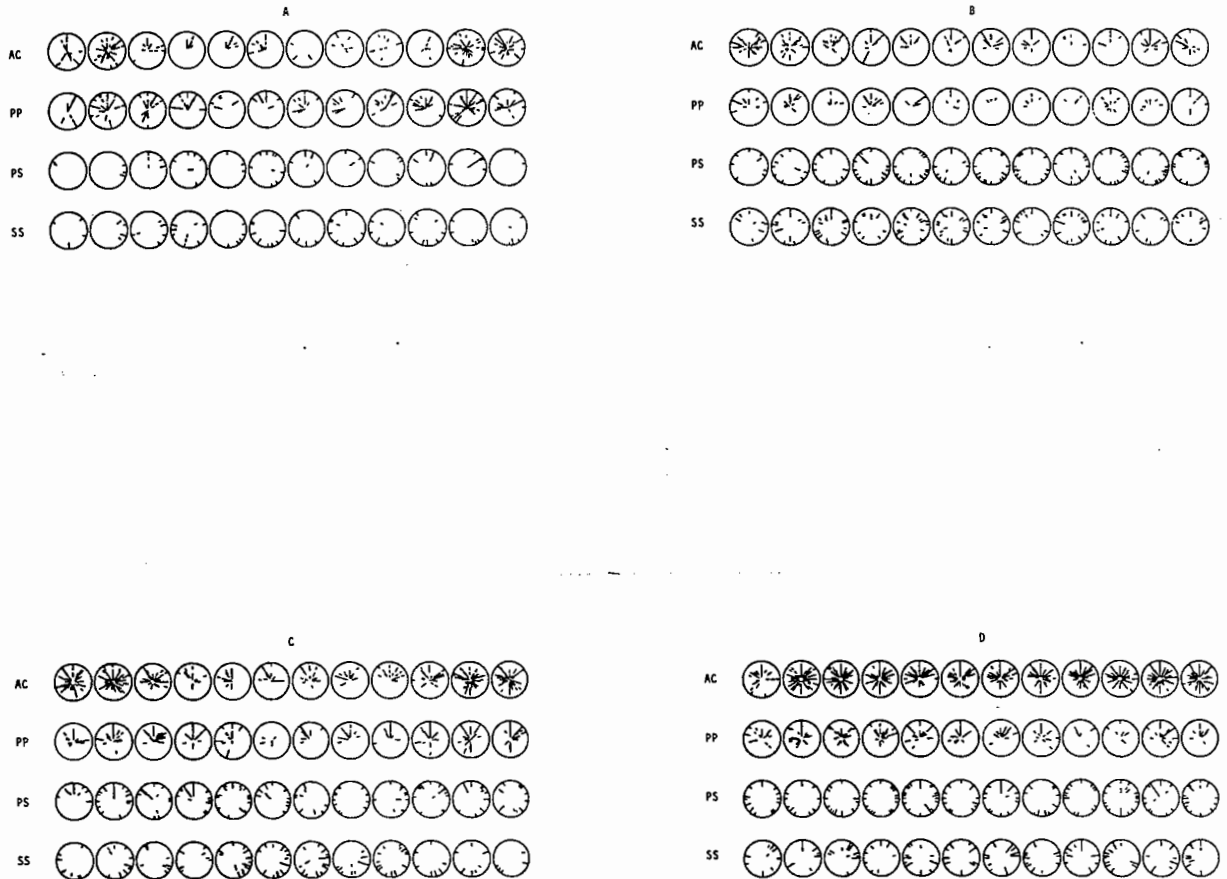


Figure IV-3. Colonization by Antrodia carbonica (AC), Postia placenta (PP), Peniophora spp. (PS), or Stereum sanguinolentum (SS) of Douglas-fir pole sections air seasoned for one (A, B) or two (C, D) years as determined by culturing. Poles from A and C were exposed in 1981 to 1983, while poles for B and D were exposed in 1982 to 1984. Each circle represents combined data of a single 15 cm thick section from 20 pole sections, with the butt of each section on the left.



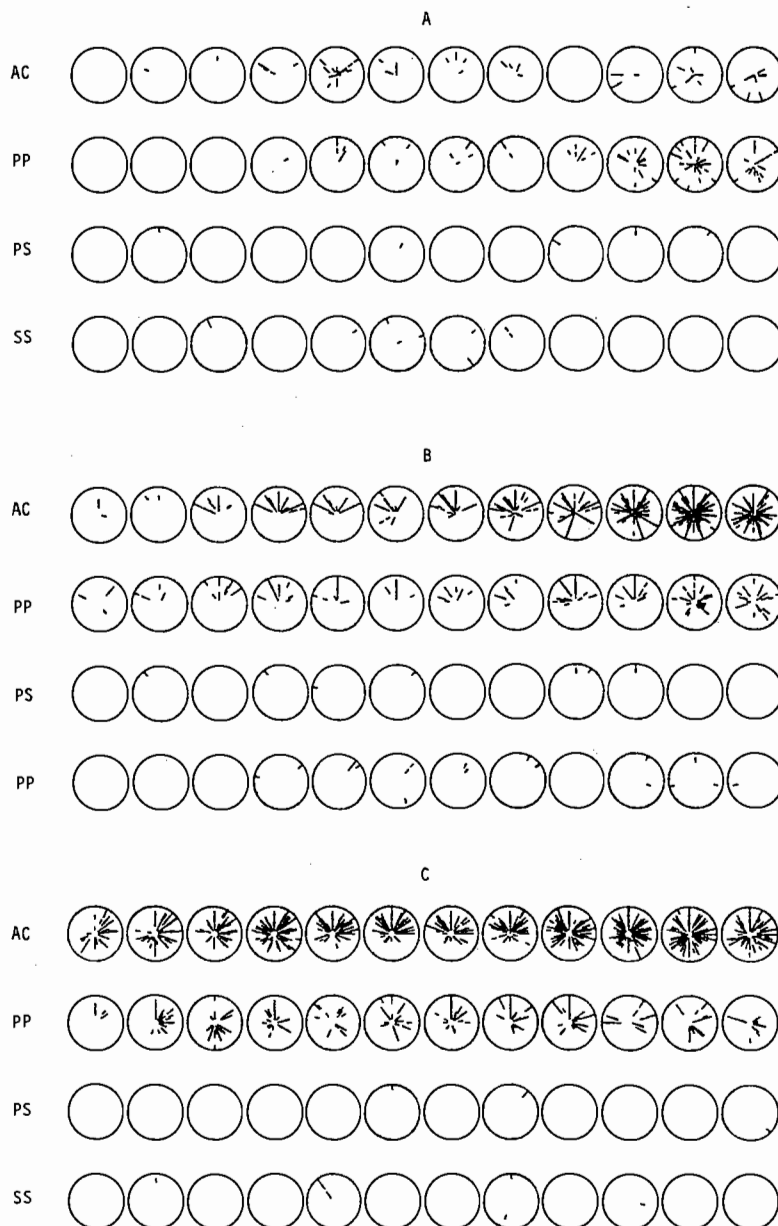


Figure IV-4. Colonization of Douglas-fir pole sections flooded with 20% ammonium bifluoride by Antrodia carbonica (AC), Postia placenta (PP), Peniophora spp. (PS), or Stereum sanguinolentum (SS) one (A), two (B), or three (C) years after treatment.

and should migrate into the wood as the pole seasons, eventually leaving the surface unprotected. This should permit renewed colonization by sapwood colonizers; however, this colonization does not occur, suggesting the moisture content and other sapwood parameters have changed to the degree that typical sapwood colonizers can no longer utilize the substrate. While ABF treatment inhibited sapwood colonizers, it had little effect on colonization by A. carbonica or P. placenta after two or three years of air-seasoning. These fungi appear to colonize through checks which open in the upper surface of the pole. ABF apparently migrates too slowly or at insufficient concentrations to inhibit colonization by these heartwood colonizing organisms.

