

ABSTRACT

Evaluation of previously established field trials of remedial internal treatments demonstrates the continued performance of chloropicrin, Vorlex, and methylisothiocyanate (MITC). While the degree of protection afforded by these treatments has declined with time, residual fungitoxic levels remain in many tests. Field trials of gelatin encapsulated MITC indicate that gelatin had no negative effect on fumigant performance even when no water was added at the time of treatment.

Closed tube bioassays, chemical analyses, and culturing of Douglas-fir and southern pine poles treated with glass encapsulated MITC (MITC-Fume) indicate that this chemical is outperforming metham sodium 3 years after application. While the glass vials lost chemical very slowly, the slow release rate did not appear to adversely affect MITC performance.

Trials to evaluate the performance of fused borate rods were sampled after 1 or 2 years of exposure. Chemical analysis of cores removed from the test poles revealed that none of the treatments contained boron at levels which would be considered adequate for arresting or preventing colonization by wood decay fungi. Interestingly, boron levels in poles exposed in Hilo, Hawaii were highest above the treatment hole, suggesting that some upward diffusion of this chemical is possible. The low boron levels in these poles are reason for concern, since a number of utilities are considering the using this formulation for remedial treatment at the groundline.

Evaluations of new solid fumigants are progressing. Trials with Basamid indicate that the addition of copper compounds improved the rate of decomposition to produce MITC. Simultaneous addition of copper sulfate and Basamid may be useful for accelerating the decomposition of this compound, making it practical for control of internal decay fungi.

Trials have been established to evaluate the performance of gelled and pelletized metham sodium and a sodium fluoride/boron rod. These trials will be evaluated in future reports. A third field trial to evaluate the performance of a copper naphthenate/boron paste for internal treatment of Douglas-fir poles is currently be evaluated to determine chemical levels 3 years after treatment.

The performance of gelled metham sodium was further evaluated under laboratory conditions to better understand the performance of this chemical. Gelled metham sodium provided improved fungal control in comparison with liquid metham sodium and appeared to produce increased MITC levels under a variety of test conditions. The improved performance of this formulation may reflect the ability of the gell to retain moisture for longer periods of time than the liquid metham sodium formulation. Further studies of this formulation are underway.

Laboratory studies were also performed to evaluate the effects of various additives on the performance of Basamid. Once again, the addition of

copper compounds enhanced the production of MITC. A number of other compounds shifted decomposition to the production of carbon disulfide and carbonyl sulfide, two less fungitoxic compounds. Further studies are underway to identify non-sulfur products which may provide some protection against wood decay fungi.

Evaluations of the effects of artificial voids on performance of fumigants in Douglas-fir poles indicate that voids had little or no effect on fumigant distribution. As a result, fumigant treatment of solid wood around voids represents a viable strategy for improving pole service life.

Evaluation of timbers treated with metham sodium indicate that detectable levels of MITC were present one year after treatment. These timbers will be evaluated in subsequent years to determine the protective period provided by fumigants in sawn material.

We continue development of a fumigant movement model using data previously developed on MITC. This year, we evaluated a previously developed system, ANSYS. Results of preliminary trials are similar to data previously developed on MITC-Fume treated poles and indicate that modeling MITC movement should be possible. Further trials are underway to confirm and expand this model.

The effect of wood moisture content, temperature and wood species on metham sodium decomposition was investigated under laboratory conditions. The efficiency of decomposition to MITC

varied widely, but was most affected by temperature and wood moisture content. The results suggests that there is considerable potential for improving decomposition efficiency to enhance performance of this fumigant. Further studies to characterize the relationship between chemical content of the wood species and decomposition are underway.

Field trials to identify safer treatments for preventing decay of cedar sapwood and protecting field drilled bolt holes are continuing. Diffusible treatments continue to provide excellent protection for field drilled bolt holes.

A study to develop estimates of the extent of decay above the groundline in Douglas-fir poles in the Pacific Northwest is underway. The data from this study will be used to develop estimates of the potential for damage and provide some insight into the extent of this problem.

Studies to develop guidelines for sterilization of Douglas-fir poles following air-seasoning are continuing. Evaluations of internal temperature development during kiln-drying were completed this year and indicate that internal temperatures during typical pole drying schedules were more than adequate for achieving sterilization. Further evaluations of the data are underway to develop reliable heating curves for this process.

Evaluations of groundline preservative systems have been established at Corvallis, OR and Merced, CA. The results indicate that all of the formulations are moving well through the wood in a manner similar to that found with pentachlorophenol-based systems.

Chemical levels in some treatments; however, are beginning to decline 30 months after treatment. Studies are now underway to establish thresholds for combinations of the various formulations.

Copper naphthenate treated western redcedar stakelets continue to perform well in fungus cellar trials. Stakes weathered prior to treatment are degrading slightly faster, while freshly sawn stakelets continue to perform well. Field trials have also been established to evaluate the performance of copper naphthenate treated Douglas-fir utility poles in California and Oregon. The chemical levels and fungal colonization will be monitored in these poles to provide a guide to performance of this chemical in western wood species.

ACKNOWLEDGEMENTS

The cooperative depends heavily upon the assistance of others in utilities, wood treatment facilities and allied disciplines to complete the outlined tasks. These contributions are essential for the success of the program and we gratefully acknowledge the numerous groups which have assisted us in the past year. We look forward to continued collaboration to enhance the performance of wood in utility systems.

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OBJECTIVE I

DEVELOP SAFE, ENVIRONMENTALLY ACCEPTABLE CHEMICALS FOR CONTROLLING INTERNAL DECAY OF WOOD POLES

A. EVALUATE PREVIOUSLY ESTABLISHED TESTS OF VOLATILE REMEDIAL INTERNAL TREATMENTS

The Cooperative Pole Research Program has established a variety of field trials to evaluate the performance of various remedial treatments (Table I-1). These trials are evaluated on an annual basis by removing increment cores for culturing, bioassays, or chemical analysis. The results of these trials provide valuable information on chemical efficacy and estimated protective period provided by various formulations. At present, 15 field trials are under active evaluation (Table I-2).

1. Douglas-fir poles treated with Vapam, Vorlex, or chloropicrin in 1969: The initial Bonneville Power Administration test line located near Corvallis, Oregon to evaluate Vapam, Vorlex, or chloropicrin was not inspected in 1990 or 1991. Many of the original poles in this trial were removed due to the presence of advanced decay and the remainder of the poles were retreated with Vapam in 1987. Because of the low numbers of poles in this trial, we have decided to discontinue annual sampling of these structures.

2. Douglas-fir poles treated in 1977 with allyl alcohol, methylisothiocyanate or Vorlex: Douglas-fir poles containing small decay pockets were treated with 1 liter of allyl alcohol, 20%

methylisothiocyanate (MITC) in diesel oil, 100% MITC, or Vorlex near the groundline. The actual dosages of 100% MITC treated poles are difficult to determine due to difficulties with melting this chemical. The allyl alcohol poles were retreated with metham sodium in 1987.

The poles were treated in 1977 and have been evaluated annually by removing increment cores from 3 equidistant sites around the pole 0, 1.2, 1.8, and 2.4 m above the groundline. One set of cores was cultured on malt extract agar for the presence of basidiomycetes, a class of fungi containing many important wood decayers. A second core from each location was evaluated using a closed-tube bioassay for the presence of residual chemicals. The outer and inner 2.5 cm of each core were individually placed into test tubes containing an actively growing culture of a test fungus, Postia placenta, on malt extract agar. The tube is sealed and inverted so that any residual fumigant in the wood vaporizes and comes in contact with the actively growing fungal mycelium. The growth of the test fungus in comparison with growth of similar cultures in the absence of wood provides a relative measure of degree of inhibition provided by a given chemical. This test is only useful for volatile chemicals, but

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 ₅₀)	Source
Timber Fume (Chloropicrin)	Trichloronitromethane "	96%	205 mg/kg	Osmose Wood Preserving Inc. Great Lakes Chemical Co.
Wood Fume Chap Fume	Sodium n-methyldithio- carbamate "	32.1	1700-1800 mg/kg	Osmose Wood Preserving Inc. Chapman Chemicals Inc.
Vorlex	20% methylisothiocyanate 80% chlorinated C ₃ hydrocarbons	99%	538 mg/kg	NorAm Chemical Co.
MITC-FUME	methylisothiocyanate	96%	305 mg/kg	Osmose Wood Preserving Inc.

Table I-2. Active field trials evaluating the performance of selected remedial treatments.

Test Site	Chemicals Evaluated	Date Installed
Santiam-Toledo (BPA)	NaMDC, Chloropicrin, Vorlex®	1969
McGloughlin-Bethell (PGE) I	MITC, Vorlex	1977
Peavy Arboretum	field drilled bolt hole treatments	1981
Peavy Arboretum	cedar pole sprays	1981
Dorena Tap (BPA)	encapsulated Chloropicrin	1982
Hamburg Line (NYSEG)	encapsulated MITC	1982
McGloughlin-Bethell (PGE) II	encapsulated MITC	1983
Alderwood Tap (BPA)	encapsulated MITC	1987
Peavy Arboretum	encapsulated MITC (MITC-fume)	1987
Peavy Arboretum	Basamid	1988
Peavy Arboretum	copper naphthenate/boron	1989
Peavy Arboretum	Impel Rods	1989
Hilo, Hawaii (CSI)	Impel Rods	1990
Central Lincoln (CLPUD)	Impel Rods	1990
Peavy Arboretum	Gelled NaMDC	1992

previous trials have shown that the method is nearly as sensitive as gas chromatographic analysis.

Culturing of cores revealed that the levels of basidiomycete colonization remain low, but had increased slightly in both MITC and Vorlex treatments (Figure I-1). The 20% MITC continues to

experience higher levels of colonization than the 100% MITC treatment, but these levels are similar to those found with Vorlex (Table I-3). Three of five 20% MITC-treated poles contain at least one basidiomycete, in comparison with 2 of 5 Vorlex-treated poles. In addition, the percentage of basidiomycete infested cores was over 50% greater in the 20% MITC

treatment. Vorlex contains 20% MITC in chlorinated C₃ hydrocarbons and should perform comparably with 20% MITC in diesel. Previous studies have shown that Vorlex provides 17 to 20 years of protection against renewed fungal invasion when applied at a dosage of 1 liter per pole. The current results validate these earlier findings.

Closed-tube bioassays continue to show only minimal evidence of residual fungitoxic activity (Table I-4). The degree of inhibition as a % of control continues to remain at approximately 50%. These values suggest that the fumigants continue to provide some degree of residual protection. While this level is not sufficient to provide complete

protection against actively growing fungal mycelium, it may be sufficient to prevent spore germination in the treated wood and this residual protection may help to explain the continued low levels of basidiomycete colonization experienced in these trials.

The results indicate that MITC can provide excellent long-term protection in Douglas-fir heartwood at levels which are comparable to those achieved with Vorlex, one of the most effective fumigants previously tested.

3. New York field test of encapsulated fumigants: In 1981, twenty-four 9-year-old chromated copper arsenate treated Douglas-fir poles in a line located near Hamburg, New York were found to be

Year	Untreated	Number of poles containing decay fungi			
		Allyl Alcohol/Vapam	Vorlex	Methylisothiocyanate	
				20% ²	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 ⁵	6 ⁶	0 ⁴	1 ⁵	0 ⁵
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	0	2	1
1989	3	3	1	2	0
1990	-	-	1	1	0
1991	-	-	2	3	1

¹Poles 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.

²Diluted in diesel oil.

³These poles were remedially treated with Vapam and were excluded from further testing.

heavily colonized by decay fungi. These poles were used to evaluate the effectiveness of gelatin encapsulated MITC. Groups of 6 poles each were treated with 475 ml of gelatin encapsulated MITC plus 1 liter of water, 950 ml of encapsulated MITC plus 900 ml of water, or 950 ml of Vapam. Six poles were left untreated to serve as controls. In 1986, the control poles in this test were treated with gelatin encapsulated Vorlex in a study designed to test the effectiveness of this chemical for controlling carpenter ant infestations. Water was added to aid in release of MITC from the gelatin.

The treatment holes were drilled in a spiral pattern offset by about 70 degrees around the pole and at about 0, 15, 30, 45, and 60 cm above groundline. The capsules measured 2.5 cm in diameter by 8.75 cm long and contained 30 ml of MITC. Water was added to each treatment hole and the holes were plugged with tight fitting wooden dowels.

The treated poles were resampled annually by removing increment cores from three equidistant sites around the pole 0, 0.6, and 1.2 m above the groundline. These cores were plated on malt extract agar and observed for the presence of basidiomycetes. In addition, a single core was removed from one side of each pole at each of the three sampling heights. These cores were used in a closed tube bioassay test. Examination of treatment holes over the first 3 years revealed that complete release of MITC occurred between 1 and 2 years after treatment.

Both dosages of MITC remain free of decay fungi 10 years after fumigant treatment, as did the Vorlex treated poles 5 years after chemical application (Table I-5). One of 6 Vapam treated poles contained decay fungi near the groundline;

however, the overall degree of infestation in this treatment remains low (Fig. I-2). These results represent an improvement over those obtain 7 years after treatment and suggest that the chemicals continued to diffuse through the poles to eliminate established decay fungi. These results closely follow those obtained in previous field tests of unencapsulated MITC and indicate that gelatin encapsulation did not alter chemical performance.

Closed-tube bioassays indicate that relatively high levels of inhibition remain in the inner cores from both MITC treatments 0 and 0.6 m above the groundline and in all 3 zones for the Vorlex treatment (Table I-6). Zones of inhibition were generally sparse in the outer zones, reflecting the absence of an oil treated shell to retain chemical near the surface. As expected from previous trials, cores removed from Vapam treated poles were generally associated with small zones of effect. Once again, the results indicate that both MITC and Vorlex continue to provide adequate protection to the interior of poles.

The results indicate that gelatin encapsulation does not adversely affect the performance of either MITC or Vorlex for arresting internal decay fungi and preventing their reinvasion.

4. Effect of moisture addition on MITC release from gelatin capsules in Douglas-fir poles: Previous laboratory studies have shown that moisture can play a significant role in fumigant movement and activity. Wet wood tends to bind less chemical, and fumigant diffusion can be adversely affected at very high moisture levels (>80%). Dry wood binds higher amounts of chemical, which can provide a long-term reservoir for later protection when moisture conditions become suitable

Meters above ground	Segment location from surface (cm)	Growth of the assay fungus (as % of control)								
		Vorlex			Methylisothiocyanate ² 20%			MITC 100%		
		1989	1990	1991	1989	1990	1991	1989	1990	1991
2.4	0-2.5	81	96	89	70	93	59	-	76	44
	12.5-15	65	93	63	76	100	42	65	100	70
1.8	0-2.5	49	90	57	100	87	54	57	83	93
	12.5-15	62	100	42	89	93	65	59	100	54
1.2	0-2.5	32	67	71	86	96	75	29	72	81
	12.5-15	92	99	62	98	90	42	62	100	38
0	0-2.5	54	96	65	81	72	57	27	79	69
	12.5-15	68	79	46	57	93	53	73	100	64
Control ³	(no wood)	37	29	23	mm ²					

¹For 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.

²In diesel oil.

³Average growth in 7-10 tubes.

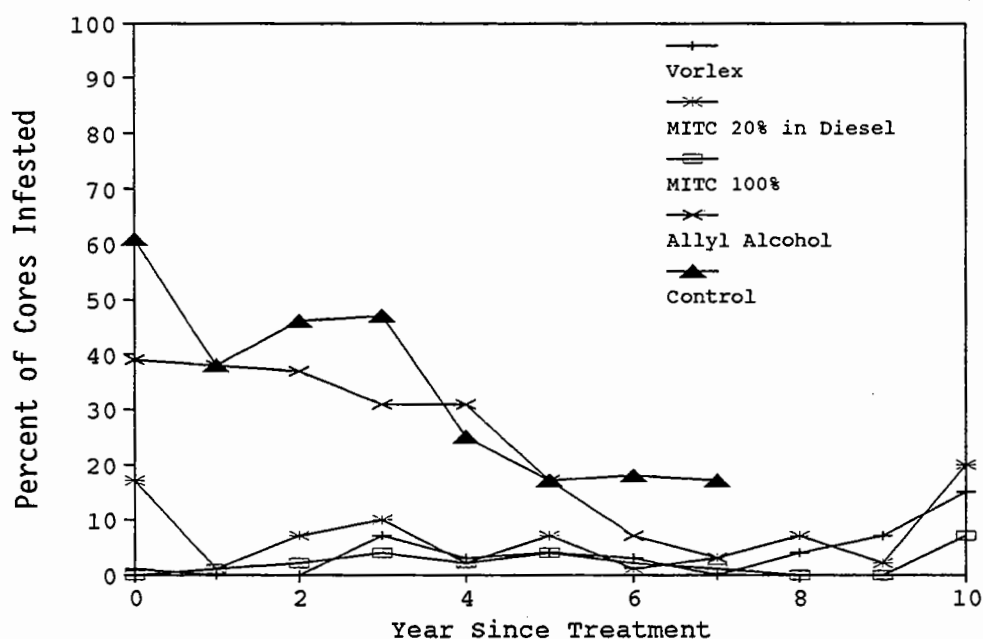


Figure I-1. Percent of cores removed from various sites on Douglas-fir transmission poles treated with Vorlex, 20% MITC in diesel oil, 100% MITC, allyl alcohol, or left untreated control which contain basidiomycetes.

for fungal invasion. The presence of a gelatin capsule around MITC might alter these relationships by slowing the release rate, particularly in dry wood. In 1983, a test was begun to evaluate the effect of moisture addition on MITC release from gelatin capsules.

Sixteen poles were selected from among a larger sample of Douglas-fir poles based upon the presence of active fungal infestations. The poles were treated with 528 ml of gelatin encapsulated MITC (22 ml per capsule) equally distributed among 6 holes beginning at groundline and spiraling around the pole at 120-degree intervals and 0.9 m upward. Each hole received 88 ml of MITC in 4 gelatin capsules along with 0 (dry), 40 (moist), or 70 ml (wet) ml of water prior to being plugged with tight fitting wood dowels.

The initial degree of fungal colonization was determined by culturing drill shavings collected from each hole. The poles were then sampled annually by removing increment cores from 3 locations around each pole 0, 0.9, 1.8, 2.7, 3.6, 4.5, and 5.4 m above the groundline. The outer and inner 2.5 cm of each core were evaluated for residual MITC using the closed-tube bioassay; while the remainder of the core was cultured for the presence of decay fungi.

Over the course of the study, several poles have inadvertently been retreated by commercial inspectors; however, sufficient numbers of poles remain in the test to provide meaningful results. Culturing of increment cores indicates that all three MITC treatments continue to limit the degree of fungal infestation 8 years after treatment although decay fungi were isolated from 2 cores in the latest sampling

(Table I-7). These results reflect earlier findings that the presence of occasional basidiomycete colonization is typical of this test. Initially, there were slight differences in degree of fungal control between the three moisture regimes, but these differences disappeared 2 years after treatment. Moisture level at time of treatment does not appear to be influencing the results. The cultural results are comparable to those obtained in other MITC trials and indicate that this fumigant should provide excellent protection both in groundline and above.

Closed-tube bioassays also continue to show a high degree of fungal inhibition in all three treatments, although the dry treatment was associated with the highest overall degree of inhibition (Table I-8). Interestingly, inhibition in these cores was highest in the zone adjacent to the treated shell. In most other studies, inhibition was greatest near the pith, reflecting the directional application of fumigant in downward sloping holes towards the pith. The reasons for this deviation are unclear.

Internal decay above the groundline is a particularly difficult problem in the Pacific Northwest, where large quantities of wind-driven rain during the winter months create higher moisture levels above the groundline which in turn create ideal conditions for development of decay fungi. Controlling this problem has posed a major challenge to utilities since the label instructions for most conventional liquid fumigants limit application to the groundline zone. Our results suggest that encapsulated MITC represents one method for effectively arresting these infestations (Figure I-3).

5. Treatment of through bored Douglas-fir poles with gelatin encapsulated MITC or chloropicrin: Trials to evaluate the

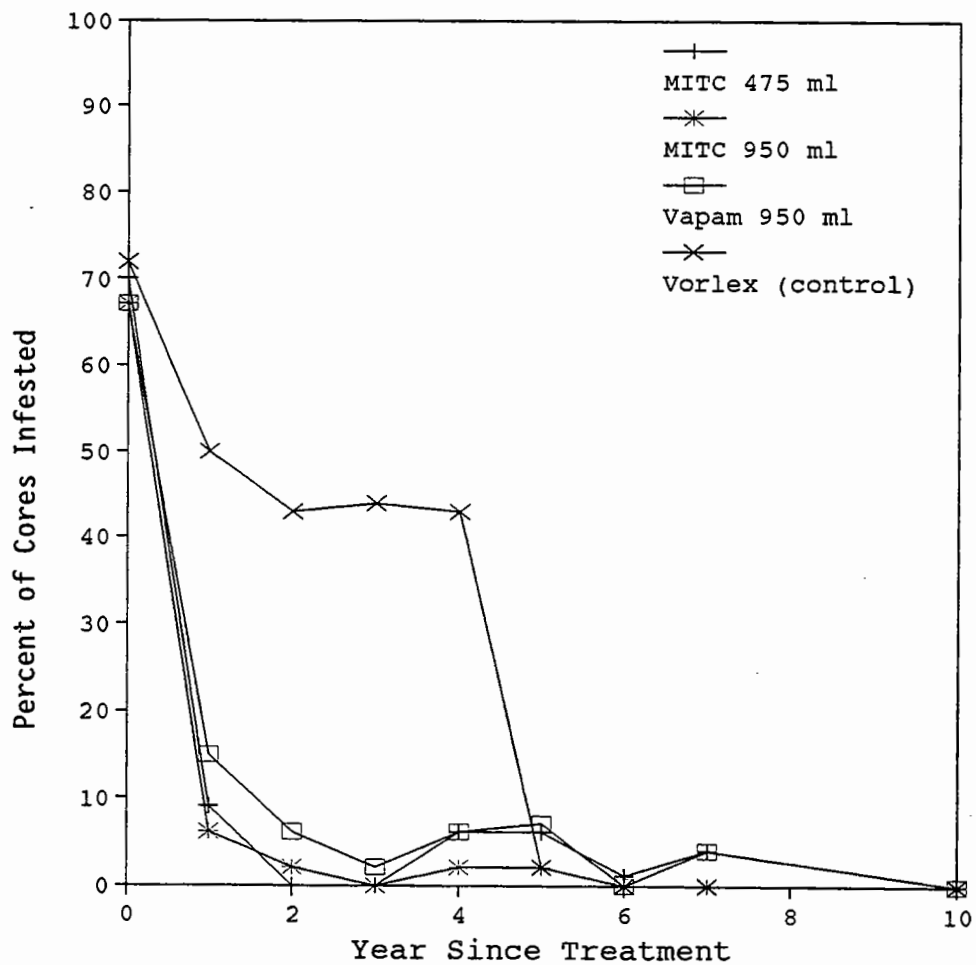


Figure I-2. Frequency of basidiomycetes in Douglas-fir poles 10 years after remedial treatment with 475 or 950 ml of gelatin encapsulated MITC or 950 ml of Vapam, or 5 years after treated with 950 ml of gelatin encapsulated Vorlex.

Table 1-5. Incidence of decay fungi in Douglas-fir poles in New York prior to and after treatment with Vapam or gelatin-encapsulated methylisothiocyanate (MITC).					
Sampling Date	Meters above groundline	Cores with decay fungi (%)			
		No Fumigant ^a (Vorlex 950 ml)	Vapam 950 ml	Encapsulated MITC	
				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	79	22	22	6
	0.6	54	17	0	6
	1.2	17	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 ^c	0	39	0	0	6
	0.6	61	0	6	0
	1.2	28	17	11	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
July 1991	0	0	0	0	0
	0.6	0	0	0	0
	1.2	0	0	0	0

^aControl poles were later treated with gelatin-encapsulated Vorlex.

Table I-6. Closed-tube bioassays of cores removed from New York poles after treatment with Vapam, gelatin-encapsulated MITC, or Vorlex.^a

Chemical	Dosage (ml)	Years Since Treatment	Sampling Height (m)	Average growth of <i>P. placenta</i> . (as a % of control)					
				Core Zone ^a					
				Outer			Inner		
				1987	1988	1991	1987	1988	1991
MITC	475	10	0	24	33	40	14	8	28
			0.6	5	61	37	17	16	0
			1.2	7	30	76	0	16	36
MITC	950	10	0	0	17	34	0	0	0
			0.6	0	34	60	0	0	20
			1.2	0	5	10	0	1	0
Vapam	950	10	0	57	78	58	77	47	16
			0.6	77	93	97	54	96	46
			1.2	70	86	77	69	85	72
Vorlex	950	5	0	18	0	0	0	0	0
			0.6	13	23	60	0	0	0
			1.2	22	35	0	0	0	0

^aOuter zone corresponds to 0 to 2.5 cm from the surface, while inner represents inner 2.5 cm.

efficacy of gelatin encapsulated chloropicrin or MITC in through-bored Douglas-fir were established in 1982 and will be evaluated in 1992 to develop 10 year efficacy data.

6. Above ground treatment with gelatin encapsulated or pelletized MITC: Douglas-fir poles treated near the underbuilt crossarms with pelletized or gelatin encapsulated MITC will be sampled in 1992. Results will be reported in 1993.

7. Effectiveness of glass encapsulated MITC in Douglas-fir and southern pine poles: Solid MITC is highly concentrated

(96% active ingredient) and sublimates at room temperature. It is, however, caustic and must be kept in a sealed container to avoid human contact prior to application. Previous trials have suggested that gelatin encapsulation is effective for containing the fumigant, but the process is not economical. Instead, the registered formulation, MITC-Fume[®], is delivered in borosilicate tubes plugged with teflon[®] caps. Although the fungitoxic properties of MITC are well known, the effect of the borosilicate tube on MITC diffusion, and thus, MITC-Fume's[®] efficacy as a fumigant compared to other formulations has not been established. The following field and laboratory trials tested both the

ability of MITC to diffuse from the MITC-Fume[®] tubes and the performance of MITC-Fume[®] at various dosages compared to a standard dosage of metham-sodium (32.1% sodium n-methyldithiocarbamate). Metham-sodium, which decomposes to MITC, typically has been used for pole treatment because of its low volatility and ease of handling, although its protective effects are sharply lower than those of chloropicrin or pure MITC.

Laboratory trials: In an effort to establish the rate of MITC release from MITC-Fume[®] tubes, eighteen 25-cm diameter by 75-cm long Douglas-fir pole sections were end-coated with an elastomeric paint. Nine of these pole sections were then air-seasoned prior to treatment to a 25% moisture content 5.0 cm below the wood surface, and the remainder were treated while still green (MC > 25%). Near the center of each pole section, a single hole, 1.9-cm diameter by 20.5-cm long, was drilled at a 45-degree angle, and an MITC-Fume[®] tube containing 30 g MITC was inserted, open-end down, in the hole. The holes were plugged with rubber stoppers, and sets of three pole sections from each of the moisture-content groups were placed in one of the following locations: a cold room (5°C), a hot wet room (30°C, 90% relative humidity), or outdoors at ambient temperature.

At periodic intervals, the MITC-Fume[®] tubes were removed from the treatment holes, weighed (nearest 0.01 g) to determine the amount of chemical remaining, and returned to the holes. Several tubes whose weight indicated they had completely lost the MITC were extracted with 5.0 ml ethyl acetate. The extract was analyzed for residual MITC content with a Varian 3700 gas chromatograph equipped with a flame

photometric detector and filters specifically for sulfur compounds. Residual MITC content was quantified by comparison with prepared standards.

Field trials: The efficacy of MITC-Fume[®] compared to metham-sodium was investigated as follows. Thirty-six Douglas-fir and 36 loblolly pine pole sections (25 to 30 cm in diameter, 3.6 m long) were obtained locally. The poles were pressure-treated to a nominal retention of 6.4 kg/m³ with chromated copper arsenate (CCA) Type C and then painted with an elastomeric paint to retard vapor loss. (Previous studies have shown that MITC diffuses readily through CCA-treated wood and is better retained in wood treated with pentachlorophenol in P9 Type A oil). The poles were then set to a depth of 0.9 m at a site 16 km north of Corvallis, Oregon. This site receives approximately 112 cm of precipitation annually, mostly during the winter months.

Into each of six poles per wood species, a series of two, four, six, or eight holes, 1.9 cm in diameter and 20.5 cm long, was drilled at steep angles, beginning at groundline and spiraling upward at 120-degree-by-15-cm intervals. One tube of MITC-Fume[®], containing approximately 30 g 96% MITC, was inserted, open-end down, into each hole. The holes were then plugged with tight-fitting, preservative-treated wood dowels to retard fumigant loss. In addition to these sets of poles (which, depending on the number of holes drilled, received 60, 120, 180, or 240 g MITC), an additional set of six poles of each species was treated with 500 ml metham-sodium equally distributed among three holes drilled as described for the

Table I-7 Frequency of decay fungi isolated from Douglas-fir poles treated with gelatin-encapsulated methylisothiocyanate (MITC).

Sampling Date	Meters above Groundline	Cores with decay fungi (%) ¹		
		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	5.5	20	20	40
	0	0	0	0
	0.9	0	0	0
	1.8	0	0	0
	2.8	0	0	0
	3.7	0	0	0
Sept. 1986	4.6	20	0	0
	5.5	0	0	0
	0	-	-	-
	0.9	40	0	0
	1.8	0	40	60
	2.8	20	0	20
Sept. 1987	3.7	40	0	20
	4.6	20	0	0
	5.5	40	0	0
	0	0	0	0
	0.9	0	0	0
	1.8	0	0	0
Sept. 1988	2.8	0	0	0
	3.7	0	0	0
	4.6	0	0	0
	5.5	0	0	10
	0	0	0	0
	0.9	0	0	10
Sept. 1989	1.8	0	0	0
	2.8	0	0	0
	3.7	0	0	0
	4.6	0	0	10
	5.5	0	10	0
	0	10	0	0
Sept. 1990	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	0	0	0
Sept. 1991	0	0	0	0
	0.9	0	0	20 (1 core)
	1.8	0	0	0
	2.8	0	0	0
	3.7	0	0	0
	4.6	0	0	0
5.5	0	0	0	

¹The 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 to 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.

Table I-8. Fungal inhibition of increment cores removed Douglas-fir poles treated with 588 ml of MITC and varying degrees of water as shown by a closed-tube bioassay using *Postia placenta* as the test fungus.

Meters Above Groundline	Core Segment ^b (cm)	Avg Growth of Test Fungus (as % of control) ^a		
		DRY	MOIST	WET
0	0 to 2.5	20	53	69
	10 to 12.5	45	45	42
0.9	0 to 2.5	0	67	49
	10 to 12.5	66	32	15
1.8	0 to 2.5	54	57	49
	10 to 12.5	19	30	12
2.8	0 to 2.5	0	50	33
	10 to 12.5	5	15	24
3.7	0 to 2.5	0	42	26
	10 to 12.5	0	4	0
4.6	0 to 2.5	24	49	20
	10 to 12.5	0	12	0

Control tubes (no wood): Avg. = 8.3 mm^c (1987)/26 mm (1988)/24 mm (1991)

^aThe 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 low numbers have higher fumigant levels.

^bIncrement 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.

^cControl tubes showed poor growth in 1987, ranging from only 5 mm to 20 mm after 7 day's growth.

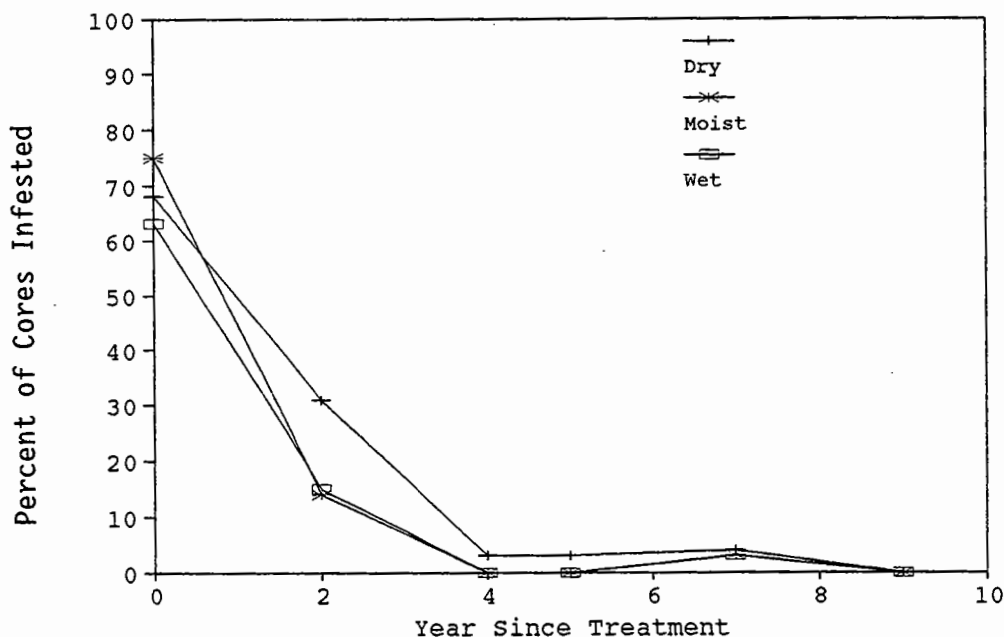


Figure I-3. Fungal infestation in Douglas-fir poles treated with gelatin-encapsulated MITC and various moisture levels as shown by culturing increment cores removed from the wood.

MITC-Fume[®]-treated poles. A final set of six poles of each species, the control group, received no chemical treatment. The ability of MITC, applied as either MITC-Fume[®] or metham-sodium, to diffuse through the poles and eliminate fungi was evaluated 6, 12, 24, and 36 months after treatment. The evaluation included two types of fungal bioassays—dowel and closed tube—as well as fungal culturing and chemical analysis.

The dowel bioassays provided an approximate measure of the extent of fumigant diffusion through the test poles over the study period. To perform these bioassays, pressure-soaked western hemlock dowels were placed in moistened vermiculite in plastic bags with a semi-permeable patch. The bags were then sterilized (20 min. at 121 °C). A 1% malt extract solution, inoculated 2 weeks earlier with *Postia placenta*, was then added to the vermiculite; the bags were sealed; and the dowels were incubated for at least 4 weeks or until the dowels were thoroughly colonized by the test fungus.

At 6, 12, 24, and 36 months after the test poles were treated with fumigant, the colonized dowels were inserted into sets of three 15-cm-deep holes, 120° apart, that had been drilled in the poles 0.0, 0.3, 0.9, and 1.5 m above the highest treatment hole. (Dowel bioassays were not conducted for sites between treatment holes because the high levels of fumigant expected in this zone would have made it difficult to resolve any treatment differences accurately.) These holes were then plugged with tight-fitting rubber stoppers to minimize fungal desiccation during the exposure period. Initially, dowels were exposed for a period of 6 months prior to removal; however, due to a low fungal survival rate in dowels in the untreated poles (presumably because of drying), the exposure period was reduced

to 3 months in subsequent tests. Following removal from the test poles, the dowels were plated onto potato dextrose agar and observed for evidence of regrowth of the test fungus.

Closed-tube bioassays represent a slightly different approach to assessing fumigant distribution. With dowel bioassays, the test fungus is exposed to fumigant vapors diffusing through the wood over several months. With closed-tube bioassays, the test fungus is exposed to all of the fumigant (both bound and vapor) in the wood in a short time (7 to 10 days). Previous studies have shown that closed-tube bioassays are very sensitive to low levels of fumigant.

In our study, closed-tube bioassays were performed 12, 24, and 36 months after pole treatment by removing two 15-cm-long increment cores, 180° apart, from each test pole 0.3 m below groundline, and sets of three increment cores of the same size, 120 degrees apart, from sites 0.0, 0.3, 0.9, and 1.5 m above the highest treatment hole. (Cores were not removed from sites between treatment holes because, as with the dowel bioassays, it was felt that the high levels of fumigant expected in this zone would prevent accurate resolution of any treatment differences.) The inner and outer 2.5-cm sections of each of the 14 cores were placed in separate tubes containing an actively growing culture of *Postia placenta*. The tubes were then sealed and incubated in an inverted position to allow fumigant vapors released from the core sections to come into contact with the test fungus. The rate of test fungus growth in the presence of fumigant-treated wood, compared to its growth rate in the absence of wood, provided a measure of the degree to which the treated wood inhibited fungal growth.

The middle section of each of the closed-tube bioassay cores was used for a culturing analysis. These sections were plated onto malt extract agar and, after 1 month of incubation at room temperature, were examined for evidence of fungal growth. If growth occurred, it was identified as either decay fungi (fungi with characteristics typical of basidiomycetes, a class of fungi containing many important wood decayers) or as nondecay fungi. No attempts to further identify the fungi were made.

For the chemical analysis of fumigant diffusion in the test poles, a second set of 15-cm-long increment cores was removed from each pole at locations adjacent to those sampled for the closed-tube bioassays. The outer and inner 2.5 cm of these cores were placed in separate test tubes containing 5.0 ml ethyl acetate. The tubes were stored for a minimum of 48 hours, and then, the extract was chromatographically analyzed as for the residual MITC in the laboratory trials, to determine the MITC level in each wood section. The results were quantified by comparisons with analyses of solutions of known MITC content.

Laboratory trials: Examination of MITC-Fume[®] tubes over a 2-year period indicated that MITC was released most rapidly from tubes in poles exposed to hot humid conditions—in these conditions, complete release occurred within 1 year (Fig. I-4). Although tubes in poles exposed to ambient temperatures had not released all of their fumigant by the end of the 2-year period, the data for the 40% MC wood indicated a release period of about 3 years. MITC was released most slowly in poles exposed to cool conditions. A slow MITC release rate is not, in itself,

a negative characteristic, provided a sufficient level of chemical is released to eliminate any fungi established in the wood—and previous studies have suggested that the levels required for fungitoxicity are fairly low.