Along with the general colonization trends noted in the combined samples, colonization also differed at the four exposure sites. In general, colonization was lowest at the Oroville, CA site, reflecting the drier conditions at this site (Figure IV-5). Colonization patterns in the heartwood were similar at Arlington and Scappoose with A. carbonica as the most dominant organism, and P. placenta being relatively infrequent (Figure IV-7,8). Antrodia carbonica was also dominant at the Eugene site, but P. placenta was also abundant at this site (Figure IV-6). The Eugene site is located around a variety of associated forest products industries and wood debris from these operations may provide substrate for growth of P. placenta which increases inoculum potential for this organism.

One parameter which was not explored in the field study was the effect of weather patterns on colonization. While weather data was not available from the actual test sites, weather collecting stations were located near all four exposure sites. Data from these stations indicated that Oroville had the warmest climate over the study period, with average monthly temperatures up to 20°F higher than the other three test sites. Temperatures at the remaining sites were

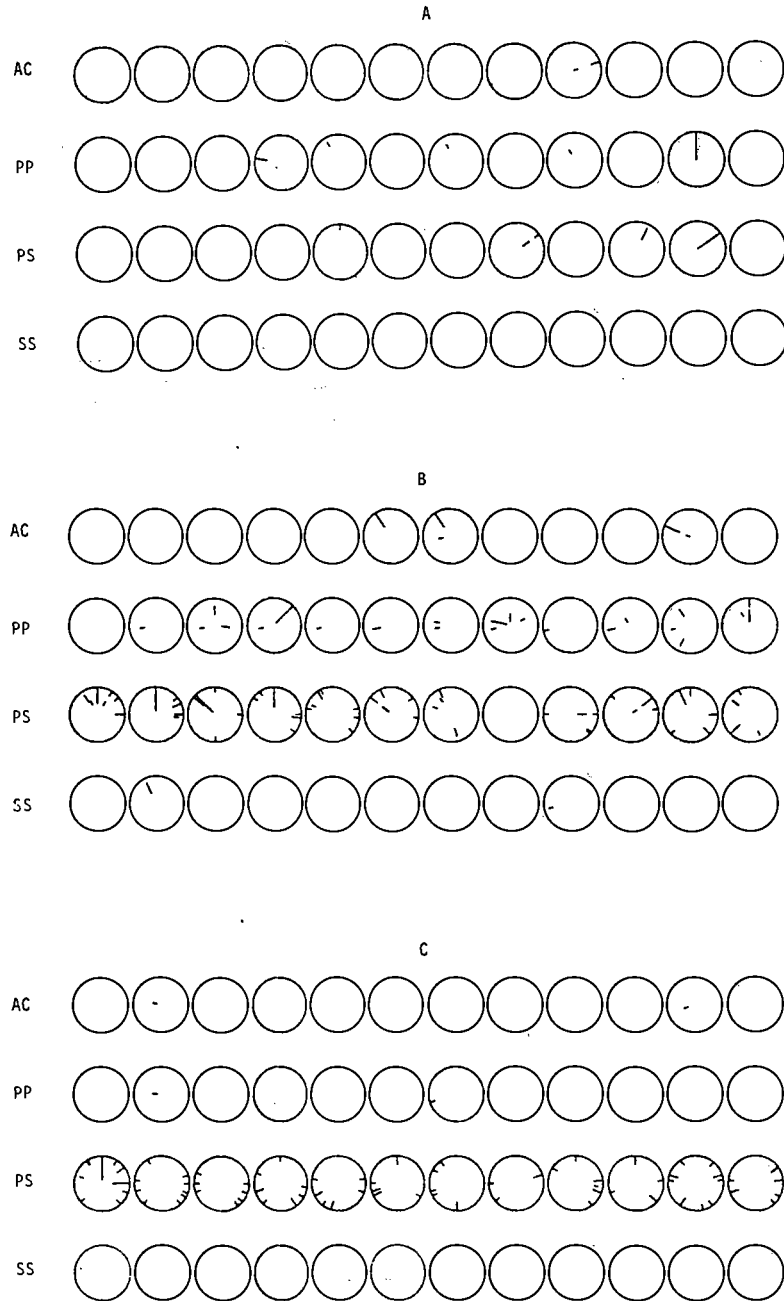


Figure IV-5. Fungal colonization of Douglas-fir pole sections by Antrodia carbonica (AC), Postia placenta (PP), Peniophora spp. (PS), or Stereum sanguinolentum (SS) after one (A), two (B), or three (C) years of air-seasoning at Oroville, CA.