Higher wood moisture content accelerated MITC release significantly only for ambient temperature exposures; and this effect continued throughout the 2-year period, even though the moisture content of the two groups of poles became equivalent within 6 months of pole treatment. These results suggest that MITC diffusion was negatively affected by the conditioning of the drier poles, which might have increased the degree of pit aspiration in those poles.

Gas-chromatographic analyses of extracts from empty tubes found only trace levels of MITC; although, the tubes did contain a coating of sulfur crystals left by the MITC decomposition. These trace levels should not pose a disposal risk, as they will volatilize rapidly when tubes are removed from the treatment holes.

Field trials: As mentioned, in the initial 6-month exposure period for the dowel bioassays, *Postia placenta* exhibited excellent survival in the untreated (control) southern pine poles; in contrast, survival in the control Douglas-fir poles was only half as high. This marked difference indicated that moisture conditions were not uniformly suitable for survival of the test fungus across both wood species, and so the exposure period for the dowels was reduced to 3 months to decrease the possibility of fungal desiccation.

The *P. placenta* survival percentages for the dowel bioassays (Table I-9)

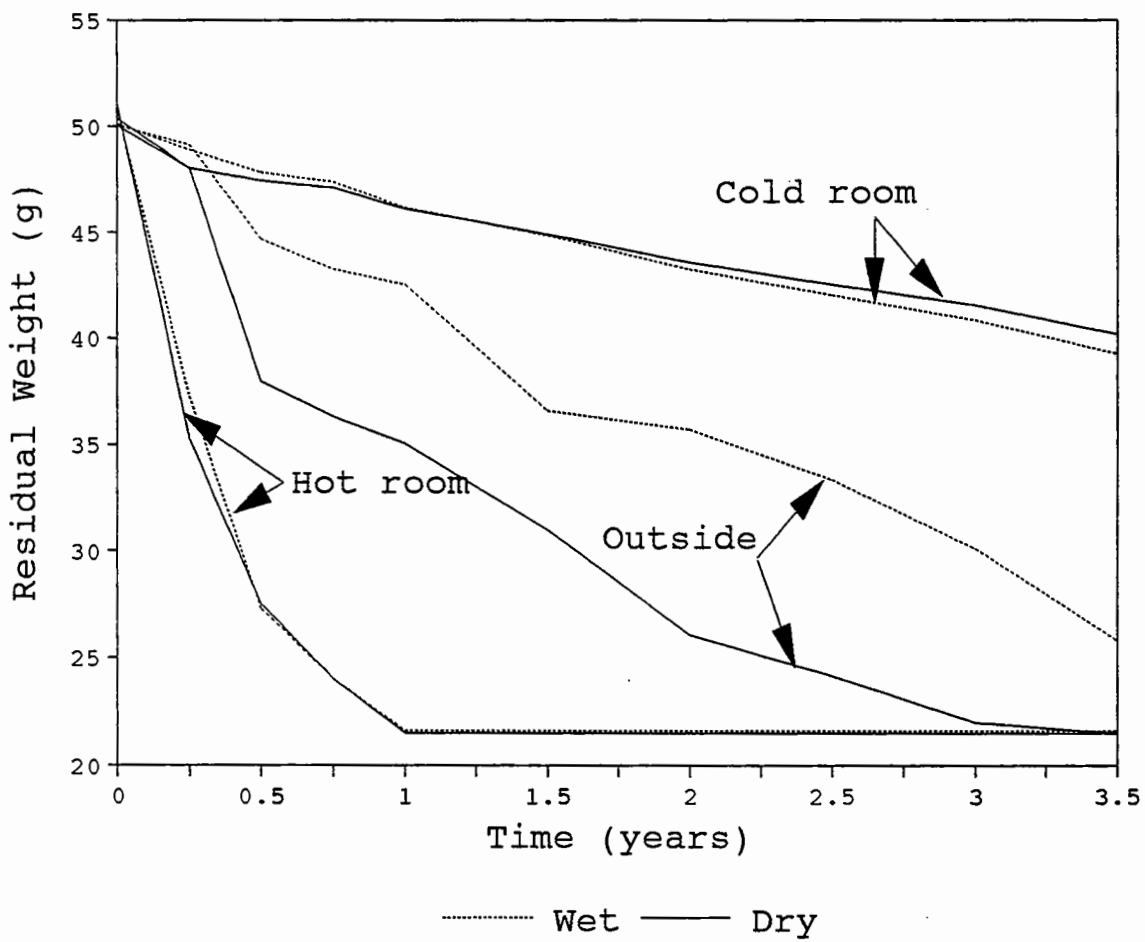


Figure I-4. Rate of MITC release from MITC-Fume[®] tubes (as determined by residual weight of tubes) in Douglas-fir pole sections with initially different moisture contents, exposed for 3-1/2 years to cold, ambient, and hot/wet conditions.

indicate that in both wood species the MITC-Fume[®] and metham-sodium treatments were well distributed to 0.3 m above the highest treatment hole within 6 months of pole treatment. With the Douglas-fir poles, low survival percentages 0.9 m above the treatment hole suggest that the fumigants had reached this level by 6 months.

Dowel bioassay results generally must be viewed with caution, however, because external environmental conditions can affect both the degree of chemical diffusion and fungal survival in different wood species. For example, hot dry conditions would increase fungal desiccation, reducing survival rates. Something of this nature probably occurred for the southern pine poles in our study, as illustrated by the fact that 1 year after treatment, fungal survival in dowels in the untreated southern pine poles was extremely low as compared to that in the untreated Douglas-fir poles. For this reason, the fungal survival data for the fumigant-treated southern pine poles from 1 year onward is suspect and will not be discussed.

Fungal survival rates in MITC-Fume[®] treated Douglas-fir poles 1 year after treatment suggest that, as at the 6-month point, fungitoxic levels of MITC were present to 0.3 m above the highest treatment hole, but MITC levels 0.9 m above the highest treatment hole were insufficient to completely eliminate the test fungus. Fungal survival rates in metham-sodium treated Douglas-fir poles 1 year after treatment suggest that this fumigant no longer was producing fungitoxic levels of MITC. Metham-sodium must decompose to produce MITC. It is possible that by 1 year after treatment, the decomposition reactions had ceased and that most of the

chemical had dissipated through the wood and was therefore less available for diffusion into the fungal-colonized dowels.

Dowel bioassays for the Douglas-fir poles 2 and 3 years after treatment produced results similar to those for the 6-month and 1-year bioassays; both of these later samplings indicated that fungitoxic levels of MITC continued to be present just above the highest treatment hole and that fungal survival rates increased with distance from this site. Our data suggest that MITC continues over time to diffuse from very high concentrations near treatment sites and to gradually lose its fungitoxic effects with distance from these sites.

Closed-tube bioassays of cores removed from poles 1, 2, or 3 years after MITC-Fume[®] treatment showed that fungitoxic levels of MITC were present up to 0.3 m above the highest treatment hole at all fumigant dosages and for both wood species (Table I-10). As with the dowel bioassays, fungal inhibition (measured as % fungal growth) appeared to be slightly higher with Douglas-fir than with southern pine, particularly at the 1-year sampling time. In general, the inner portions of the cores produced a higher degree of fungal inhibition than the outer portions, reflecting the fact that the MITC-Fume[®] tubes, by opening inward, tend to direct chemical inward. However, some degree of inhibition was consistently noted in the outer sections of the cores, suggesting that outward diffusion from the glass tubes does occur. Bioassay results after 3 years showed continuing declines in fungal inhibition in all treatments on both species; although, the differences between the 2- and 3-year bioassays were often slight. In contrast to the MITC-Fume[®] results, bioassays of cores removed from metham-sodium treated poles of

Table I-9. Survival of <i>Postia placenta</i> in hem-fir dowels inserted in southern pine and Douglas-fir poles treated with MITC-Fume® or metham-sodium 6, 12, 24, or 36 months prior to dowel insertion. ^a															
Fungal survival (%) at different vertical distances from treatment zone															
Chemical Treatment	Dosage	0.0 m			+0.3 m			+0.9 m			+1.5 m				
		mos.	36 mos.	6 mos.	12 mos.	24 mos.	36 mos.	6 mos.	12 mos.	24 mos.	36 mos.	6 mos.	12 mos.	24 mos.	36 mos.
Southern Pine															
MITC-Fume ^b	60	50	0	27	0	12	0	33	17	40	22	50	6	75	89
	120	0	0	27	11	0	0	33	17	56	13	44	11	40	43
	180	0	0	5	0	0	11	39	0	73	32	62	11	75	5
	240	0	0	16	6	0	0	67	39	82	6	83	33	100	6
Metham-sodium ^c	500	20	0	13	6	62	25	67	1	67	58	67	17	100	54
Control	-	80	0	27	6	80	6	44	0	70	50	50	6	87	11
Douglas-fir															
MITC-Fume ^b	60	0	0	5	0	0	0	5	11	25	0	22	33	33	11
	120	0	0	5	0	20	0	14	33	14	10	38	78	60	20
	180	0	0	0	6	0	6	5	22	33	0	56	28	50	6
	240	0	0	0	0	0	0	11	33	10	0	50	67	12	7
Metham-sodium	500	0	0	0	77	33	0	13	80	67	13	20	87	83	7
Control	-	40	27	33	100	71	0	39	100	73	11	39	100	45	83

^aWood dowels colonized by *Postia placenta* were inserted in sets of three holes, 120' apart, drilled in the poles at selected heights above the highest treatment hole. The dowels were removed after 3 or 6 months and cultured on malt agar/benomyl plates.

^bDosage in grams.

^cDosage in ml.

both species indicated that fungitoxic levels of MITC were present only near the highest treatment hole. Two years after pole treatment, cores removed from sites 0.3 m below the lowest treatment hole in southern pine poles produced complete fungal inhibition, but cores removed from the same sites in Douglas-fir only partially inhibited fungal growth. Three-year results continued to show declining levels of residual protection in both species.

The closed-tube bioassays provided an indication of the degree of protection afforded by the two fumigant treatments relative to one another. The test results indicated that the MITC-Fume[®] treatment produced fungitoxic MITC levels up to 0.3 m above the highest treatment hole, while the metham-sodium treatment were more confined to the zone immediately surrounding the treatment site. The lesser effectiveness of metham-sodium may be explained by this chemical's shorter residual time in wood and the relatively small amounts of MITC generated by the chemical's decomposition.

Culturing provides an ultimate measure of fumigant efficacy because ineffectively treated wood will, if conditions are conducive, eventually be colonized by decay fungi. In our study, although the cores of untreated southern pine poles showed no evidence of colonization by basidiomycetes, virtually all cores contained at least one nondecay microfungus (Table I-11). For treated southern pine poles, levels of nondecay fungi colonizing the zone immediately adjacent to the highest treatment hole and 0.3 m below the lowest hole were much lower than levels in zones above the treatment holes, suggesting that for all treatments, MITC was present at fungitoxic levels in the lower zones. These results corroborate those of other studies. Extensive colonization by

microfungi is typical of southern pine and these fungi also tend to reinvade fumigant-treated southern pine early in the treatment cycle although their effects on treatment efficacy at this stage are unknown. In contrast to the southern-pine poles, untreated Douglas-fir poles were gradually colonized by basidiomycetes during the 3-year study although the levels of colonization remained relatively low throughout that period. Interestingly, decay fungi were also isolated from several MITC-Fume[®] treated Douglas-fir poles 1 year after treatment but could not be reisolated 2 years after treatment. Because the poles used for this study were not sterilized during treatment, these isolated fungal colonies may have been present at the time of installation and were subsequently killed by the MITC-Fume[®] treatments.

Initially it was thought that the MITC-Fume[®] tube design, with only one small opening near the tip, would hinder fumigant diffusion; however, the chemical analysis results suggest that fumigant diffusion through poles occurred rapidly after treatment. According to the chemical analysis, MITC from the MITC-Fume[®] treatments was capable of diffusing up to 0.9 m above the highest treatment hole in southern pine and to 1.5 m above the highest treatment hole in Douglas-fir (Table I-12). Trace levels of MITC were detected 1.5 m above the highest treatment hole in southern pine poles, but these levels were too low to be quantified. Chemical levels tended to be highest in the inner sections of the poles, probably due to the insertion of the MITC-Fume[®] tubes with their opening inward as well as to the more rapid loss of fumigant nearer the poles' surfaces. Chemical levels in MITC-Fume[®] treated poles of both species generally increased with increasing dosage, microfungi is typical of southern pine and these fungi also tend to reinvade fumigant-treated southern pine early in the treatment cycle although their effects on

Table I-10. Incidence of fungal growth, as measured by closed-tube bioassays of increment core segments, in southern pine and Douglas-fir poles 12, 24 and 36 months after treatment with MITC-Fume® or metham-sodium. ^a													
Vertical distance from treatment zone	Core segment tested ^b	Months after treatment	Fungal growth (as % of control) ^b										
			Southern pine					Douglas-fir					
			MITC-Fume®					MITC-Fume®					
			60g	120g	180g	240g	500 ml	60g	120g	180g	240g	500 ml	
-0.3 m		12	12	0	0	0	0	23	34	25	4	0	77
		24	17	0	20	0	0	100	16	6	20	0	20
		36	55	41	33	32	0	78	25	21	20	22	82
		12	0	0	0	0	0	14	0	12	0	0	49
		24	0	0	0	0	0	0	0	0	0	0	16
		36	14	1	3	0	0	7	1	14	13	16	69
		12	16	3	11	0	0	40	0	0	0	0	10
		24	0	7	30	0	0	100	16	0	0	0	12
		36	38	12	24	10	0	69	19	21	26	21	76
		12	0	0	0	0	0	0	0	0	0	0	0
		24	0	0	0	0	0	0	0	10	0	0	0
		36	13	3	7	3	0	5	8	2	1	0	82
0.3 m		12	80	0	21	41	63	63	65	32	4	0	67
		24	83	36	33	33	100	40	23	0	0	0	0
		36	51	25	28	27	67	24	19	15	7	91	0
		12	40	0	0	0	0	45	16	12	0	0	15
		24	0	0	13	0	13	13	16	13	0	0	33
		36	5	6	19	1	23	23	8	20	14	3	84
		12	100	73	95	100	90	79	64	64	27	19	70
		24	90	77	94	100	100	43	43	23	24	24	60
		36	101	77	63	85	84	37	31	29	13	83	0
		12	60	33	92	100	86	27	26	22	8	39	33
		24	57	63	35	48	60	20	0	16	0	0	33
		36	78	49	43	36	50	38	54	41	15	15	90
1.5 m		12	100	100	100	100	100	63	100	100	62	48	86
		24	97	100	100	100	87	53	47	60	100	100	0
		36	88	91	89	85	93	74	71	72	86	92	0
		12	100	100	100	50	97	95	100	68	50	84	0
		24	100	94	80	57	70	77	43	30	67	67	0
		36	99	83	74	61	57	76	74	74	77	102	0

^aCores were removed from selected locations at different vertical distances above and below the treatment site.

^bValues represent the growth of *Postia placenta* in tubes containing treated wood cores as a percentage of its growth in tubes to which wood cores were not added. Complete inhibition (0% growth) represents fungitoxic chemical levels.

^cWhere outer represents 2.5 cm from pole surface and inner represents 12.5-15.0 cm from pole surface.

Table I-11. Incidence of decay and nondecay fungi in southern pine and Douglas-fir poles 12, 24, and 36 months after treatment with MITC-Fume ^a or metham-sodium. ^a																
		Percentage of cores containing decay (nondecay) fungi ^b														
		-0.3 m ^c			0.0 m			0.3 m			0.9 m			1.5 m		
Chemical Treatment	Dosage	24 mos.	36 mos.	12 mos.	24 mos.	36 mos.	12 mos.	24 mos.	36 mos.	12 mos.	24 mos.	36 mos.	12 mos.	24 mos.	36 mos.	
Southern Pine																
MITC-Fume ^{a,d}	60	0(50)	0(67)	0(67)	0(0)	0(17)	0(100)	0(100)	0(100)	0(39)	0(100)	0(100)	0(100)	0(100)	0(88)	
	120	0(50)	0(42)	0(83)	0(17)	0(8)	0(100)	0(83)	0(100)	0(17)	0(100)	0(100)	0(100)	0(100)	0(56)	
	180	0(28)	0(57)	0(30)	0(57)	0(14)	0(100)	0(100)	0(100)	0(67)	0(100)	0(100)	0(100)	0(100)	0(52)	
	240	0(0)	0(58)	0(50)	0(0)	0(17)	0(100)	0(100)	0(38)	0(100)	0(100)	0(100)	0(100)	0(100)	0(94)	
Metham-sodium ^a	500	0(40)	0(70)	0(40)	0(40)	0(40)	0(100)	0(80)	0(73)	0(100)	0(100)	0(100)	0(100)	0(100)	0(87)	
Control	-	0(100)	0(92)	0(100)	0(100)	0(83)	0(100)	0(100)	0(83)	0(100)	0(100)	0(100)	0(100)	0(100)	0(83)	
Douglas-fir																
MITC-Fume ^{a,b}	60	0(0)	0(42)	0(25)	0(33)	0(0)	0(33)	0(50)	0(0)	0(0)	0(50)	0(100)	0(50)	0(100)	6(39)	
	120	0(57)	0(17)	0(29)	0(29)	0(0)	0(71)	0(100)	0(17)	0(17)	0(64)	7(100)	0(10)	0(100)	10(29)	
	180	0(50)	0(17)	0(16)	0(17)	0(8)	0(58)	0(67)	0(10)	0(75)	0(67)	0(67)	0(17)	0(67)	0(22)	
	240	0(33)	0(33)	0(29)	0(17)	0(0)	0(25)	0(67)	0(8)	0(8)	0(100)	0(100)	0(0)	0(100)	0(13)	
Metham-sodium ^a	500	0(60)	0(40)	0(60)	0(40)	10(50)	0(40)	10(50)	13(7)	10(50)	10(80)	10(80)	0(40)	10(80)	0(0)	
Control	-	33(100)	33(75)	0(100)	33(100)	42(67)	0(50)	25(100)	28(50)	8(33)	8(100)	28(50)	0(33)	0(100)	6(6)	

^aCores were removed from selected locations at different vertical distances above and below the treatment site. The middle segment of cores was used for this analysis.

^bValues reflect an average of 15 total cores per dosage/position. Figures in parentheses represent non-decay fungi isolated from the same cores.

^cTwelve-month data not taken for -0.3 m cores.

^dDosage in grams

^eDosage in ml.