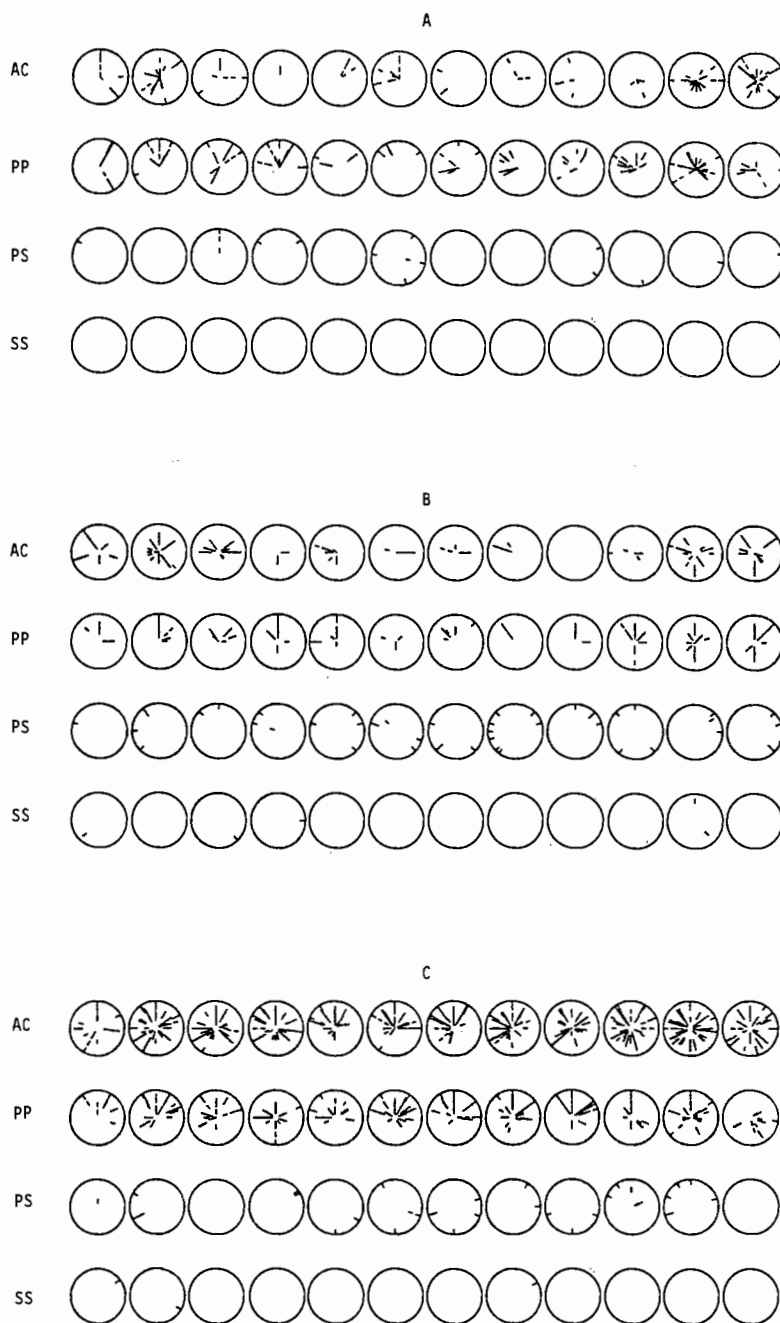


Figure IV-6. Fungal colonization of Douglas-fir pole sections by *Antrodia carbonica* (AC), *Postia placenta* (PP), *Peniophora* spp. (PS), or *Stereum sanguinolentum* (SS) after one (A), two (B), or three (C) years of air-seasoning at Eugene, OR.

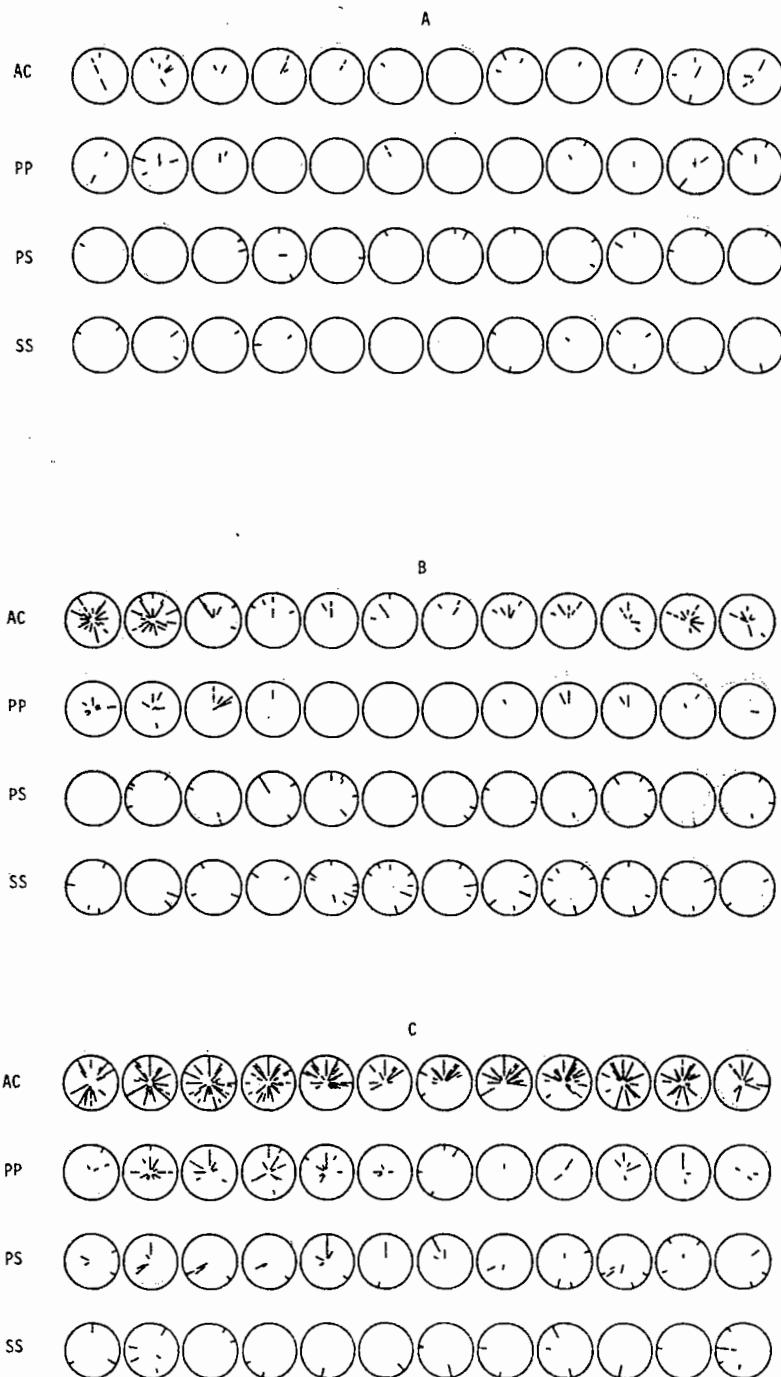


Figure IV-7. Fungal colonization of Douglas-fir pole sections by *Antrodia carbonica* (AC), *Postia placenta* (PP), *Peniophora* spp. (PS), or *Stereum sanguinolentum* (SS) after one (A), two (B), or three (C) years of air-seasoning at Scappoose, OR.