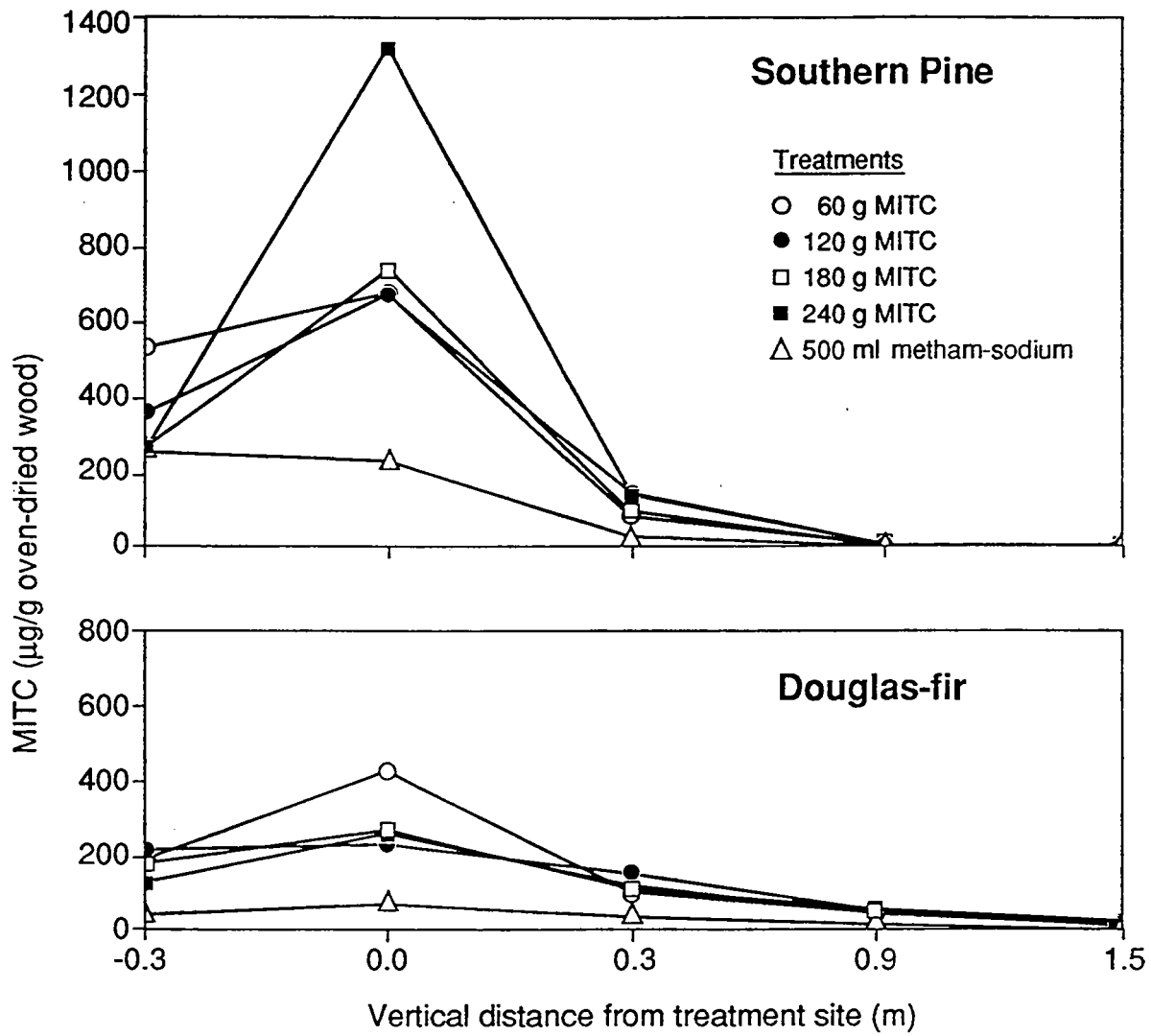


Figure I-5. Residual MITC at selected locations in Douglas-fir and southern pine poles 3 years after treatment with 500 ml metham-sodium or 60-240 g MITC-Fume.*

Table I-12. Residual MITC content as measured by gas chromatographic analysis of increment cores in southern pine and Douglas-fir poles 6, 12, 24 and 36 months after treatment with MITC-Fume® or metham-sodium.^a

Vertical distance from treatment zone	Core segment tested ^c	Months after treatment	MITC content ($\mu\text{g}/\text{oven-dried g of wood}$) ^b										
			Southern pine					Douglas-fir					
			MITC-Fume® dosage				Metham-sodium dosage	MITC-Fume® dosage				Metham-sodium dosage	
			60g	120g	180g	240g	500 ml	60g	120g	180g	240g	500 ml	
-0.3 m	Outer	12	105	179	170	320	10	164	346	401	439	-	
		24	125	306	204	185	213	140	168	404	273	15	
		36	30	31	56	163	2	18	81	28	55	2	
	Inner	12	369	1534	1282	1644	147	292	270	1327	441	-	
		24	203	1996	2028	1754	535	132	154	2161	1240	143	
		36	536	368	284	277	257	186	219	182	127	44	
	0.0 m	Outer	12	93	147	169	275	95	119	485	280	1500	41
			24	127	120	426	140	18	219	200	192	322	31
			36	138	62	176	62	1	61	59	51	78	3
Inner		12	2031	2777	2009	3425	1986	2525	2879	3745	3985	978	
		24	2054	1798	2033	2381	319	1191	1928	1600	1242	34	
		36	675	673	736	1332	227	418	223	260	251	68	
0.3 m	Outer	6	0	1	3	2	0	5	84	132	132	4	
		12	38	94	30	29	9	26	12	149	206	11	
		24	T	40	33	13	T	46	94	177	311	22	
	Inner	6	21	42	34	36	2	37	48	63	99	8	
		12	1	14	12	6	2	132	296	534	624	352	
		24	239	316	212	184	96	128	349	1052	262	105	
	0.9 m	Outer	24	285	353	322	281	54	256	459	363	554	306
			36	77	139	91	135	19	92	142	108	107	24
			6	0	0	0	0	0	0	2	0	0	0
Inner		12	T	12	13	10	0	34	94	25	34	10	
		24	T	T	T	T	0	84	60	40	72	T	
		36	1	4	6	5	T	26	40	17	20	4	
1.5 m	Outer	6	0	0	0	0	0	2	115	4	2	2	
		12	T	12	9	T	0	24	198	26	31	102	
		24	T	T	T	46	0	149	117	92	165	49	
	Inner	36	2	12	12	8	T	34	26	28	48	8	
		6	0	0	0	0	0	0	0	0	0	0	
		12	0	0	0	0	0	5	T	T	T	T	
	Outer	24	0	0	0	0	0	T	T	T	49	0	
		36	0	T	T	2	T	3	3	T	4	T	
		6	0	0	0	0	0	0	0	0	0	0	
12		0	0	0	0	0	T	T	T	21	0		
24		0	0	0	0	0	T	T	T	120	0		
36		0	0	T	2	T	3	6	3	2	T		

^aCores were removed from selected locations at different vertical distances above and below the treatment site.

^bValues represent the growth of *Postia placenta* in tubes containing treated wood cores as a percentage of its growth in tubes to which wood cores were not added. complete inhibition (0% growth) represents fungitoxic chemical levels.

^cWhere outer represents 2.5 cm from pole surface and inner represents 12.5-15.0 cm from pole surface.

treatment efficacy at this stage are unknown. In contrast to the southern-pinepoles, untreated Douglas-fir poles were gradually colonized by basidiomycetes during the 3-year study although the levels of colonization remained relatively low throughout that period. Interestingly, decay fungi were also isolated from several MITC-Fume[®] treated Douglas-fir poles 1 year after treatment but could not be reisolated 2 years after treatment. Because the poles used for this study were not sterilized during treatment, these isolated fungal colonies may have been present at the time of installation and were subsequently killed by the MITC-Fume[®] treatments.

The apparently more extensive diffusion of MITC in Douglas-fir compared to southern pine is perplexing because southern pine is a more permeable wood species. Possibly, southern pine's greater permeability simply resulted in a faster rate of fumigant loss in zones relatively distant from the treatment sites. Previous studies with chloropicrin treatment of southern pine and Douglas-fir have shown that while southern pine poles experience a nearly complete loss of chemical within 5 years, chloropicrin remains at detectable levels for over 20 years in Douglas-fir. Further studies of the differences between MITC diffusion in southern pine and Douglas-fir are planned.

Initially it was thought that the MITC-Fume[®] tube design, with only one small opening near the tip, would hinder fumigant diffusion; however, the chemical analysis results suggest that fumigant diffusion through poles occurred rapidly after treatment. According to the chemical analysis, MITC from the MITC-Fume[®]

treatments was capable of diffusing up to 0.9 m above the highest treatment hole in Douglas-fir (Table I-12). Trace levels of MITC were detected 1.5 m above the highest treatment hole in southern pine poles, but these levels were too low to be quantified. Chemical levels tended to be highest in the inner sections of the poles, probably due to the insertion of the MITC-Fume[®] tubes with their opening inward as well as to the more rapid loss of fumigant nearer the poles' surfaces. Chemical levels in MITC-Fume[®] treated poles of both species generally increased with increasing dosage, particularly in the region immediately surrounding the treatment holes, but this phenomenon generally declined with increasing distance from the treatment sites. In zones 0.9 m or farther above the highest treatment site, it was not possible to clearly distinguish between dosages by comparing chemical levels (Fig. I-5).

The chemical analysis showed that in both wood species, fumigant levels gradually increased over the first year for all treatments, but then declined sharply over the next 2 years as chemical diffused from the wood. This relatively rapid decline may reflect the use of CCA treatments instead of oilborne preservatives, which lose fumigant more slowly. A previous study using closed-tube bioassays suggested that Douglas-fir retains MITC at detectable levels for up to 13 years, although the levels were not quantified in that study.

Compared to the MITC levels in the MITC-Fume[®] treated poles, which increased during the first part of the 3-year exposure period, MITC levels detected by chemical analysis in the metham-sodium

treated poles remained low throughout the exposure period. This effect may partly be explained by the relatively low yield of MITC per unit weight of metham-sodium. Theoretically, metham-sodium contains 32.1% active ingredient, which decomposes to MITC at a 40% efficiency. Thus, 500 ml of formulated metham-sodium should have yielded about 64.2 g of MITC. This means that the MITC levels in the metham-sodium treatments should have been comparable to those found in the 60 g MITC-Fume[®] treatment. Although MITC levels in both wood species were similar for the 60 g MITC-Fume and metham-sodium treatments at the 6-months sampling, MITC levels in metham-sodium treated poles tended to be lower than in MITC-Fume[®] treated poles at subsequent sampling points. This result suggests that the MITC yield from metham-sodium is lower than 40% and corroborates a previous study of actual versus theoretical MITC yield. Of the several metham-sodium decomposition products with fungitoxic effects, MITC is the most effective, and any loss in its yield would reduce the long-term treatment efficacy of metham-sodium.

One of the original goals of this investigation was to develop dosage recommendations for MITC-Fume[®] by comparing the effects of different dosages with those of a standard metham-sodium dosage. Our results suggest that as little as 60 g of MITC-Fume[®] provide chemical protection comparable to that of a 500-ml metham-sodium dosage. In practice, however, higher MITC-Fume[®] dosages should provide a larger reservoir of fumigant and therefore longer-term chemical diffusion. In any case, the use of three MITC-Fume[®] tubes, equally spaced around the pole, is recommended to promote a uniform chemical distribution.

The results of this study indicate that MITC-Fume[®] provides comparable or better protection to both southern pine and Douglas-fir poles than metham-sodium. Although differences were noted in the degree of fumigant diffusion for the two wood species, the nature of these differences could not be discerned by the testing methods we employed. Further studies are planned to more fully determine the differences in fumigant diffusion between Douglas-fir and southern pine.

B. EVALUATE PREVIOUSLY ESTABLISHED TRIALS OF NON-VOLATILE REMEDIAL INTERNAL TREATMENTS

1. Ability of fused borate rods to diffuse through Douglas-fir heartwood: While a majority of our research has evaluated volatile remedial chemicals, there are many instances where less volatile chemicals may provide equivalent protection. One currently available

formulation employs sodium octaborate tetrahydrate in a fused borate rod. These glass-like rods release boron when wetted, and this boron can then diffuse to control decay fungi present in the wood.

In 1990, a trial was established to evaluate the efficacy of fused borate rods in Douglas-fir heartwood. Fifty Douglas-fir pole sections (1.05 m long by 25 to 30 cm in diameter) were surface dried and dipped for 5 minutes in a 2.0% solution of chromated copper arsenate Type C. The dipped poles were stored under cover for 24 hours to allow the fixation process to proceed, then air-dried. A 1.9 cm diameter hole was drilled through each pole section 40 cm from the top and a galvanized bolt with a slot cut perpendicular to the threads was inserted into the hole. A 1.9 cm diameter by 20 cm long hole was then drilled 15 cm directly above the bolt hole. The holes received 40 or 80 g of fused borate rod (1 or 2 rods) and plugged with a tight fitting wood dowel. The pole sections were capped with plywood to limit end-grain wetting and exposed on a rack above-ground in either Corvallis, Oregon or Hilo, Hawaii. The Corvallis site is a typical Pacific Northwest location receiving approximately 112 cm of rainfall per year, primarily in the winter months. The Hilo site is an extremely wet, humid site receiving over 400 cm of rainfall per year.

The poles were sampled one year after treatment by removing increment cores from 2 sites 90 degrees around from and 7.5 cm below the treatment hole, as well as 7.5 cm below the bolt hole. The cores were segmented into zones corresponding the outer and inner 5 cm. The segments were ground to pass a 20 mesh screen and analyzed for residual boron content by extraction and Ion Coupled Plasma Spectroscopic analysis. In addition, one core was removed from a site 7.5 cm above the treatment. This core

was ground as one sample and similarly analyzed. A second set of cores was removed from sites 7.5 cm below each bolt hole and cultured on malt extract agar for the presence of decay fungi.

Culturing of increment cores revealed that none of the poles were infested by decay fungi in the zone near the bolt hole. Chemical analysis revealed that boron levels at all locations were less than 0.7 kg/m³ (Table I-13). It is difficult to determine the exact threshold of boron for fungal control; however, previous studies on hardwoods suggest that a threshold ranging from 0.6 to 1.2 kg/m³ (as boron) will prevent colonization by basidiomycetes. Our results suggest that these levels are present only in the zone above the original treatment hole.

As expected, boron levels in the inner zone were higher than those nearer to the surface, although these differences were sometimes slight. Chemical levels in pole sections exposed at Hilo tended to be lower than those in similar sections exposed in Corvallis. Since Hilo receives considerably more precipitation, boron leaching losses might account for these differences. Generally, chemical levels below the treatment holes were lower than those found in the single core removed from above the treatment hole. This difference is perplexing since we considered downward movement to be the more likely pathway for movement of this chemical. Chemical dosage also appeared to have only a minimal effect on subsequent boron levels. The absence of a dosage effect suggests that the rate of boron release from the two treatments is similar. In general, however, the boron levels present in these pole sections are far

lower than would be required to effectively arrest established internal decay fungi and suggest that considerable caution should be exercised in the application of this chemical.

2. Performance of fused borate rods in groundline treatments of Douglas-fir poles in Owego, New York: In 1989, increment cores were removed from a series of pentachlorophenol treated Douglas-fir pole sections located near Owego, NY. These cores were cultured for the presence of decay fungi, and poles containing a range of degrees of fungal infestation were divided into 4 treatment

groups of 6 poles each. These poles received either 3 (120 g) or 6 (240 g) fused borate rods and 0 or 150 ml of distilled water equally distributed among the treatment holes. The holes were then plugged with tight fitting wood dowels. The poles were sampled 16 months after treatment by removing increment cores from 3 sites around the pole 0, 0.3, and 0.9 m above the groundline. The outer, preservative treated zone from each core was discarded, and the untreated remainder was divided into two equal zones corresponding to the outer and inner zone. These segments were combined for

Table I-13. Average retention of boron in Douglas-fir pole sections exposed in Corvallis, OR or Hilo, Hawaii for 1 year after treatment with fused borate rods^a

Dosage (g)	Boron content (Kg/m ³)				
	7.5 cm below treatment		22.5 cm below treatment		7.5 cm above treatment
	Outer	Inner	Outer	Inner	Combined
CORVALLIS, OREGON					
40	0.05(0.03)	0.55(1.03)	0.05(0.04)	0.06(0.09)	0.26(0.30)
80	0.04(0.03)	0.04(0.02)	0.02(0.02)	0.06(0.10)	0.70(0.63)
HILO, HAWAII					
40	0.03(0.09)	0.25(0.57)	0.01(0.01)	0.01(0.01)	0.69(1.87)
80	0.08(0.09)	0.01(0.01)	0.01(0.04)	<0.01(0.01)	0.62(0.88)

^aValues represent means of 10 replicates per treatment. Figure in parentheses represent 1 standard deviation. Untreated control poles contained 0.002 kg/m³ of boron.

a given height on each pole and ground to pass a 20 mesh screen prior to extraction. The resulting extracts were analyzed for boron content using Ion Coupled Spectroscopic Analysis. A second core removed from the same site on each pole was cultured on malt extract agar for the presence of decay fungi.

Cultural results indicate that decay fungi were only present in the inner zone near the groundline of the low dosage treatment (Table I-14). The remaining cores did not contain decay fungi. Chemical analysis revealed that boron levels were extremely low in all positions and at both dosages with levels ranging from 0.001 to

0.004% by weight. These values fall far below those required for effective wood protection and suggest that remedial treatment with boron rods will not result in rapid diffusion of boron at levels adequate to arrest existing fungal infestations. These tests will be reevaluated in the coming years to determine if boron distribution improves; however, the similarity of these results with those of the Hilo and Corvallis trials would suggest that diffusion through more refractory species such as Douglas-fir will require far longer periods to produce adequate chemical loadings than previously presumed.

C. EVALUATE PROMISING NEW REMEDIAL TREATMENTS IN FIELD TRIALS

1. Preliminary field trials using the solid fumigant Basamid amended with selected additives: A potential new wood fumigant, Basamid (3,5-dimethyltetrahydro-1,3,5,2H-thiadiazine-2-thione, also called Dazomet and Mylone), is a crystalline flowable powder that has been used extensively as a soil sterilant. It is stable at normal temperatures when moisture is excluded. In soil, Basamid decomposes to form methylisothiocyanate (MITC), carbon disulfide, hydrogen sulfide, and formaldehyde. Potentially, it can decompose to nearly a dozen volatile or nonvolatile compounds that have fungitoxic properties. This array of decomposition products could provide both immediate and long-term fungal control; however, preliminary field tests with Basamid in pure form have indicated that

decomposition proceeds too slowly to arrest internal decay in utility poles.

The continued development of Basamid as a wood fumigant will depend upon identifying methods for enhancing decomposition into fungitoxic compounds in wood. Some metals can enhance decomposition rates of various dithiocarbamate fungicides. Basamid decomposition was enhanced in laboratory trials when it was amended with copper sulfate and a powdered pH 12 buffer. Complete control of Antrodia carbonica was effected in small blocks within 4 weeks, suggesting that additives can be used to manipulate decomposition rates. Subsequent laboratory trials have indicated that copper has a greater enhancing effect on Basamid decomposition than several other metal additives. This note reports 2-year results of field trials with Basamid

and selected additives in Douglas-fir poles stubs.