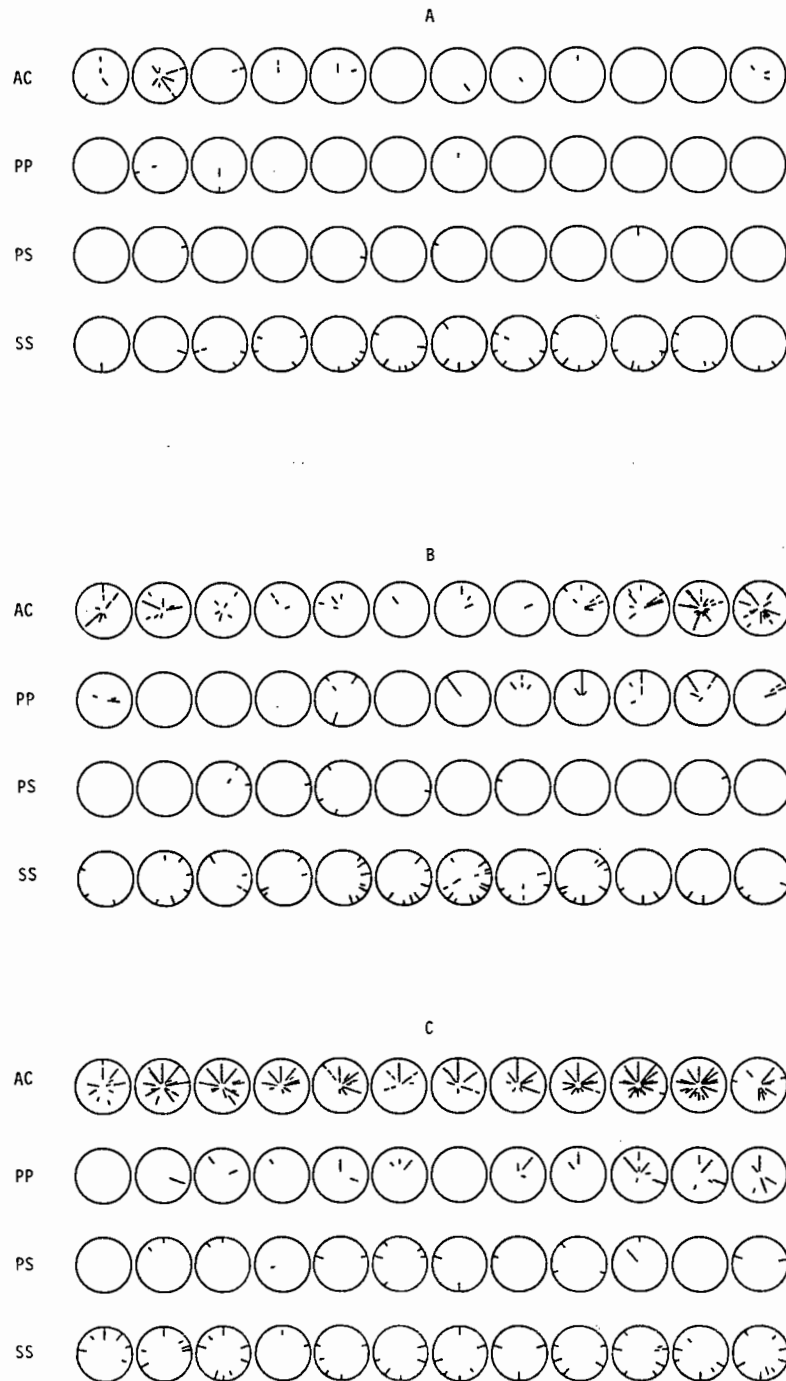


Figure IV-8. Fungal colonization of Douglas-fir pole sections by *Antrodia carbonica* (AC), *Postia placenta* (PP), *Peniophora* spp. (PS), or *Stereum sanguinolentum* (SS) after one (A), two (B), or three (C) years of air-seasoning at Arlington, WA.

fairly uniform. While Oroville had the highest average monthly temperatures, it generally had the lowest average rainfall, although there were occasional precipitation extremes at this test site. Rainfall tended to vary widely at the various sites, suggesting that average monthly rainfall did not provide a relevant measure of the risk of fungal colonization. Further evaluation of the weather data is underway to determine the number of days with both measurable precipitation and temperatures which were conducive to fungal growth. This information should provide a relative measure of the potential risk of colonization for a given test site.

**B. ABILITY OF SODIUM OCTABORATE TETRAHYDRATE TO LIMIT FUNGAL COLONIZATION OF DOUGLAS-FIR POLES DURING AIR-SEASONING**

The decay development studies have clearly shown that Douglas-fir poles are rapidly colonized by decay fungi during air-seasoning. The presence of this microflora places added emphasis on eliminating this fungus at some point during or after the treatment process, before the pole is placed in service. Alternatively, treatments applied shortly after bark removal might help to prevent initial fungal colonization.

Previously, application of a 20% (w/w) solution of ammonium bifluoride shortly after peeling was shown to reduce the degree of fungal colonization ('86 Ann. Rept., pg. 86-93); however, potential users expressed concern about the risk for fluoride contamination of the air-seasoning yard. Because of these concerns, we explored safer diffusible chemicals for protecting air-seasoning. Boron was selected because it is safe, readily available, and has demonstrated ability to control basidiomycetous decay fungi.

The ability of boron to prevent colonization by fungi during air-seasoning was explored by spraying or dipping freshly peeled 1.8-m-long Douglas-fir pole

sections with boron as sodium octaborate tetrahydrate by spraying or dipping each pole section in a variety of combinations (Table IV-2).

Following initial treatment, the pole sections were exposed at the OSU Peavy Arboretum test site. An additional set of poles treated by dipping was exposed at Oroville, CA, a drier test site where fungal colonization patterns differ markedly from those found in the Pacific Northwest.

Pole sections have been sampled annually by removing increment cores from numerous locations around and along each section. These cores have been cultured on a nutrient medium, and any fungi growing from the cores have been examined for characteristics typical of Basidiomycetes, a class of fungi containing many important wood decayers.

Pole sections have been examined after 1 and 2 years of air-seasoning. As expected, untreated pole sections at the Oregon site were experiencing high levels of fungal colonization, with the degree of colonization rising by almost 250 percent between 1 and 2 years (Table IV-2; Figure IV-9,10). Spraying at the time of peeling or 6 months after had little effect on colonization, with levels approaching or exceeding those found in untreated controls. While application of sprays at 0 and 6 months reduced colonization slightly, application at 0 and 12 months provided a higher degree of protection. This difference may reflect a more even replenishment of boron near the surface, providing additional chemical to migrate further into the wood as checks open.

Retreatment at 6-month intervals or dipping in a more concentrated treatment solution at the start of air-seasoning produced the most dramatic reductions in the degree of colonization. Dipping delivers a high concentration of chemical to the wood surface. This chemical can then migrate inward and protect any checks which open as the wood seasons. Respraying at 6-month



Table IV-2. Basidiomycete colonization of Douglas-fir pole sections treated with sodium octaborate tetrahydrate by various schedules and sampled 12 or 24 months after treatment.