Eighty untreated air-seasoned Douglas-fir pole stubs (20-25 cm diameter by 1.6 m long) were top-capped with roofing felt to prevent excessive end-grain absorption of water. Three holes (2.2 cm diameter by 30.5 cm deep) were drilled at approximately 60-degree angles and at equal 10-cm vertical spacing around a center treatment zone on each pole. Each hole received 50 g of Basamid alone or of Basamid amended with either 1% copper sulfate, 10% glucose, 10% ammonium lignin sulfonate, or 5% sodium octaborate tetrahydrate in powdered form; or with 50 ml of ethanol, methanol, acetone, or water. All powdered additives were tested with or without 5% powdered pH 12 buffer. The liquids were tested because increased decomposition of the fumigant (as Dazomet) has been found in their presence. Boron was tested because it is a metal and because of the alkaline buffering capacity of the formulation. Control poles received either no chemical or metham sodium (150 ml per hole) as a commercial standard.

Five poles per treatment were exposed vertically above ground for 2 years at the Peavy Arboretum test site of Oregon State University, near Corvallis. All poles were sampled 6 months after installation by removing three equally spaced increment cores (0.5 cm diameter to the pith) 15 cm above and below the treatment zone. The poles were sampled again 1 and 2 years after treatment by removing increment cores 15 and 45 cm above and below the treatment zone. The cores were then broken into inner and

outer halves, and each half was placed in a test tube containing 5 ml of ethyl acetate and extracted for at least 48 hours at room temperature. After 48 hours, the tubes were stored at 5°C until analysis for MITC content. Five ml of the extract were injected into a Varian 3700 gas chromatograph equipped with a flame photometric detector under the following conditions: 150°C injector temperature, 100°C column temperature, 240°C detector temperature, 30 ml/min nitrogen carrier flow rate, and a glass column, 2 m long by 2 mm inner diameter, packed with 10% Carbowax 20M on 80/100 Supelcoport. Concentrations were determined by comparison to known standards of MITC dissolved in ethyl acetate. The data were compared statistically with a one-way analysis of variance and least square differences ($\alpha = 0.05$) of the means for each treatment group at each exposure time (SAS Institute, Inc., Cary, North Carolina).

MITC was detected in all poles at 6, 12, and 24 months, which indicates that Basamid was decomposing (Table I-15); however, most MITC levels were low. A one-way analysis of variance indicated significant differences among treatments at all sampling periods; however, least square differences ($\alpha = 0.05$) indicated that the relative effects of the additives on MITC levels changed over time. After 6 months, poles treated with metham sodium had the highest MITC levels, significantly higher than those treated with Basamid amended with copper sulfate plus buffer. MITC levels in all other treatments were significantly lower

24

44
38
28
109

Table I-14. Residual boron levels and percent basidiomycete colonization in pentachlorophenol-treated Douglas-fir poles 16 months after remedial treatment with fused borate rods.

Sampling position (m)	Zone ^a	Water ^b	Dosage			
			120 g		240 g	
			Boron level (%)	Fungal Infestation (%)	Boron level (%)	Fungal Infestation (%)
0	Inner	150	0.004	0	0.004	0
		0	0.004	66	0.003	0
	Outer	150	0.003	0	0.004	0
		0		0	0.002	0
0.3	Inner	150	0.001	0	0.004	0
		0	0.001	0	0.001	0
	Outer	150	0	0	0.001	0
		0	0.001	0	0.001	0
0.9	Inner	150	0	0	0	0
		0	0	0	0	0
	Outer	150	0	0	0	0
		0	0	0	0	0

^aUntreated sections of each increment core sample were divided in half to produce inner and outer zones.

^bWater was added to dome treatment holes at the time of chemical application.

than those with copper sulfate plus buffer. Addition of pH 12 buffer increased MITC levels in all except the boron treatment. It is unclear why boron with buffer reduced MITC production.

After 1 year, copper sulfate plus buffer produced significantly higher MITC levels than any other treatment, including metham sodium. This trend continued after 2 years of exposure. Interestingly,

MITC levels in poles treated with metham sodium were not significantly different from levels in other amended-Basamid treatments after 2 years, indicating that levels of decomposition to MITC, which were high initially, declined rapidly over time. This trend has been found in laboratory trials with metham sodium in different species and helps to explain the need for retreatment after 5 to 7 years. Although MITC levels declined between 1

and 2 years with Basamid amended with copper sulfate plus buffer, the decline was less dramatic than with metham sodium. It was also noteworthy that MITC in the copper sulfate treatment was more equally distributed throughout the pole stubs (Table I-15), providing an evenly distributed protective barrier rather than high levels only in the zone adjacent to treatment holes. Zahora found that low residual levels of MITC provided long-term protection against invasion from decay fungi. Other studies have shown that over long exposures, Basamid is effective in controlling fungal growth. Application of Basamid to poles before internal decay has caused substantial wood loss may greatly increase the service life of poles made from western U.S. softwood species.

The results of these field tests indicate that copper sulfate plus a pH 12 buffer can significantly enhance decomposition of Basamid to MITC, thereby increasing the prospects for successful elimination of established decay fungi. MITC levels with that treatment declined much less rapidly and were more evenly distributed throughout pole stubs than in treatments with metham sodium indicating that longer more complete internal protection may be afforded to wood poles with this treatment. These results suggest that simultaneous application of Basamid and additives can increase MITC production from this solid, less volatile compound, substantially increasing applicator and environmental safety.

2. Field trials with gelled and pelletized metham sodium: This past Fall a trial of gelled metham sodium was

established. Gelled metham sodium minimizes the risk of spilling during application, and our laboratory trials suggest that the gell markedly improves the performance of this chemical.

Fifty ACZA-treated Douglas-fir pole sections (25 to 30 cm in diameter by 3.6 m long) were obtained from local cooperators and set at the Peavy Arboretum test site. Three 1.9 cm diameter by 22.5 cm long steeply angled holes were drilled into the pole beginning 0.9 m above their base and extending around the pole at 120 degree intervals and upward at 15 cm increments. These poles were treated in groups of 5 with 100, 200, 300, 400, 500, or 750 g of 40% gelled metham sodium. Previous laboratory trials suggested that this formulation provided improved protection over comparable 40% liquid formulation of the same chemical. The 750 ml dosage required the use of slightly larger treatment holes. Following treatment, the holes were plugged with tight fitting preservative treated wood dowels. Two additional sets of 5 poles received 100 or 200 g of a solid, pelletized formulation of metham sodium containing 25% active ingredient.

Chemical movement in the poles will be assessed 6 months after treatment and thereafter at 1, 2, 3, and 5 years after treatment. Increment cores will be removed from 3 equidistant sites 0.3, 0.9, and 1.5 m above the highest treatment site. The outer and inner 2.5 cm of each core will be placed in ethyl acetate, extracted for a minimum of 48 hours, and analyzed for residual MITC using gas chromatographic methods. The middle 2.5 cm of each core will be evaluated

using the closed tube bioassay to determine if the wood contains fungitoxic vapors.

The results will assist in evaluating the efficacy of the gelled formulation and will also be used to confirm the performance of a fumigant movement model which will be discussed in a subsequent section.

3. Evaluation of a copper naphthenate/boron paste for internal treatment of Douglas-fir posts: A copper naphthenate/boron paste previously employed for surface treatments of decaying utility poles has been proposed for internal treatment of decaying Douglas-fir poles; however, there is little data on the efficacy of this formulation for internal applications.

Twenty five pentachlorophenol-treated Douglas-fir poles (20 to 25 cm in diameter by 2.0 m long) were installed at the Peavy Arboretum test site. Three holes (2.1 cm in diameter) were drilled at a 45 degree angle to depths of 10 or 17.5 cm beginning at the groundline, spiraling around the pole 120 degrees and upward 15 cm. Ten poles with 10 cm long holes received 150 g; while 10 poles with 17.5 cm long holes received 300 g of a paste containing 18.16% amine based copper naphthenate and 40% sodium tetraborate decahydrate applied from a grease gun. The treatment holes were plugged with tight fitting preservative treated wood dowels. Five poles were left untreated to serve as controls.

The poles will be sampled 3 and 5 years after treatment by removing duplicate sets of 3 increment cores from equidistant sites around the pole 7.5 cm

above and below the treatment zone and two cores 120 degrees around the pole from the middle treatment hole. The cores will be segmented into outer and inner zones along the untreated heartwood and the respective zones will be combined at a given level for each pole. The segments will be analyzed for residual copper content using an ASOMA x-ray fluorescence analyzer then the ground material will be water extracted. The resulting extracts will be analyzed by residual boron using the Azomethine H method. The initial sampling of these poles will take place this summer.

The results should provide some indication of the ability of the copper naphthenate and boron components to migrate through Douglas-fir heartwood. A separate study will be described under a subsequent section addressing the threshold values for these chemicals for protecting wood against decay fungi.

4. Evaluation of a sodium fluoride/boron rod for internal treatment of Douglas-fir poles: A sodium fluoride/boron rod developed in Australia has shown some promise for preventing and arresting fungal attack of wood; however, no data on the efficacy of this formulation on U.S. species is available. In this trial, the effects of dosage and pattern on performance will be investigated using preservative treated Douglas-fir poles.

Douglas-fir pole sections (25 to 30 cm in diameter by 2 m long) will be treated with pentachlorophenol in P9 Type A oil. The poles will be set to a depth of 0.6 m at the Peavy Arboretum test site.

Sets of five poles each will be drilled using the following patterns:

1. Three holes beginning at groundline and spiraling upward at 120-degree intervals and 0.3 m-height increments.
2. Three holes beginning at groundline and spiraling upward at 90-degree intervals and 0.3 m-height increments.
3. Six holes beginning at groundline and spiraling upward at 120-degree intervals and 0.15-m height increments.
4. Six holes beginning at groundline and spiraling upward at 90-degree intervals and 0.15-m height increments.

The holes may need to be angled slightly to accommodate the rod and plug. Each hole should receive a single rod containing 24.3% sodium fluoride and

58.2% disodium octaborate tetrahydrate (Preschem Pty Ltd, Cheltenham, Victoria, Australia) and be plugged.

The poles will be sampled annually by removing increment cores from site 120 degrees on either side of the treatment holes and from three equidistant locations around the pole at points equidistant between the various treatment heights. In addition, a set of 3 cores each shall be removed from 15 cm below ground and 15 cm above the highest treatment hole. Each sample will be divided into 3 equal size samples corresponding to outer, middle, and inner zones. Zones from a given location on each pole will be combined for each of the 5 poles per treatment group and the samples will be ground for analysis of boron and fluoride. Boron analysis will be performed using the Azomethine H method; while, the fluoride analysis will be performed using the method described in AWWA Standard A5.

D. IDENTIFY NEW REMEDIAL TREATMENTS FOR INTERNAL DECAY CONTROL

1. Performance of gelled metham sodium as a wood fumigant: Metham sodium is the most commonly used fumigant for controlling internal decay of large wood structures in North America. Application of this chemical results in elimination of established decay fungi within 1 year and provides protection for an additional 7 to 10 years in Douglas-fir poles and 3 to 5 years in southern pine. While metham sodium is widely used, it has several disadvantageous properties which have limited use and encouraged the

search for safer formulations. As a liquid, metham sodium can be spilled during application, posing a potential worker exposure hazard and, when spilled on skin, causes burns. In addition to these worker-exposure concerns, metham sodium provides relatively little long-term protection in terms of residual chemical levels in the wood. Finally, metham sodium must decompose to become an effective fungicide, and laboratory trials suggest that the decomposition efficiency ranges from 12 to 26% of the total amount

of chemical applied. Each hole drilled into the wood for fumigant application diminishes wood strength. Therefore, utilities must seek chemical treatments which maximize dosage while minimizing strength effects. At present, the low decomposition efficiency of metham sodium makes it less attractive as a wood fumigant.

One approach to minimizing applicator risk and improving chemical performance is to gel the liquid formulation. Gels could be easily applied and might retain moisture near the treatment site, thereby enhancing the degree of metham sodium decomposed to produce methylisothiocyanate (MITC), the primary fungitoxicant of metham sodium.

In this report, we describe the preliminary experiments performed with a 40% gelled metham sodium formulation.

Gelled metham sodium was obtained from ICI Americas Inc. in small caulking tubes. The formulation was evaluated in 3 laboratory trials and has been installed in a field test site.

In the laboratory trials, metham sodium decomposition was evaluated in small glass chambers containing measured amounts of wood or in small wood blocks colonized by a decay fungus. In the first test, 0.5 g of Douglas-fir heartwood sawdust was placed into a 40 ml borosilicate screwcap tube along with 10 or 25 ug of gelled or liquid metham sodium. The tubes were sealed with tight-fitting teflon-lined caps and incubated at 5, 23, or 32°C for 24, 48, 72, or 144 hours. Each dosage was replicated in 3 tubes per time point, per temperature. At each time

point, an air sample was removed from each vial and injected into a Varian 3700 GC equipped with a flame photometric detector with specific for sulfur. Although carbon disulfide and carbonyl sulfide were detected in these analyses, only MITC was quantified by comparison with prepared standards. Three ml of ethyl acetate was then added to each vial, and 5 ul of this extract was analyzed for MITC after 0.5 and 24 hours of extraction.

In the second test, Douglas-fir heartwood blocks (2.5 by 2.5 by 10 cm long) were pressure soaked with water and inoculated with *Antrodia carbonica*, a common brown rot fungus. The blocks were incubated at room temperature for 4 to 6 weeks, then measured amounts of gelled or liquid metham sodium were applied through small holes drilled in the tangential face of each blocks. The holes were plugged with tight-fitting rubber serum caps, and the blocks were incubated for 1 to 28 days at room temperature. At each time point, the outer 5 mm of each end was removed, and two additional 5-mm-thick sections were cut. The two sections from each end were cut into 16 equal-sized squares, and the inner four squares of the outermost section were placed on potato dextrose agar and observed for evidence of fungal growth which served as a measure of chemical effectiveness. The 4 inner squares from the innermost section were placed into 5 ml of ethyl acetate and analyzed for MITC as described above.

Application of gelled metham sodium to Douglas-fir heartwood sawdust resulted in high air levels of MITC at all treatments (Table I-16). Airborne MITC levels generally peaked 48 hours after

application and declined thereafter. In general, MITC levels in the wood were approximately 1000 times greater than those found in the air, reflecting the preferential sorption of this chemical onto wood. This preferential sorption helps to explain the excellent performance afforded by MITC-based fumigants. Airborne levels of MITC in gelled metham sodium treatments were similar to those found with liquid metham sodium at 5 or 23°C, but were substantially higher at 32°C. Short-term extractions of metham sodium-treated wood produced variable results; however, 24-hour extractions indicate that MITC levels were consistently higher in gelled metham sodium treatment and suggest that gelled metham sodium provided a more efficient decomposition to MITC resulting in higher levels of this chemical in the wood.

Treatment of Douglas-fir heartwood blocks with gelled or liquid metham sodium produced variable results (Table I-17, 18). The degree of fungal survival declined substantially in the gelled metham sodium treatments, while survival varied in the liquid treatments. In the initial trial, 250 to 400 mg of liquid metham sodium was required per block to control the test fungus with a 7-day period, while gelled metham sodium affected 90% of control at 50 mg per block (Figure I-6). In a second trial, however, 90% control was affected at 100 mg (Table I-17), suggesting some variability in chemical effectiveness. In general, gelled metham sodium produced a higher degree of fungal control, although some fungal survival was noted in the two highest dosages 28 days after application. This variation may reflect incomplete MITC diffusion since chemical analyses revealed that the wood contained high levels of MITC 7 days after treatment.

Chemical levels in gelled metham sodium treatments 7 days after application were 2 times higher than those found with comparable dosages of liquid formulation.

In a second test, the relative degree of control associated with 250 mg of gelled or liquid MITC was evaluated over a 28-day period (Table I-18). In this trial, fungal survival initially declined more rapidly with the liquid metham sodium while chemical levels increased more rapidly. After 5 days; however, fungal survival declined rapidly in gelled treatments while MITC levels remained at slightly higher levels for a longer period of time than in the liquid treatments.

The field trials of gelled metham sodium, with the exception of the two highest dosages, have been established at the OSU Peavy Arboretum test site. This site also has a number of previous trials of commercial fumigants and was established to produce data to support commercialization of internal wood treatments. These poles will be assessed for chemical level and fungal colonization beginning 6 months after installation.

Gelled metham sodium appears to have a number of properties which make it attractive for wood treatment. The gel should reduce the risk of spilling during application and, thereby, diminish the possibility of skin burns due to inadvertent chemical contact. The gel also appears to decompose more efficiently than comparable dosages of liquid metham sodium. While liquid metham is an effective fumigant, its residual protective period is sharply lower than that found with chloropicrin or pure MITC. Enhancing the performance of this product through improved decomposition might encourage more widespread use.

Dosage (mg)		Temp (C)		Time (hr)		Gelled Metham Sodium				Liquid Metham Sodium			
						MITC Air Concentration ng/ml		MITC Wood Conc. (µg/g)		MITC Air Concentration ng/ml		MITC Wood Conc. (µg/g)	
								0.5 hr Extr.	24 hr Extr.			0.5 hr Extr.	24 hr Extr.
10	5	24	5	377.3 (312.9)	638 (261)	3646 (0)	1195.7 (174.1)	852 (98)	2541 (205)	24 hr Extr.	24 hr Extr.		
				520.8 (329.5)	102 (15)	5714 (0)	142.3 (41.1)	393 (147)	1513 (284)				
				66.3 (81.6)	50 (68)	5714 (0)	182.4 (39.5)	442 (69)	1313 (324)				
				59.2 (99.9)	674 (166)	2903 (1465)	284.0 (70.1)	459 (28)	3703 (2099)				
	21	24	24	21	1048.7 (1138.6)	449 (509)	3105 (743)	1359.8 (70.1)	810 (413)	1666 (991)	24 hr Extr.	24 hr Extr.	
					609.2 (626.3)	237 (62)	5703 (9)	1621.1 (142.2)	607 (187)	1581 (133)			
					2010.8 (2050)	407 (361)	5150 (977)	236.0 (240.4)	381 (221)	1089 (555)			
					977.3 (1018.7)	686 (197)	5714 (4)	253.3 (237.9)	287 (347)	1011 (219)			
	32	24	24	32	8159.3 (2867.1)	557 (0)	3646 (0)	3028 (597)	-	3484 (486)	24 hr Extr.	24 hr Extr.	
					16791.6 (16.8)	1059 (1157)	5713 (0)	2614 (1408)	335 (108)	2545 (275)			
					6287.5 (4540.1)	1511 (308)	5348 (635)	1189 (138)	314 (261)				
					5343.4 (1908.5)	69 (70)	5710 (6)	68 (0)	-				
25	5	24	5	526.7 (306.6)	1105 (357)	3646 (0)	3494.8 (693.5)	1559 (165)	6458 (154)	24 hr Extr.	24 hr Extr.		
				1626.8 (1396.8)	1136 (701)	5713 (0)	796.7 (261.5)	2413 (1463)	5985 (9)				
				269.0 (445.0)	601 (623)	5115 (719)	1436.0 (310.6)	2029 (250)	4156 (150)				
				414.4 (577.8)	925 (801)	4455 (1256)	880.0 (196.0)	1239 (910)	4959 (382)				
	21	24	24	21	7227.5 (2617.4)	1978 (1172)	3646 (0)	2843 (246)	998 (220)	4857 (328)	24 hr Extr.	24 hr Extr.	
					10795.5 (5690.5)	2144 (1649)	5714 (0)	1212 (506)	1959 (927)	3506 (1426)			
					8383.5 (7100.3)	2095 (1116)	5714 (0)	489 (443)	443 (232)	2628 (1213)			
					4942.4 (0)	484 (837)	1905 (3297)	368 (262)	1144 (806)	1246 (742)			
	32	24	24	32	8210.8 (3465.8)	2315 (1208)	3646 (0)	6264 (450)	-	5218 (34)	24 hr Extr.	24 hr Extr.	
					20884.1 (5884.0)	2825 (831)	5713 (0)	1493 (496)	631 (122)	1083 (454)			
					14829.7 (15,512.5)	4625 (1283)	5714 (0)	1174 (189)	454 (205)	-			
					8045.1 (3913.0)	1217 (1031)	5738 (22)	22 (0)	-	219 (296)			

Table I-17. Residual MITC levels and percent fungal survival in Douglas-fir heartwood blocks treated with selected dosages of gelled and liquid metham sodium and incubated for 7 or 28 days.