Fungal Species	Percentage of cores containing each fungus																
	Spray Schedule <sup>a</sup>																
	Corvallis, OR						Oroville, CA										
	0	0-6	6	0-12	0-6-18	0-6-12-18	Dip	Untreated	Untreated	Dipped	Untreated						
	1 yr.	2 yr.	1 yr.	2 yr.	1 yr.	2 yr.	1 yr.	2 yr.	1 yr.	2 yr.	1 yr.	2 yr.					
Unidentified with clamps	4.1	19.4	4.8	14.3	4.1	27.0	6.4	16.9	5.8	1.6	5.9	8.1	22.6	0.7	0.5	0.3	-
Unidentified without clamps	4.3	13.5	6.2	9.2	5.5	14.1	5.3	10.1	8.3	8.5	9.7	9.1	12.5	3.9	0.5	2.7	1.5
<i>Stereum sanguinolentum</i>	-	-	2.3	0.3	0.7	0.8	1.1	0.5	-	-	-	0.5	-	-	-	-	-
<i>Antrodia carbonica</i>	1.1	3.4	0.3	0.9	0.2	4.8	3.9	3.4	0.7	6.2	0.3	10.8	-	-	-	-	-
<i>Peniophora</i> spp.	2.3	9.1	3.5	16.7	3.1	6.3	13.6	5.9	14.1	0.5	0.4	3.2	2.4	-	-	-	-
<i>Stereum hirsutum</i>	0.7	0.7	-	0.3	0.2	2.8	1.1	0.7	-	-	-	0.5	1.7	-	-	-	-
<i>Postia placenta</i>	0.2	1.2	-	-	-	2.0	0.3	1.1	-	-	3.2	0.5	2.4	-	-	0.5	-
<i>Trametes versicolor</i>	-	-	1.1	-	0.5	0.3	-	-	-	-	-	0.5	0.3	-	-	-	-
<i>Schizophyllum commune</i>	-	0.2	-	0.6	-	-	1.9	-	-	-	-	0.3	1.0	-	-	4.9	-
<i>Sistotrema brinkmanii</i>	0.5	-	0.8	-	0.5	3.5	-	0.5	-	0.2	1.6	0.5	4.9	0.3	0.3	0.5	-
<i>Gloeophyllum saepiarium</i>	-	0.2	-	1.2	-	1.5	-	-	-	-	-	-	0.3	-	-	-	-
<i>Heterobasidium annosum</i>	-	-	-	-	-	-	-	0.2	-	-	-	-	-	0.3	-	-	-
Total Basidiomycetes	13.1	47.8	18.8	43.4	14.6	63.1	33.6	39.2	29.0	8.0	27.8	23.3	59	5.2	1.3	8.8	1.5
No. cores examined	444	408	372	336	419	336	360	444	396	436	252	407	288	408	371	408	348

<sup>a</sup> Pole sections were sprayed with 10% sodium octaborate tetrahydrate dipped in a 20% BAE solution at the start of air seasoning at 0, 6, 12, and 18 months or left unsprayed.

**Frequency of isolation of basidiomycete  
from boron treated pole sections**

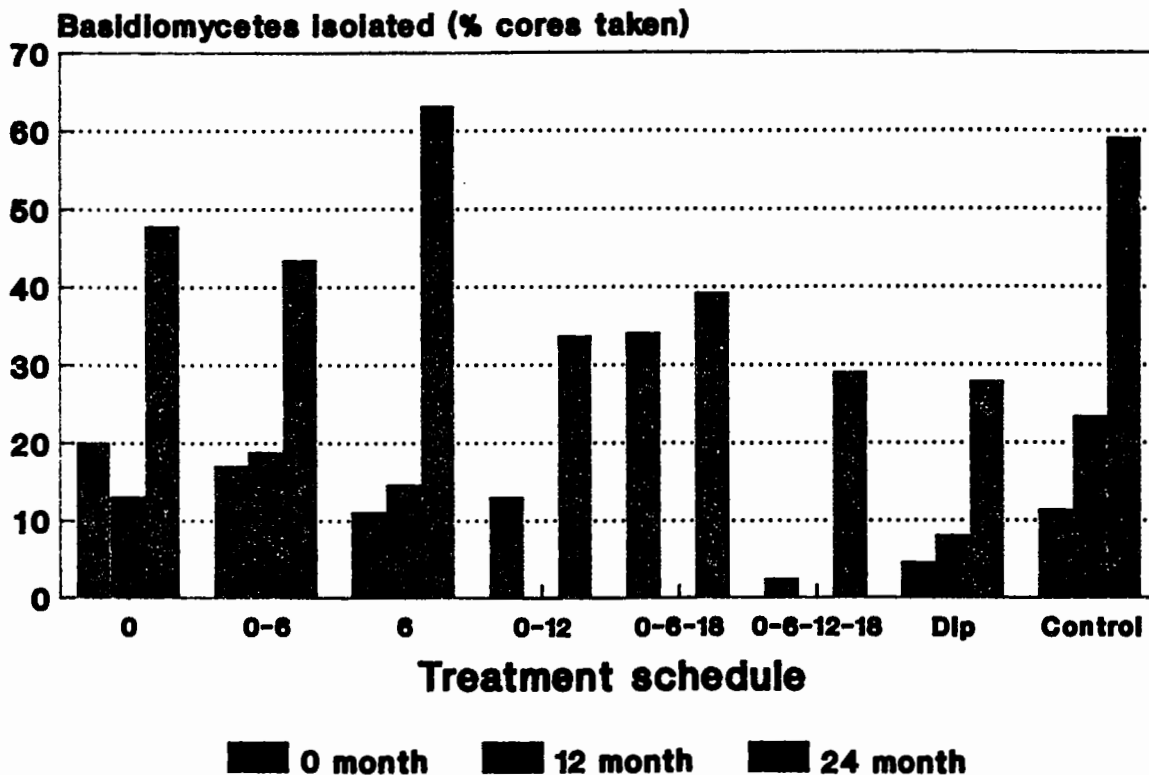


Figure IV-9. Percentages of increment cores removed from Douglas-fir pole sections treated with sodium octaborate tetrahydrate by dipping or spraying which contain Basidiomycetes after 1 or 2 years of air-seasoning near Corvallis, OR.

**Frequency of isolation of basidiomycete  
from boron treated pole sections**

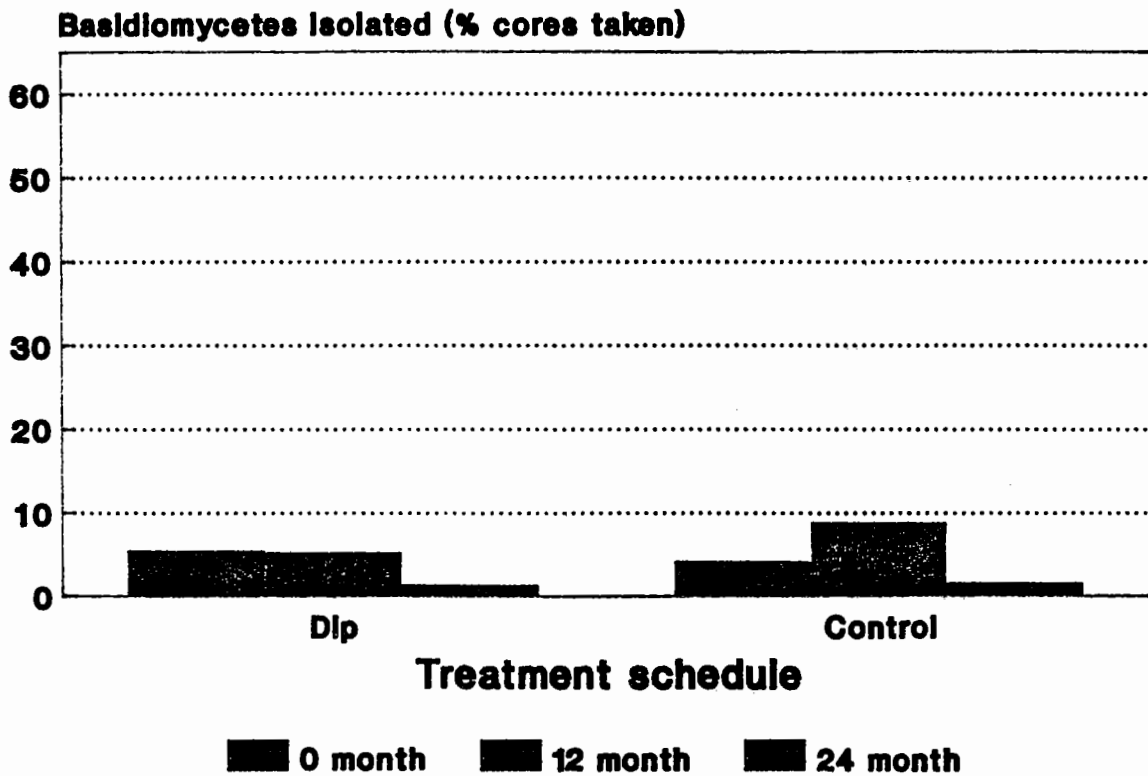


Figure IV-10. Percentage of increment cores removed from Douglas-fir pole sections dipped in a 20% (BAE) solution of sodium octaborate tetrahydrate which contain Basidiomycetes after 1 or 2 years of air-seasoning at Oroville, CA.

intervals may provide the same degree of replenishment, although this practice would certainly be more labor intensive and provide the potential for more chemical exposure to workers and the environment. Boron is an extremely safe compound; however, efforts still must be made to minimize the potential for environmental contamination and human exposure. Our dip tests used a 20% boric acid equivalent (BAE) treating solution; however, higher concentrations could be used to provide additional protection against fungal invasion.

Both treated and untreated pole sections exposed at Oroville, CA, experienced declines in the degree of colonization between 1 and 2 years (Figure IV-10). These results reflect those found previously, illustrating the beneficial effects of Oroville's extremely hot, dry summers which are not conducive to fungal colonization. While application of boron by dipping was associated with slight reductions in the degree of colonization, it is doubtful that such treatments are cost effective under conditions at this site.

The results after 2 years suggest that application of boron by initial dipping of a concentrated solution or regular respraying at 6-month intervals with more dilute solutions can reduce the potential for colonization by fungi during air-seasoning. While boron treatments would not completely eliminate the need for some type of sterilization process during preservative treatments, reductions in the degree of colonization would decrease the possibility that a fungus might survive the sterilization process. In addition, delays in fungal colonization would reduce any potential effects on wood strength properties. Additional pole sections will be evaluated this summer after 3 years of air-seasoning.

C. ABILITY OF CURRENT TREATMENT PRACTICES TO ELIMINATE DECAY FUNGI FROM DOUGLAS-FIR POLES

1. Internal temperatures during Cellon treatment of Douglas-fir poles:

The high frequency of Basidiomycetes in air-seasoned Douglas-fir pole places added importance on the need to sterilize the wood at some point during or after the preservative treatment process. In previous reports, we have detailed the internal temperatures found in Douglas-fir pole sections during treatment with pentachlorophenol in oil or ammoniacal copper arsenate ('88 Ann. Rept., pg. 98-106). The thermocouple data from these treatments is currently undergoing more detailed analysis in cooperation with the Department of Chemical Engineering to improve the heating prediction curves and provide more precise guidelines for insuring sterilization of utility poles.

This past year we examined internal temperatures achieved in Douglas-fir poles during treatment by the Cellon process. While this treatment is now infrequently used, many poles treated by this process are already in service and we wondered if these poles would be expected to have higher levels of fungal colonization than poles treated using conventional pentachlorophenol in heavy oil. The Cellon process consisted of a vacuum (15 min.), purge (10 min.), vacuum (35 min.), fill and begin pressure period (2 hrs.), press charge (9 hrs. at 82.2°C), empty cylinder (3 hrs. at 82.2°C), Vapor recovery (3.5 hrs. at 85.0-87.8°C), and final vacuum (3 hrs.). An oil wash was then applied to remove any pentachlorophenol crystals on the wood surface. This wash consisted of filling the vessel (1 hr.), raising oil temperature (82.2°C), pumping out (1.5 hr.), drawing a vacuum (0.5 hr.), steaming (4-5 hrs. at 110°C), venting (0.5 hr.) and pulling a final vacuum (1.5 hrs.).

The results indicated that temperatures of 122°F or greater were maintained for 15 hours at the pith center of the pole sections (Figure IV-11). None of the thermocouples reached 65.6°C for 75 minutes, the suggested time/temperature period for sterilization. Despite this apparent failure to achieve adequate heating conditions, increment cores removed from these poles after treatment contained no decay fungi. The absence of fungi in poles which were not adequately heated during treatment suggested that other factors in the treatment process might be influencing fungal survival.