Dosage	Liquid			Gelled		
	7 days		28 days	7 days		28 days
	Fungal Survival (%)	MITC level (ug/g wood)	Fungal Survival (%)	Fungal Survival (%)	MITC level (ug/g wood)	Fungal Survival (%)
50	37.5	50(41)	20.8	16.7	-	0
100	29.2	61(8)	16.7	8.3	417(100)	0
250	37.5	98(38)	16.7	8.3	164(55)	0
400	4.2	361(248)	12.5	29.2	618(399)	4.2
500	0	342(145)	0	12.5	757(293)	4.2

Table I-18. Residual MITC levels and percent fungal survival in Douglas-fir heartwood blocks treated with 250 mg of 40% gelled or liquid metham sodium as measured 1 to 28 days after chemical application.

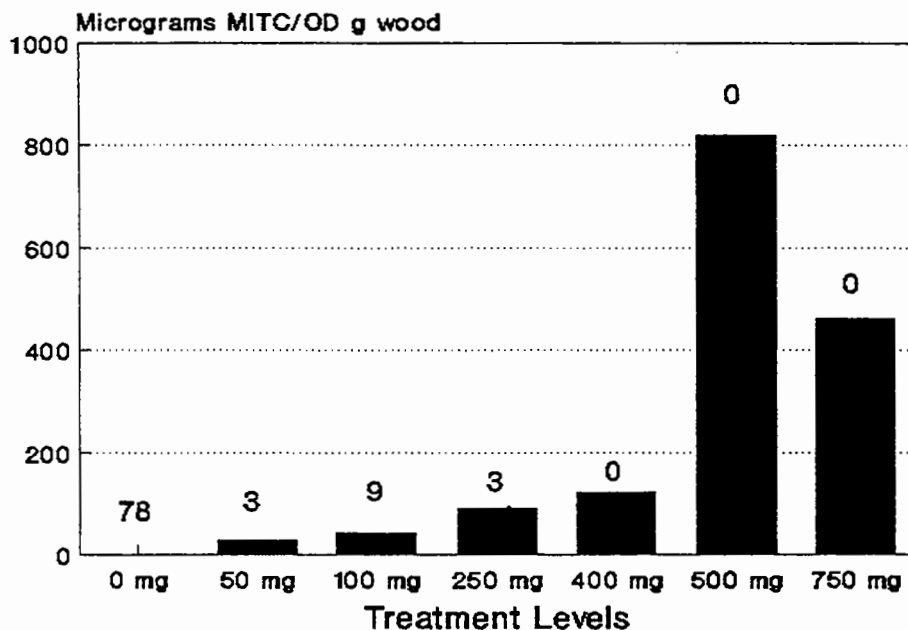
Incubation Period (days)	Control		Gelled Metham Sodium		Liquid Metham Sodium	
	Fungal Survival (%)	MITC level (ug/g wood)	Fungal Survival (%)	MITC level (ug/g wood)	Fungal Survival (%)	MITC level (ug/g wood)
1	50.0	-	91.7	415(240)	66.7	543(275)
3	-	-	58.3	489(221)	16.7	485(246)
5	-	-	50.0	519(268)	29.2	321(426)
7	28.8	-	8.3	218(166)	0	109(108)
10	-	-	12.5	10(5)	4.2	22(13)
14	29.2	-	37.5	-	125	-
28	45.8	-	0	-	-	-

E. EVALUATE BASIC PROPERTIES OF REMEDIAL INTERNAL TREATMENTS

1. The effect of selected additives and conditions on the decomposition of Basamid in Douglas-fir heartwood:

Identifying safer fumigants for remedial treatments would enhance applicator safety while permitting more widespread use of these treatments. One promising chemical, Basamid (tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione; also known as Mylone or Dazomet), not only decomposes to form MITC, but also overcomes both problems encountered with the existing registered fumigants; i.e., it is a solid and does not decompose or sublime when kept dry. As with most wood fumigants, Basamid was developed as a soil sterilant. Soil studies show that Basamid decomposes to form

formaldehyde, methylamine, hydrogen sulfide, and MITC; however, decomposition in wood has until now been too slow to be effective. Some studies in wood have shown that long exposures to Basamid are effective in controlling fungal growth. In fact slow decomposition could be useful if the chemical was applied to non-decayed wood at the time of installation when immediate fungal eradication is not of concern. However, most fumigants are applied to older poles which may already contain actively growing decay fungi. Basamid decomposes too slowly in pure form to rapidly eliminate an actively growing fungal colony.



Numbers are % survival.

Figure I-6. Residual MITC levels and percent fungal survival in Douglas-fir heartwood blocks treated with selected dosages of gelled metham sodium and incubated for 7 days at room temperature. Values above bars represent percent fungal survival.

Decomposition of several dithiocarbamates can be enhanced by the addition of certain metals; e.g., methamsodium decomposition increases in the presence of as copper, manganese, iron, or zinc. It has been suggested that soil minerals may catalyze the primary step of Basamid decomposition. Previously, we have found that pH 10 to 12 buffers also increased MITC production and decreased fungal survival rates in wood blocks. Complete control of *Antrodia carbonica* was effected in small blocks within four weeks of applying Basamid amended with powdered pH 12 buffer. These results suggest that Basamid decomposition can be enhanced to rates capable of rapidly eradicating decay fungi in utility poles.

The following tests were performed to determine the effect of moisture and temperature as well as selected additives on the decomposition of Basamid in Douglas-fir heartwood. An initial screening of additives was performed to determine which additives warranted further study. Two additives were further studied to determine both the rate of decomposition and the effects of additives on the balance of decomposition products.

Initial Additive Screening: The following powdered additives were tested for their ability to enhance Basamid decomposition as indicated by the production of MITC:

- 5% pH 12 buffer
- 1% copper sulfate
- 1% copper chloride
- 1% manganese sulfate
- 1% magnesium sulfate

Amounts are given as the percentage of metal added based on the weight of

Basamid. Douglas-fir heartwood ground to pass a 3 mm screen and adjusted to 30 moisture content (MC) was used in all tests. Vials that received only pH 12 buffer as an additive were tested at 12, 30, and 60% MC. Tests were performed by placing 3 oven-dry (OD) g sawdust that had been adjusted to the proper MC into a 40 ml glass vial. One-hundred twenty mg of Basamid amended with the test additive was placed on top of the sawdust in an evenly distributed layer and covered with an additional 3 g of sawdust. The vials (3 per combination) were then tightly capped with a Teflon-lined silicone septum and stored at 23°C.

Basamid decomposition was determined 1, 3, 5, 7, 10, and 14 days after treatment by removing an air sample through the septum with an gas-tight syringe. The sample was injected into a Varian 3700 gas chromatograph equipped with a flame photometric detector at the following conditions: injector temperature, 150°C; oven temperature, 100°C; detector temperature, 240°C; nitrogen carrier flow rate 30 ml/minute; column, 10% Carbowax 20M on 80/100 Supelcoport. MITC concentration was quantified by comparison with injections of known amounts of MITC dissolved in ethyl acetate.

Decomposition study: Trials were established to determine the decomposition products of Basamid alone or amended with 5% pH 12 buffer and/or 1% copper sulfate. The powdered additives were measured as a percentage of Basamid by weight and were mixed thoroughly before treatment. Using vials as described above, 120 mg Basamid amended with the appropriate additive was placed in an evenly distributed layer in the bottom and covered with 1 OD g of sawdust that had

been adjusted to 6 or 30% MC. A fine-meshed plastic screen was placed on top of the sawdust, and an additional MC-adjusted 2 OD g of sawdust were placed on top. Each vial was capped with a Teflon-lined silicone septum and stored at 5, 23, and 32°C for up to 30 days. Controls were assembled using either no chemical or no wood to detect volatile components from untreated wood and stability of Basamid with additives in the absence of moisture.

Two air samples were removed from the vials (3 per combination) at selected times and one was injected into a Varian 3700 gas chromatograph and analyzed for sulfur-containing compounds as described above. The other sample was analyzed for non-sulfur compounds using a flame ionization detector on a second Varian 3700 gas chromatograph at the same operating conditions except: column temperature, 110°C; column, 4% Carbowax 20M on 0.8% KOH 60/80 Carbopack B.

Following air sampling, the vials were placed into a freezer for later analyses of non-volatile decomposition products. The portion of sawdust above the plastic screen will be removed and extracted with selected solvents. Each extract will be analyzed by high performance liquid chromatography and the extracted wood will be analyzed for residual sulfur content by inductively coupled plasma (ICP) spectrometry. The wood and chemical below the screen will also be analyzed by ICP for total sulfur content. Decomposition efficiencies and mass balances will be calculated from these analyses.

Initial screening: Moisture greatly enhanced the decomposition of Basamid to

MITC (Figure I-7). No MITC was detected in any vial containing wood at 12% MC. MITC production from Basamid was consistently greater in wood at 60% MC than at 30% MC. Using a pH 12 buffer also greatly enhanced MITC production, confirming previous results although the MITC levels associated with pH 12 buffer were still quite low. Both copper sulfate (Cu^{+2}) and copper chloride (Cu^{+1}) had a far greater enhancing effect on MITC production from Basamid than manganese or magnesium (Figure I-8). The different copper compounds were evaluated to determine if valence state affected decomposition, but no differences were noted. These results confirm field test data obtained using Basamid amended with various additives. In those tests, copper sulfate with a pH 12 buffer outperformed several other additives in elevating MITC production in Basamid-treated Douglas-fir pole sections over a 2-year period. The results of the screening tests indicated that one of the copper-containing additives warranted further study; we chose copper sulfate.

Decomposition study: Analyses for both methylamine and dimethylamine in the headspace of the test vials were inconclusive. If present, these compounds were below the limits of detection. There were, however, several unidentified compounds produced in small quantities in the higher MC and temperature exposures.

The presence of copper sulfate resulted in MITC production from Basamid even in the absence of wood or moisture. This makes it likely that this additive would have to be mixed with Basamid immediately prior to treatment to prevent premature fumigant decomposition.

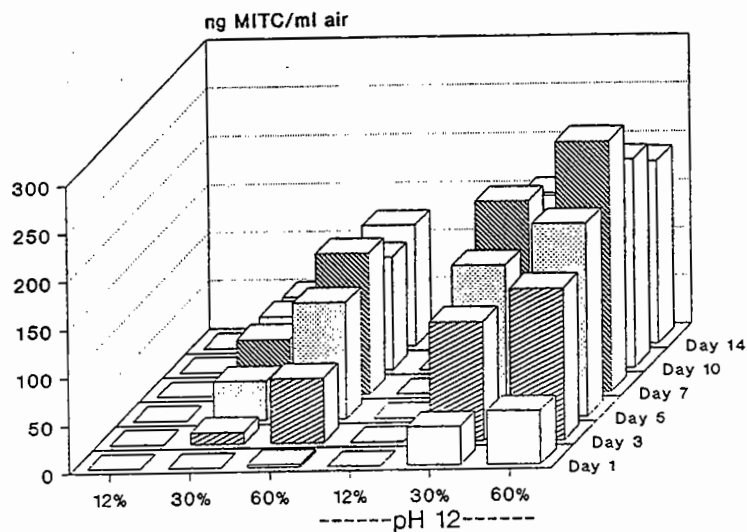


Figure I-7. MITC levels at selected times in the headspace of sealed vials containing Douglas-fir heartwood at 12, 30, and 60% MC that was treated with Basamid alone or amended with a powdered pH 12 buffer.

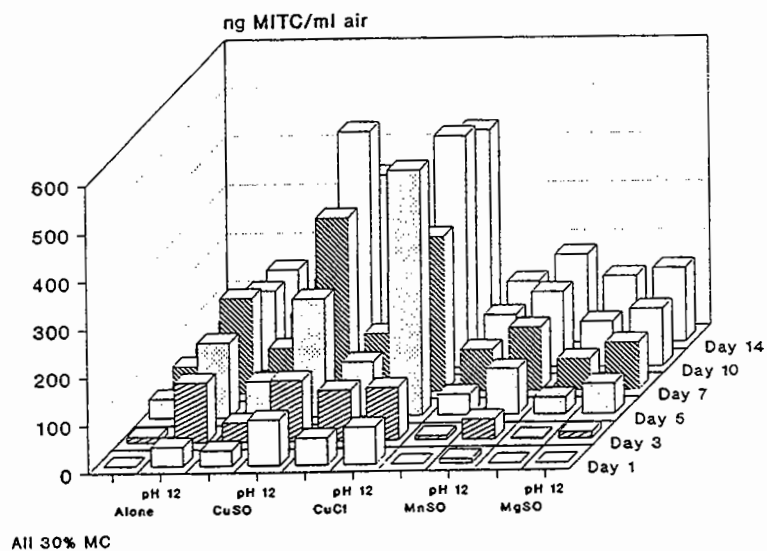


Figure I-8. MITC levels at selected times in the headspace of sealed vials containing Douglas-fir heartwood at 30% MC that was treated with Basamid alone or amended with pH 12 buffer, copper sulfate, copper chloride, manganese sulfate, or magnesium sulfate.

Both MITC and carbon disulfide (CS_2) were identified in the headspace of the test vials. As in the screening experiments, higher MC's resulted in higher MITC production (Figure I-9) regardless of the additive or temperature used. Higher temperatures also enhanced MITC production. These results were not unexpected as a number of tests with metham sodium have achieved similar results. Corresponding trends were noted for CS_2 production (Figure I-10); however, these levels were much higher than those found for MITC on a weight to weight basis. It is evident that levels for both compounds were decreasing after 30 days in most treatments. This decline may be due to recombination of various decomposition products to form non-volatile compounds. Analyses of extracts from the wood are planned to examine this possibility.

The effects of pH and copper sulfate on decomposition were repeated as in the initial screening tests. Trends in MITC production when pH 12 buffer was added to Basamid were nearly identical to those without the buffer, but the levels were much higher. Addition of copper had the same enhancing effect, but the effects were delayed, and the levels of MITC did not decline as rapidly as those treatments receiving no copper. Once again, these results reflect those from Basamid field tests. Adding both buffer and copper sulfate had a synergistic effect on initial and prolonged MITC production, especially at 30% MC and 32°C.

CS_2 production was increased by the addition of pH 12 buffer and copper in some treatments; however, CS_2 release in relation to MITC was not as dramatic when copper was added. One goal of this research was to identify additives to

enhance Basamid decomposition; however, decomposition must produce effective fungicides. These compounds must also interact sufficiently with wood and not immediately volatilize, leaving the wood unprotected. While copper increased CS_2 production slightly, it increased MITC levels markedly causing the ratio of CS_2 to MITC detected to decrease an order of magnitude in many instances (Figure I-11). There are two possible pathways for MITC production through cleavage of the Basamid ring. One of these pathways involves the same carbon atom involved in CS_2 evolution, explaining their diametric production rates. Although CS_2 is an effective fungicide, it volatilizes rapidly providing no residual wood protection. MITC, conversely, has been shown to remain in wood for long periods of time providing long-lasting protection. This demonstrates that the efficiency of decomposition is equally important to the rate of that breakdown.

The results indicate that:

1. Increasing temperature and moisture content enhance Basamid decomposition.
2. Decomposition of Basamid is enhanced by addition of powdered pH 12 buffer; however, this additive greatly favors the production of CS_2 over that of MITC.
3. Copper sulfate enhances the production of MITC from Basamid while reducing CS_2 evolution. This is especially true when copper sulfate is used in combination with the pH 12 buffer.
4. Methylamine and dimethylamine were not detected in our study.

5. Basamid is not stable in the presence of copper sulfate, even without moisture, making it necessary to keep this additive separate from the fumigant until immediately prior to treatment.

Laboratory tests are in progress to further elucidate the decomposition of Basamid in wood with and without selected additives under various conditions. Field tests are continuing to determine the release and distribution of MITC in pole sections treated with Basamid amended with various additives.

2. Effect of decay voids on fumigant movement and effectiveness in Douglas-fir poles:

Fumigants are often applied to poles containing small decay pockets or voids. While most utility specifications require that the inspector drill into sound wood above or below the pocket to apply fumigants, there is considerable debate concerning the effects of these voids on fumigant movement and efficacy. To provide more information on this topic, 12 pentachlorophenol treated Douglas-fir poles were cut in half and a 5 cm diameter by 15 cm long hole was cut into the exposed, untreated cross section of each half. The void was filled with boron rotted wood, and the pole halves were reassembled. The joint was sealed with an elastomeric paint to retard lateral fumigant loss. The poles were then treated with 80 or 160 ml of metham sodium or chloropicrin applied to holes drilled above the void. Each treatment was applied on 3 poles and the poles were exposed outdoors, but protected from rain at the Forest Research Laboratory.

The poles were sampled 3, 4, and 5 years after treatment by removing increment cores from 3 equidistant sites

around the pole 0.3 and 0.9 m above and below the void. The outer and inner 2.5 cm of each core were extracted for 48 hours in ethyl acetate for metham sodium treated wood or hexane for chloropicrin treatments. The extracts were analyzed for residual fumigant content by gas chromatographic methods.

The presence of voids had little effect on fumigant distribution regardless of dosage or fumigant employed (Table I-19). These results indicate that the void, while creating a gap in wood continuity which the fumigant must cross, does not act as a barrier to movement. This effect implies that once the fumigant level in the void reaches a certain concentration, diffusion across the void is the driving factor to continued fumigant movement. While the presence of a deep check intersecting the void might alter the development of a steady concentration of fumigant in the void, the rate of air exchange with the air outside the pole should be low and therefore not adversely affect diffusion. Furthermore, the strong affinity of MITC for wood should help restrict potential fumigant loss from the void zone.

Fumigant levels in this test dropped precipitously between 4 and 5 years after fumigant treatment; however, the levels after 5 years appear more in line with those found at the 3 year sampling. The reasons for the peak in detection 4 years after treatment are unclear, although it is possible that the sampling sites were closer to the original treatment sites and therefore more likely to detect higher chemical loadings. Further sampling of these poles will be necessary to more fully evaluate the effect of prolonged exposure on residual fumigant levels.

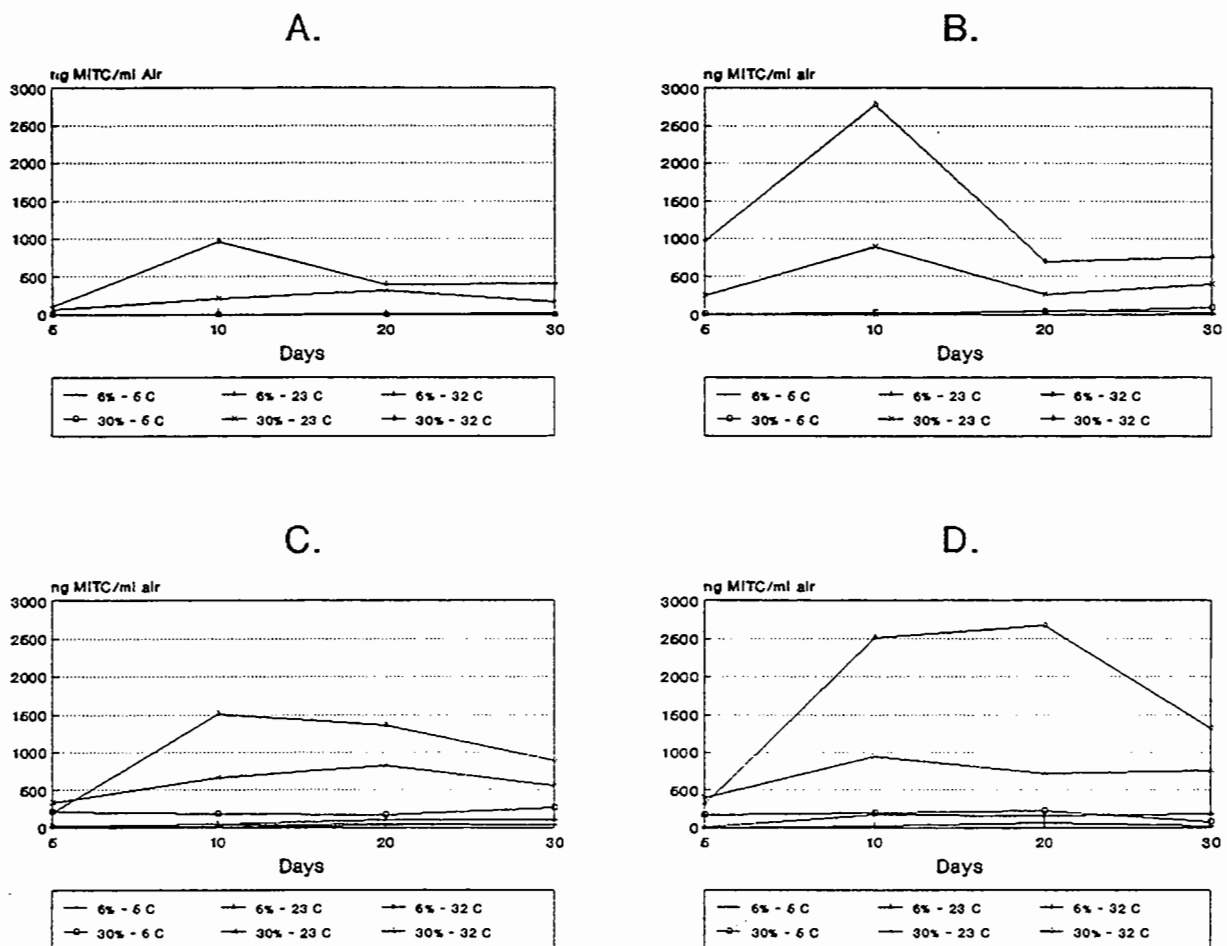


Figure I-9. MITC levels over a 30 day period in the headspace of sealed vials containing Douglas-fir heartwood at 6 and 30% MC that was treated with (a) Basamid alone or amended with (b) pH 12 buffer, (c) copper sulfate, or (d) both buffer and copper sulfate and stored at 5, 23, or 32°C.

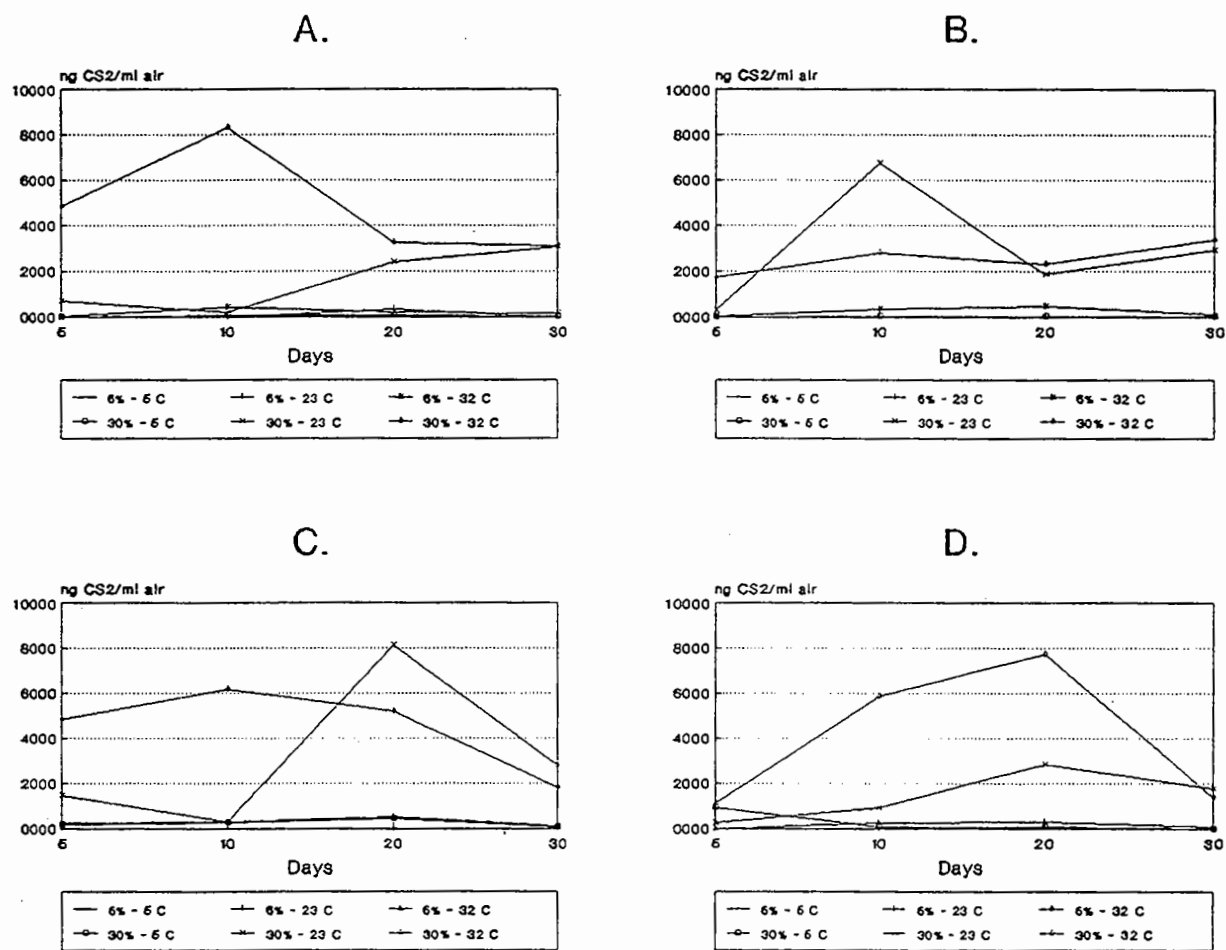


Figure I-10. CS₂ levels over a 30 day period in the headspace of sealed vials containing Douglas-fir heartwood at 6 and 30% MC that was treated with (a) Basamid alone or amended with (b) pH 12 buffer, (c) copper sulfate, or (d) both buffer and copper sulfate and stored at 5, 23, and 32°C.

The results indicate that poles containing voids can be effectively protected above and below the void by application of fumigants and that the voids do not adversely affect fumigant movement.

3. Distribution of MITC in Douglas-fir timbers following metham sodium treatment: Fumigants are increasingly employed to treat timbers and other large, sawn wood products. Fumigants are presumed to function in these materials in a manner similar to that found in poles; however, there is little performance data in sawn materials. In 1990, timber stringers in a bridge located in Marion County, Oregon, was treated with metham sodium. Chemical was added through 1.9 cm diameter holes drilled into the timbers at 1.2 m intervals. The holes were plugged with tight fitting dowels. One year after treatment, chemical levels in the timbers

were determined by removing increment cores from sites located between the treatment holes. Increment cores were removed from sites near the top and bottom edge 0.6 m from each treatment hole on each of 7 stringers. The outer preservative treated shell was discarded and the remainder of the core was divided into inner and outer zones. Each core segment was extracted for 48 hours in ethyl acetate and the extract was analyzed for MITC content by gas chromatographic methods. MITC is the presumed major fungitoxic decomposition product of metham sodium.

The results indicate that MITC was detected in virtually all samples removed from the timbers except the outer zone of one sample (Table I-20). MITC levels ranged from 0 to 100 ug/oven-dried gram of wood. Previous studies suggest that long-term exposure to these levels of

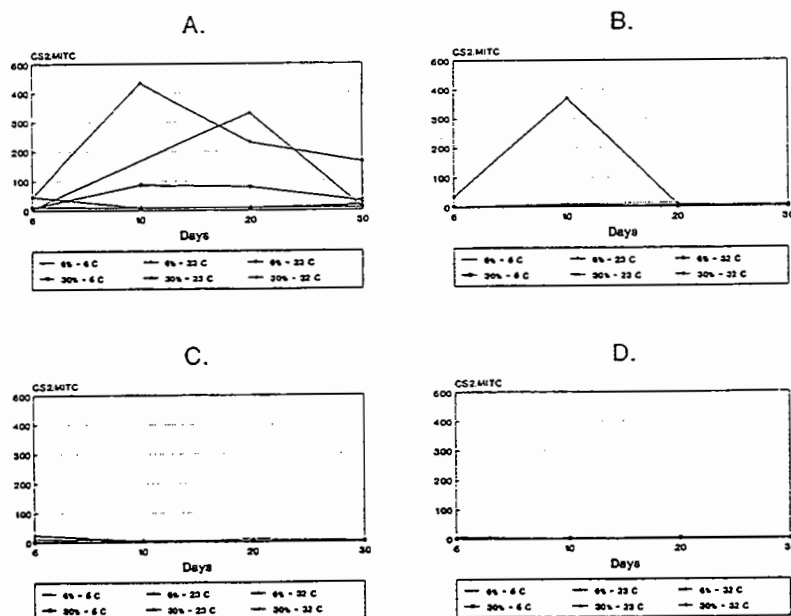


Figure I-11. Ratio of CS₂ to MITC levels over a 30 day period in the headspace of sealed vials containing Douglas-fir heartwood at 6 and 30% MC that was treated with (a) Basamid alone or amended with (b) pH 12 buffer, (c) copper sulfate, or (d) both buffer and copper sulfate and stored at 5, 23, and 32°C.

Table I-19. Residual MITC or chloropicrin concentrations at various sites above or below voids in Douglas-fir poles 3 or 4 years after treatment with selected dosages of metham sodium or chloropicrin.														
Fumigant content (ug MITC or chloropicrin/g wood) ¹														
-0.9 m														
Chemical Treatment	Dosage (g)	Void (+/-)	Outer			Inner			Outer			Inner		
			3 yr	4 yr	5 yr	3 yr	4 yr	5 yr	3 yr	4 yr	5 yr	3 yr	4 yr	5 yr
Metham sodium	80	(+)	3.7	16.7	0	3.0	14.8	0.0	9.7	148.7	3.5	15.9	121.8	1.7
		(-)	-	0	0.8	2.5	14.0	0.0	8.1	8.1	2.7	57.7	147.3	2.6
	160	(+)	4.2	0	0.0	10.5	21.5	0.0	13.1	62.5	1.2	32.4	277.5	0.0
		(-)	2.1	21.5	0.0	4.5	28.0	1.2	15.4	327.0	6.1	30.3	376.5	13.1
Chloropicrin	80	(+)	-	8.1	-	-	114.4	-	-	205.0	-	-	442.1	-
		(-)	-	14.1	-	-	55.0	-	-	150.7	-	-	507.3	-
	160	(+)	-	27.0	-	-	223.8	-	-	357.8	-	-	821.8	-
		(-)	-	11.7	-	-	215.4	-	-	166.9	-	-	585.2	-

Table I-19 (continued). Residual MITC or chloropicrin concentrations at various sites above or below voids in Douglas-fir poles 3 or 4 years after treatment with selected dosages of metham sodium or chloropicrin.														
Fumigant content (ug MITC or chloropicrin/g wood) ¹														
+0.3 m														
Chemical Treatment	Dosage (g)	Void (+/-)	Outer			Inner			Outer			Inner		
			3 yr	4 yr	5 yr	3 yr	4 yr	5 yr	3 yr	4 yr	5 yr	3 yr	4 yr	5 yr
Metham sodium	80	(+)	12.4	82.3	3.8	11.0	260.0	1.9	4.2	17.5	0.0	3.4	23.3	0.0
		(-)	9.4	46.2	1.5	15.1	136.0	1.8	-	0	0.0	3.9	13.5	0.0
	160	(+)	8.9	129.5	5.1	20.0	724.5	5.9	-	22.0	1.5	5.3	77.0	2.9
		(-)	20.4	206.3	9.2	28.1	908.7	6.7	3.4	2.5	0.0	3.9	14.8	0.0
Chloropicrin	80	(+)	-	93.3	-	-	339.0	-	-	4.3	-	-	26.3	-
		(-)	-	253.1	-	-	607.6	-	-	14.3	-	-	107.3	-
	160	(+)	-	236.3	-	-	620.9	-	-	21.7	-	-	335.5	-
		(-)	-	145.6	-	-	488.0	-	-	28.1	-	-	232.8	-

¹As determined by gas chromatographic analyses of ethyl acetate extracts of 3 increments removed from each pole at a given height.

Table I-20. Residual MITC content in Douglas-fir bridge stringers one year after metham sodium treatment as determined by gas chromatographic analysis of ethyl acetate extracts of wood samples.

Structure		ug MITC/OD g wood	
		Inner	Outer
5	Top	4.3	0.00
	Bottom	59.7	24.5
10	Top	40.2	53.2
	Bottom	75.8	39.9
15	Top	27.3	37.4
	Bottom	16.0	24.3
20	Top	26.2	65.4
	Bottom	82.7	23.2
25	Top	26.5	13.1
	Bottom	33.4	65.5
30	Top	73.2	100.3
	Bottom	83.6	75.8
35	Top	44.1	60.6
	Bottom	14.0	9.2

MITC should be lethal to established decay fungi; however, the long-term performance of this chemical remains unknown.

Previous studies have shown that metham sodium decomposes to produce MITC at a 40% efficiency rate, resulting in relatively low levels of MITC per g of metham sodium applied. Furthermore, the sawn timbers expose more torn and open tracheids which can act as conduits for loss of chemical on the wood surface. As a result, metham sodium treatments may provide shorter protective periods for these products. Continued evaluations of these timbers are planned to assess this possibility.

4. Development of a three-dimensional model to simulate MITC diffusion through Douglas fir poles:

Fumigant application, while highly effective, remains a very imprecise process. For example, fumigant dosages and treatment patterns have developed empirically, utilizing holes created during the inspection process. As a result, it is possible that obtaining a better understanding of fumigant movement could help to improve fumigant application and, thereby, enhance performance. While a large-scale field trial to evaluate as many treatment parameters as possible would accomplish this task, the size of such a test would be beyond the scope of the Cooperative. Instead, we have attempted to use basic chemical information, previously acquired through the Cooperative to develop a MITC diffusion model to calculate fumigant concentration and flow in poles under a variety of

conditions. Results of the model can be used determine fumigant dosages and to tailor application patterns to maximize chemical delivery.

In previous reports, we have described a preliminary model which was written in Turbo Pascal programming language ('91 Annual Report, pg. 44-51). Further efforts on this model were discontinued when it became obvious that even after optimizing the program code to decrease run-time, a relatively short (6-month) simulation of MIT diffusion through a 3.6 m pole section required several days of computing time. The present model utilizes the ANSYS program which is a self-contained general purpose finite element program developed and maintained by Swanson-Analysis Systems Inc. The program contains many routines for the purpose of solving engineering and mechanics problems by the finite element method. ANSYS has been developed over many years and is widely used. It is available on both personal and mainframe computers.

For the diffusion model we used the documented capabilities of the program for solving field equations of the form:

$$\nabla^2 (Kc) = C$$

This equation is used in steady-state heat conduction, flow-through porous media, steady-state electric conduction and other mechanics problems. For diffusion the following substitution of variables were made :

$$\nabla^2 (Dc) = Q$$

where: D = diffusion coefficient,
 cm^2/min
 c = MITC concentration,
 ug/cm^3
 Q = MITC flow rate,
 $\text{ug}/\text{min. cm}^3$

MITC concentration and flow rate at user-defined sites, termed elements (Figure I-12), are calculated by ANSYS. Diffusion coefficients must be supplied by the user. We have previously measured diffusion coefficients for MITC flow through Douglas-fir at several moisture contents and have observed that wood moisture strongly influences diffusion rate. Additionally, diffusion is affected to different degrees in longitudinal, radial, and tangential directions.

A 30 cm by 3.6 m long pole section was modeled and results were compared to actual pole sections that had been placed in a test site at Peavy Arboretum, treated with MITC, and monitored for fumigant concentration over a period of 2 years ('91 Annual Report, pg. 19-27). To create the model, an element grid was constructed (Figure I-12). The grid contained a 2.3 cm diameter by 31 cm long treatment hole with a 45 degree downward slope positioned at groundline. Diffusion coefficients for 22% moisture in wood above groundline and 40% moisture below groundline were entered into the model. Initial fumigant concentration in the treatment hole was $35 \text{ ug}/\text{cm}^3$, a value previously determined during the measurement of the diffusion coefficients.

MITC concentrations within the pole in the model remained constant after approximately 6 months. MITC concentrations at six months and at 40 cm

below groundline and 30, 90, 150, and 210 cm above groundline (Figures I-13, 14) were found to be very similar to MITC concentrations measured in the test poles at Peavy Arboretum 6 months after fumigant treatment (Table I-21). Some discrepancies exist because the test poles had two fumigant holes compared to the single treatment hole in the model. We are currently working on models to evaluate movement from two or more treatment holes. These models will then be comparable to the field trials and will allow us to confirm the validity of the model.

We took another approach to verify the model by modifying the original grid to simulate the release of MITC in a 30 cm-diameter by 75 cm-long pole section. We took another approach to verify 27-28). Residual fumigant amounts computed Like-sized pole sections had been treated green with MITC-Fume and stored outside at Corvallis, OR ('91 Annual Report, pg. by the model proved to approximate the actual amounts measured in the pole sections for 3 years following fumigant treatment (Figure I-15).