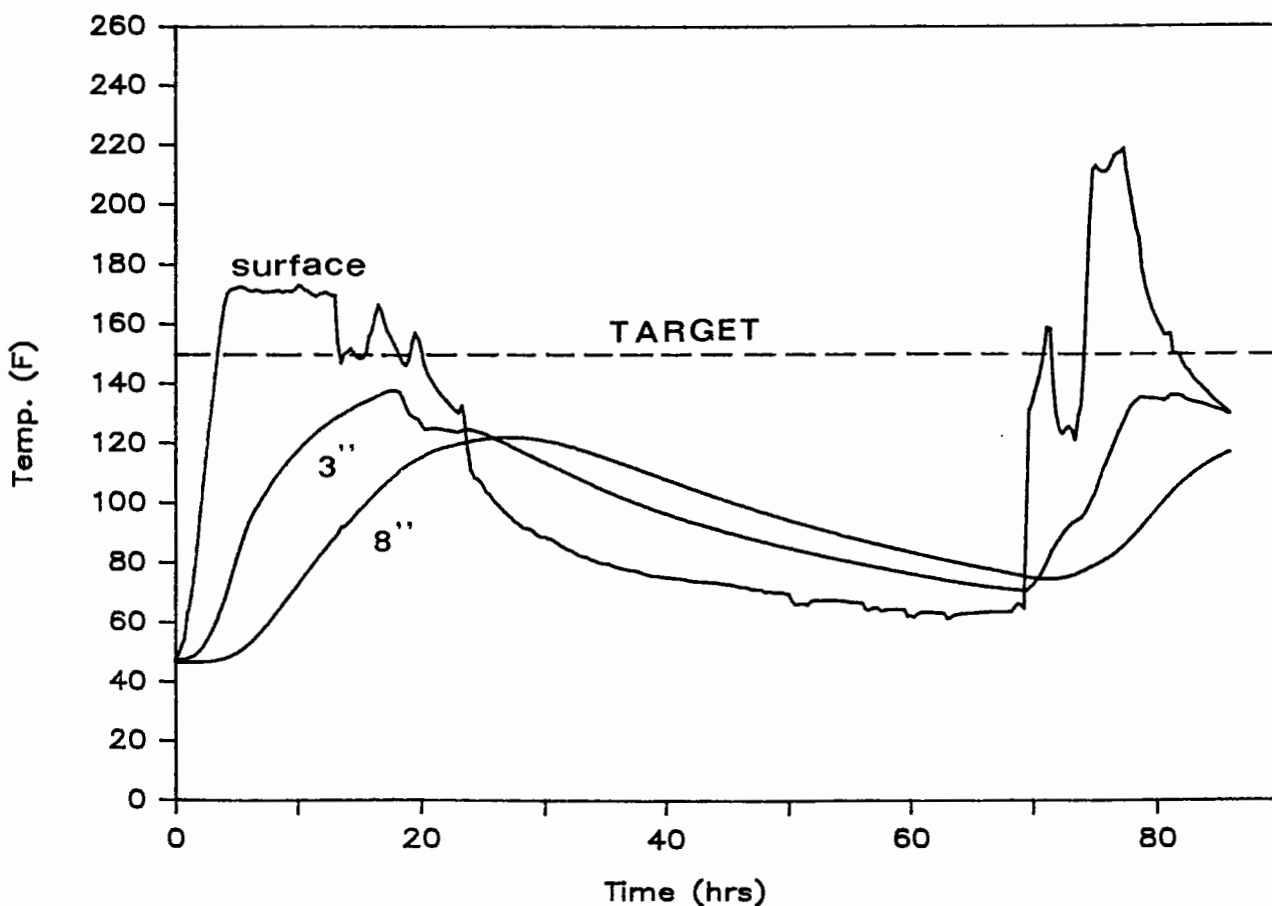


Figure IV-11. Internal temperature development at selected depths in Douglas-fir pole sections during preservative treatment by the Cellon process.

To confirm this effect, thirty-four increment cores were removed along the length of two Douglas-fir poles before and after treatment by the Cellon process. These cores were cultured for the presence of decay fungi. The results showed that the poles were moderately colonized by decay and non-decay fungi prior to treatment, but no fungi were isolated from the wood following treatment (Table IV-3). The absence of fungi following treatment suggests that some volatile component of the preservative system may be penetrating the heartwood, effecting sterilization far beyond the depth of actual preservative penetration.

The Cellon process uses a butane/isopropyl ether solvent mixture (95:5). The effect of this solvent mixture on fungal survival was investigated using Douglas-fir pole sections (20 cm diameter by 30 cm long) which were prepared for treatment by drilling a small diameter hole longitudinally into the wood to the center of the pole and inserting a 5-cm-long wooden dowel which was infested with Postia placenta. The hole was plugged with a second dowel and the top was sealed with 2 coats of an epoxy end-sealer to minimize solvent penetration. These sections were then exposed to varying periods of vacuum and pressure using the butane/isopropyl ether mixture. The maximum time period to which the wood was exposed to solvent was 4 hours. Following treatment, the dowels were removed from the pole sections, aerated to release residual chemical vapors, and cultured on nutrient agar to determine if the fungus survived the treatment conditions. Only one fungal-infested dowel survived chemical exposure; however, this dowel was in a section exposed to one of the longer pressure periods (Table IV-4). The variability makes it difficult to positively claim that the solvent affects fungal survival, but the results suggest that vapor penetration from the solvent may play a major role in sterilization of Cellon treated wood. Many utilities have commented on the presence of residual solvent near the pith of Cellon-

**Table IV-3.** Fungal population in two Douglas-fir poles before and after treatment by the Cellon process.

Pole #	Total cores removed	Cores with decay/nondecay fungi (%) <sup>a</sup>	
		Prior	After
1	34	18 <sup>97</sup>	0*
2	34	50 <sup>91</sup>	0*

<sup>a</sup> Decay fungi identified were S. sanguinolentus or S. brinkmanii. These were observed at 2.5 to 10 cm from the depth. The superscript denotes nondecay fungi.

**Table IV-4.** Fungal survival in Douglas-fir pole sections pressure treated with a Butane 5% isopropyl ether co-solvent.

Treating schedule	% of implanted <u>P. placenta</u> infested dowel
1/2 hr. vacuum 1 hr. press @ 110 psi and 145°F 2 1/2 hr. vapor recovery (20 psi each, 30 min.) 1 hr. final vacuum	0
1/2 hr. vacuum 2 hr. press @ 100 psi and 145°F 2 1/2 hr. vapor recovery (20 psi each, 30 min.) 1 hr. final vacuum	0
1/2 hr. vacuum 3 hr. press @ 100 psi and 140°F 2 hr. vapor recovery (20 psi each, 30 min.) 1 hr. final vacuum	50
1/2 hr. vacuum 4 hr. press @ 100 psi and 140°F 2 hr. vapor recovery (20 psi each, 30 min.) 1 hr. final vacuum	0

treated poles which were cut for removal or other maintenance. Further tests are now underway to evaluate the effect of exposure to ambient temperature butane/isopropyl ether on survival of P. placenta or Antrodia carbonica in small wooden dowels.

2. Effect of elevated temperatures on survival of Basidiomycetes in Douglas-fir heartwood: In earlier reports, we described results of temperature exposures of Postia placenta and Antrodia carbonica in Douglas-fir heartwood



blocks ('85 Ann. Rept., pg. 96-100). These results suggested that P. placenta exhibited some tolerance to elevated temperatures; however, both fungi were controlled upon prolonged exposure to higher temperatures. Since these tests, evaluation of thermocouple data from ammoniacal copper zinc arsenate (ACZA) treatments have suggested that poles are exposed to much lower temperatures for long time periods, yet sampling of these poles revealed the absence of Basidiomycete colonization following treatment. These results suggest that longer exposures to lower temperatures may also provide a measure of sterilization.

To investigate this prospect, Douglas-fir heartwood blocks (2.5 by 2.5 by 5.0 cm long) were inoculated with either Antrodia carbonica or P. placenta and incubated at 28°C for 6 weeks. Groups of three blocks were then sealed in air-tight plastic bags and submerged in water baths maintained at 48.9, 51.7, 54.4, 57.2, 60, 62.8 65.6, 68.4, or 71.1°F. One bag containing 3 blocks was removed at each selected interval and a 0.5-cm section was cut from the center of each block. This section was cut into 16 square cubes, and the four center cubes were plated onto a malt extract agar. These cubes were observed over a four week period for the presence of the test fungus, which was used as the measure of fungal survival.

The results indicate that both fungi were capable of surviving exposures of 48 and 1 hour at 48.9°C and 65.6°C, respectively (Table IV-5; Figure IV-12). In general, A. carbonica was more heat tolerant than P. placenta between 51.7 and 60°C. Both fungi produce thick-walled chlamyospores which make these species more resistant to adverse conditions. The tests also showed that prolonged exposure at temperatures ranging from 54.4 to 60°C eliminated both fungal species. Previous tests have shown that ACZA treatments achieved

temperatures within this range for this period. The results suggest that additional examination of the sterilization requirements for the various commercial preservative treatments is warranted. Further tests are now underway using S. sanguinolentum and Peniophora spp. to determine their relative temperature tolerances of these surface colonizers.

**Table IV-5.** Effect of elevated temperature exposure on survival of Postia placenta or Antrodia carbonica in Douglas-fir heartwood blocks.

Exposure Temperature (c)	Maximum survival time (hr.)	
	<u>A. carbonica</u>	<u>P. placenta</u>
48.9	48	48
51.7	48	24
54.4	15	12
57.2	12	6
60.0	6	4
62.8	2	1.5
65.6	1	1
68.4	0.25	0.5
71.1	0.25	0.25

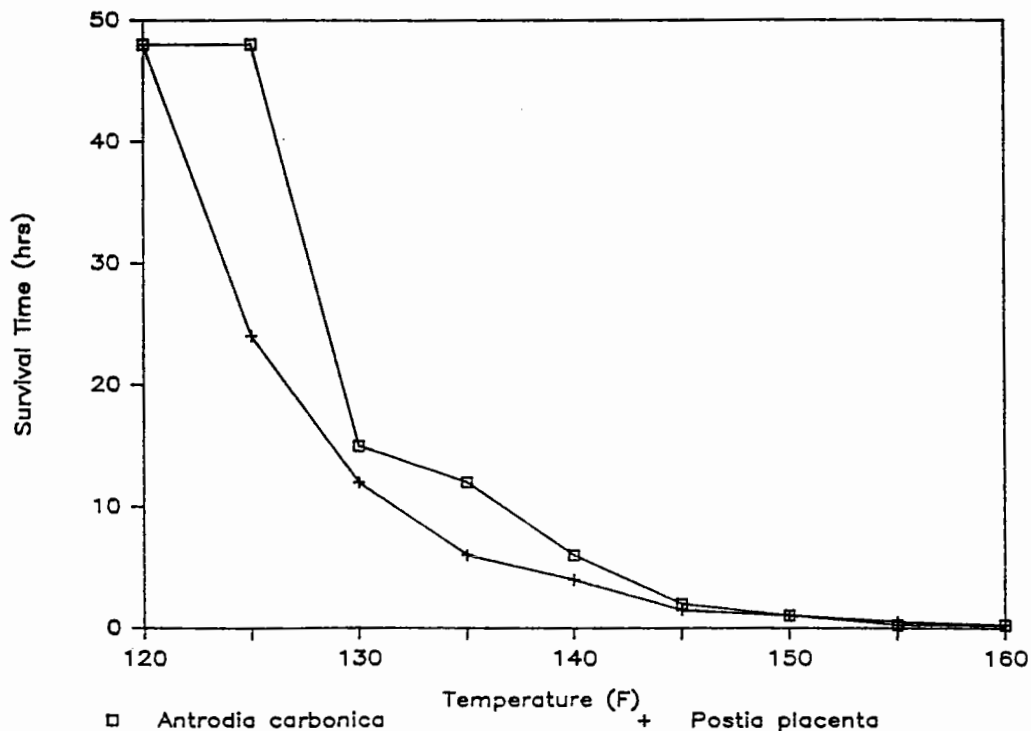


Figure IV-12. Ability of A. carbonica or P. placenta established in Douglas-fir heartwood to survive exposure to temperatures ranging from 48.9 to 71.1°C.

**OBJECTIVE V****PERFORMANCE OF MODIFIED GROUNDLINE WRAP SYSTEMS  
ON UNTREATED DOUGLAS-FIR SAPWOOD**

Preservative treatment of Douglas-fir poles generally produces a well treated outer core of sapwood that is resistant to surface decay. This protection derives from the relatively high chemical levels per unit volume of treated wood, compared to other wood species. In certain applications such as poles in concrete or poles in extreme decay hazards, however, the use of supplemental groundline protection may be advisable.

Until recently, groundline wraps were composed of mixtures of creosote, pentachlorophenol, and various water soluble, inorganic pastes. The water soluble components presumably diffuse for short distances into the wood to control any decay fungi present, while the oilborne compounds remain on the surface and provide a barrier against renewed fungal invasion. Previous studies have shown that the various groundline wrap systems provided a high degree of surface protection for southern pine and Douglas-fir. As a result, many utilities routinely apply groundline wraps during routine pole maintenance.

Increasing sensitivity to public concerns about pesticide usage and the categorization of creosote, pentachlorophenol, and certain inorganic arsenicals as restricted-use pesticides have recently led many chemical manufacturers to alter existing groundline wrap systems to remove one or more components and substitute less toxic alternatives. The most common substitutes include copper naphthenate in place of creosote and pentachlorophenol, and boron in place of the inorganic salts. Both of these compounds have long histories as successful wood preservatives in both the United States and other countries, but their effectiveness in groundline wrap systems have not been tested. For this reason,

the following trial was established to compare the performance of these modified systems with existing industry standards.

Forty-two untreated, freshly peeled Douglas-fir posts (25 to 30 cm in diameter by 1.8 m long) were obtained from cooperating wood treaters. These sections were stored above ground for 7 to 10 months to permit some microbial colonization and seasoning to occur.

The pole sections were then evaluated for resistance to Pilodyn pin penetration using an 18 joule Pilodyn equipped with a 3 mm diameter pin. Pilodyn tests were performed at 3 equidistant points around the posts at intended groundline. Moisture meter readings were taken at a depth of 2.5 cm at sites immediately adjacent to the Pilodyn test sites, using a Delmhorst electrical resistance moisture meter. These moisture content readings were used to correct Pilodyn readings.

The poles sections were then treated with one of the following groundline wrap systems:

1. CUNAP-WRAP (Tenino Wood Preservatives, Inc.): a copper naphthenate solution (2.0 % as Cu) on an absorbent pad protected by a plastic barrier. This wrap is completely prepared and is applied by peeling of the backing and applying directly to the pole.

2. CuRap 20 (Chapman Chemical Co.): a paste containing 40% borax (sodium octaborate tetrahydrate) and 18% copper naphthenate (2.0% as Cu).

3. PolNu 15-15 (Chapman Chemical Co.): a mixture containing 12.9% pentachlorophenol, 15.5% creosote, and 1.5% chlorinated phenols to serve as a standard.

4. Pol-Nu (Chapman Chemical Co.): a grease containing 10.2% pentachlorophenol and serving as a standard.

5. Cop-R-Rap (Osmose Wood Preserving Inc.): a 19.25% copper naphthenate paste (2% as Cu).

6. CRP-82631 (Osmose Wood Preserving Inc.): a paste containing copper naphthenate (2% as copper) in 45% sodium fluoride.

7. Untreated pole sections.

Six poles were treated with each formulation and all poles were set to a depth of 45 cm at the OSU Peavy Arboretum test site. At one-year intervals, the sections will be excavated and increment cores will be removed from three equidistant points sites at the groundline and 15 cm above or below the groundline. The cores will be cultured on nutrient media for the presence of decay fungi. Additional cores from the same sites will be removed for chemical analysis to determine the relative depth of penetration of the various chemicals.

In addition to microbial and chemical analysis of wood from the posts, small wood sticks (0.6 by 1.25 by 15.0 cm long) will be inserted to a depth of 7.5 cm in the soil surrounding the pole sections. Sticks will be inserted at three points around the pole, 7.5 and 15.0 cm away from the poles. Any chemical migrating away from the posts should come in contact with these sticks which will be removed at 6-month intervals and analyzed for residual chemical levels. This evaluation is intended only as a qualitative assessment of the potential for chemical migration from the various wrap systems. More quantitative studies are already underway by other research groups to evaluate potential leaching from groundline wrapped southern pine poles.