We plan to continue refining and evaluating the model as well as measuring the effect of pole moisture content and various fumigant treatment patterns on MITC concentration in the pole and on release rate of fumigant from the treatment hole. We will also look at the effect of voids and moisture pockets on fumigant concentration patterns.

5. Effect of wood species on decomposition efficiency of metham sodium: Metham sodium (32.1% sodium

n-methylthiocarbamate) is the most commonly used fumigant for controlling wood deterioration of large wood structures in North America. This chemical is not particularly fungitoxic and must decompose to become effective. Potentially, 13 decomposition products are possible, but only one, methylisothiocyanate (MITC), is considered to be of importance in fungal control in wood. MITC is a highly effective fungicide which moves readily through most wood species and appears to have some physical interactions with wood which produce long-term protection against fungal reinvasion.

Metham sodium is believed to decompose to MITC at a 40% efficiency rate; however, preliminary trials suggest that the rate is considerably lower. Metham sodium decomposition to MITC is most effective at pH 9.5 and declines with increasing acidity. Thus, the low pH of many wood species may adversely affect decomposition. These relatively low decomposition rates may help to explain the inability to detect fungitoxic levels of fumigant in metham sodium treated wood within 2 to 3 years of treatment. Since the model by modifying the original grid to simulate the release of MITC in a 30 cm-diameter by 75 cm-long pole section. Like-sized pole sections had been treated green with MITC-fume and stored outside at Corvallis, OR ('91 Annual Report, pg. 27-28). Residual fumigant amounts computed by the model proved to approximate the actual amounts measured in the pole sections for 3 years following fumigant treatment (Figure I-15). decomposition plays an important role in the use of this chemical. Preliminary small block laboratory studies of metham

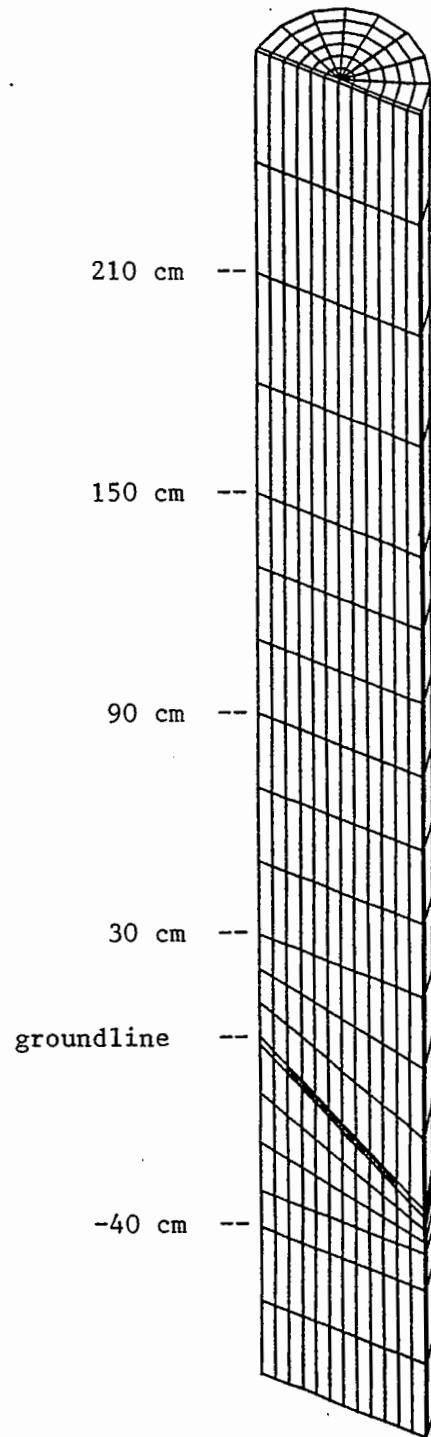
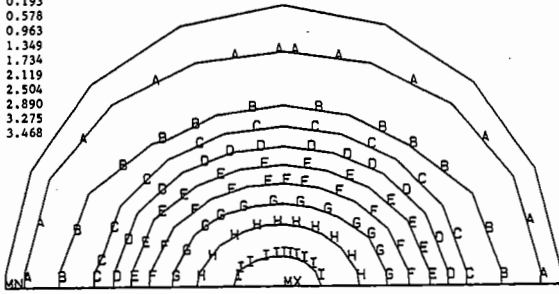
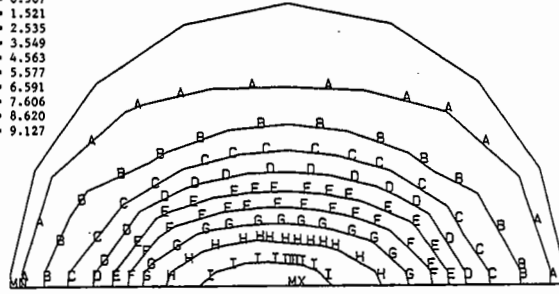


Figure I-12 Grid element used to model a 30 cm by 3.6 m long Douglas-fir pole section containing one sloping fumigant treatment hole at groundline.

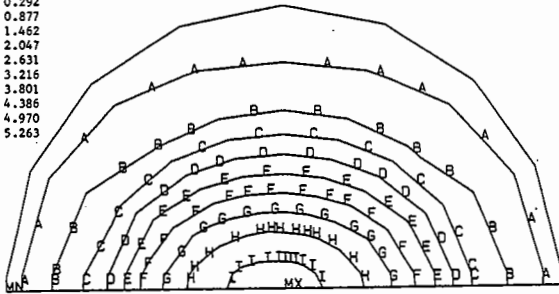
+210 cm
MITC, grams/meter³
A = 0.193
B = 0.578
C = 0.963
D = 1.349
E = 1.734
F = 2.119
G = 2.504
H = 2.890
I = 3.275
MX = 3.468



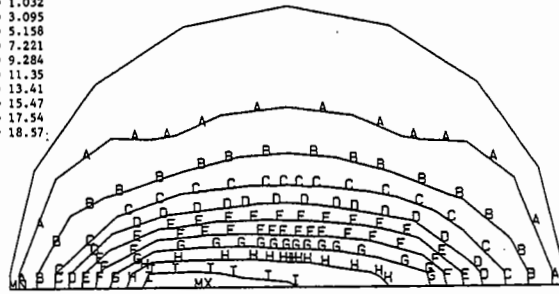
+90 cm
MITC, grams/meter³
A = 0.507
B = 1.521
C = 2.535
D = 3.549
E = 4.563
F = 5.577
G = 6.591
H = 7.606
I = 8.620
MX = 9.127



+150 cm
MITC, grams/meter³
A = 0.292
B = 0.877
C = 1.462
D = 2.047
E = 2.631
F = 3.216
G = 3.801
H = 4.386
I = 4.970
MX = 5.263



+30 cm
MITC, grams/meter³
A = 1.032
B = 3.095
C = 5.158
D = 7.221
E = 9.284
F = 11.35
G = 13.41
H = 15.47
I = 17.54
MX = 18.57



-40 cm
MITC, grams/meter³
A = 1.293
B = 3.878
C = 6.463
D = 9.048
E = 11.63
F = 14.22
G = 16.80
H = 19.39
I = 21.97
MX = 23.27

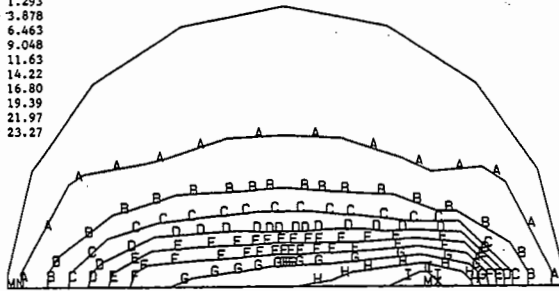


Figure I-13. Fumigant distribution at selected locations in a Douglas-fir pole section 6 months after treatment with 30 g of MITC: -40 cm, 30 cm, 90 cm, 150 cm or 210 cm above (+) or below (-) the treatment site.

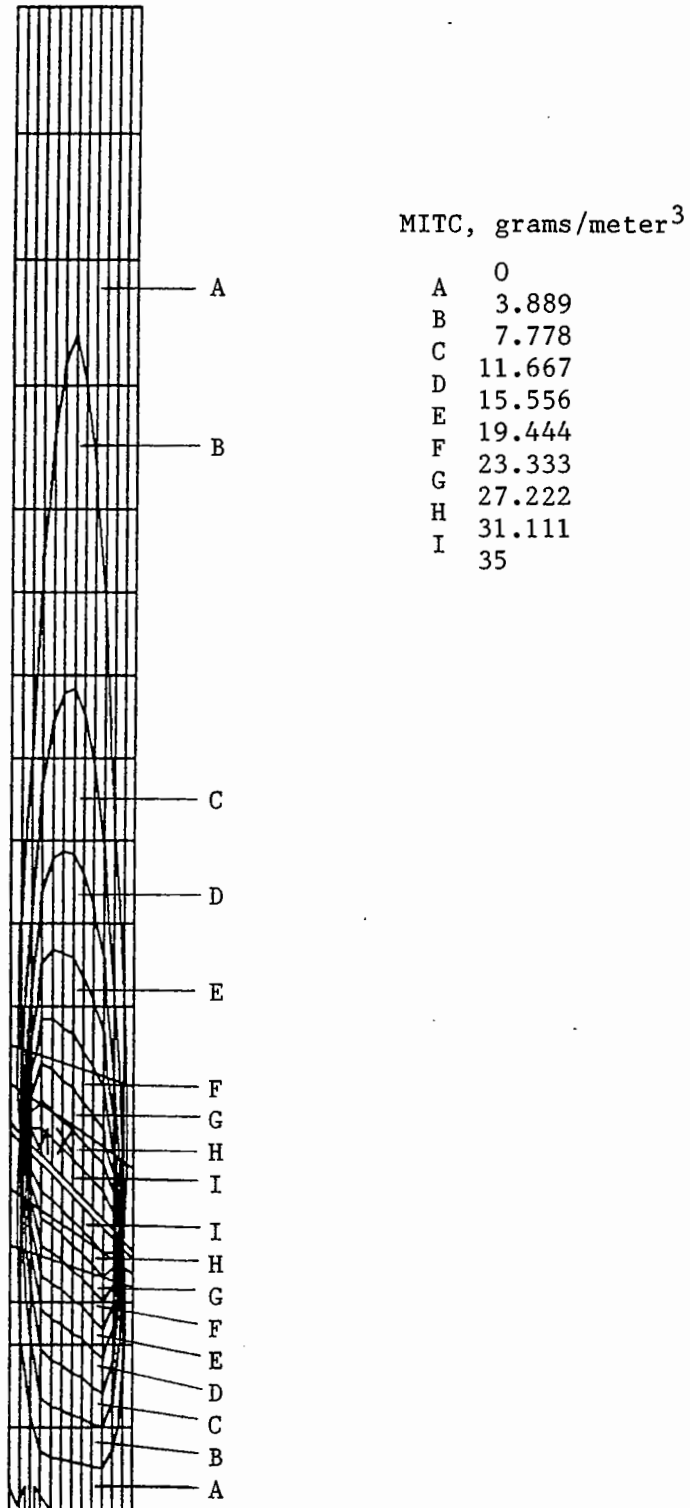


Figure I-14. Longitudinal section through a Douglas-fir pole section showing MITC distribution 6 months after treatment with 30 g of MITC

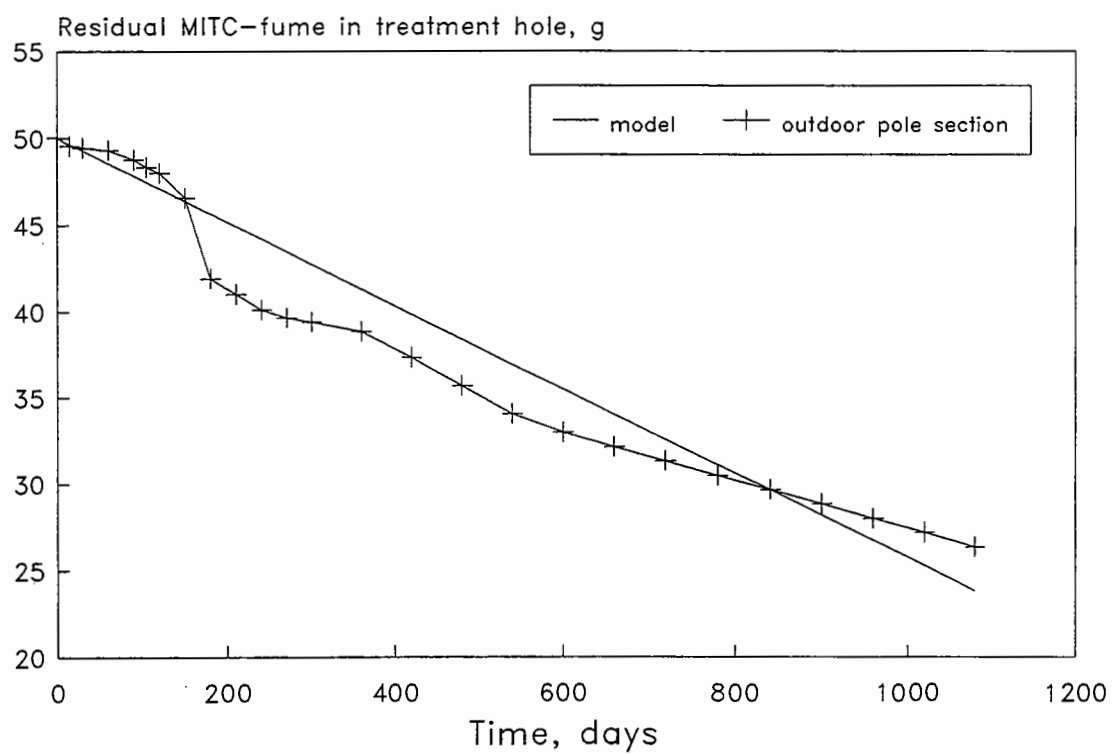


Figure I-15. Amount of MITC released from the treatment hole in a Douglas-fir pole section exposed for 36 months in Corvallis, Oregon.

Table I-21. Comparison between MITC concentration in Douglas-fir pole sections 6 months after treatment with MITC-Fume as measured by extraction of excised wood samples, and levels predicted using a computer model.

Source of Pole Sections	MITC Concentration (ug/cm ³ wood)					
	.3 m ^a		.9 m		1.5 m	
	Outer ^b	Inner	Outer	Inner	Outer	Inner
Test Site ^c	0-10	0-216	0	0-3.5	0	0
Model ^d	0-5	11.3-18.6	0-2.5	7.6-9.1	0-0.9	4.4-5.3

^aHeight above highest treatment hole.

^bOuter and inner corresponds to 0 to 2.5 cm and 12.5 to 15.0 cm from the pole surface, respectively.

^cDouglas-fir sections, each having 2 fumigant treatment holes (groundline and 15 cm above groundline). MITC analyses were performed on the outer and inner 2.5 cm segments of 15 in.-long increment cores. The range of values at each location are from 18 measurements (3 cores removed from each of 6 poles).

^dFumigant diffusion model (ANSYS). One treatment hole at groundline.

and hardwoods revealed a wide range of efficacy between the species tested, suggesting that wood characteristics might affect the efficiency of metham sodium decomposition. In this paper, the effect of wood species on metham sodium decomposition to MITC is explored. Samples were obtained from freshly sawn boards of the following species.

Alpine fir (*Abies lasiocarpa* (Hook.) Nutt.)

Douglas-fir (*Pseudotsuga menziesii* (Mirb.)

Franco) (interior and coastal)

Sitka spruce (*Picea sitchensis* (Bong.) Carr.)

Southern pine (*Pinus taeda* L)

Western hemlock (*Tsuga heterophylla* (Raf.) Sarg.)

Western larch (*Larix occidentalis* Nutt.)

White fir (*Abies concolor* (Gord. & Glend) Lindl.)

Western redcedar (*Thuja plicata* Donn)

Hardwoods

American beech (*Fagus grandifolia* Ehrh.)

Apitong (*Dipterocarpus grandiflorus* Blanco)

Bigleaf maple (*Acer macrophyllum* Pursh.)

Red alder (*Alnus rubra* Bong.)

Red oak (*Quercus rubra* L.)

Sugar maple (*Acer saccharum* Marsh.)

Sweetgum (*Liquidambar styraciflua* L.)

Sycamore (*Planatus occidentalis* L.)

Tangile (*Shorea polysperma* (Blanco) Merr.)

White lauan (*Parashorea malaanonan* (Blanco) Merr.)

The wood was ground to pass a 2 mm wide screen and air-dried for one week (7 to 9% moisture content). One half of the wood for each species was wetted to raise the moisture level to 50-100% MC. This wood was thoroughly mixed and equilibrated at 5°C for 6 weeks prior to use. One half gram of wood was added to a 40 ml vial and 15 ul of metham sodium was added. Previous studies had shown that this dosage was sufficient to provide measurable decomposition, but low enough to permit quantification. The vials were sealed with plastic caps equipped with Teflon lined septa. The vials were incubated at 5, 23, or 32°C for 24, 48 or 144 hours. At each time point, three vials per treatment combination were sampled. A headspace sample was removed from each vial and injected into a Varian 3700 Gas Chromatograph equipped with a flame photometric detector with filters specific for sulfur at the following conditions: injector temperature, 150°C; oven temperature, 100°C; and detector temperature 240°C with nitrogen as the carrier gas (30 cc/min). A glass column (2 m by 2 mm inner diameter) packed with 10% carbowax 20M on 80/100 Supelcoport solid support was employed. Sample sizes depended upon MITC

concentration present. MITC levels were quantified by comparison with standards.

Following air-sampling, the caps were removed and 3 ml of ethyl acetate was added. The vials were extracted for 15 minutes at room temperature, then the ethyl acetate extract was analyzed for MITC content as described above. Longer extraction periods were not used because residual metham sodium in the wood tended to decompose in the ethyl acetate, artificially inflating the MITC levels.

The results for headspace analysis and wood extraction were used to determine the total amount of MITC present in each vial at a given time point. These results were divided by the total weight of metham sodium applied to produce a relative decomposition efficiency for each wood species.

Metham sodium decomposition to MITC in dry wood was extremely low, ranging from 3.7 to 28.4 % of the original dosage (Table I-22). These levels are far lower than the theoretical yield. The majority of MITC was found in the wood, reflecting the high affinity this chemical has for wood. Air to wood MITC ratios were generally 1:500-1000. In general, NaMDC decomposition was greater in wet wood for all treatments and species (Table I-23). Decomposition efficiencies ranged from as low as 10.2 % for the 23 and 32 C red alder treatments 144 hours after treatment to 69.7 % for the 48 hours white fir treatment at 23 C. This improved efficiency reflects the need for some water for decomposition to proceed. Improved decomposition efficiency in wet wood is a major asset for decay control since most decay fungi would become active in wetter

wood. Increased chemical loadings would produce more rapid fungal control, thereby minimizing the risk of continued wood degradation.

MITC levels in dry wood were generally lowest in the 5 C treatments and increased with increasing incubation temperature. Although increased temperature should enhance reaction rates, differences between the 23 and 32 C treatments were sometimes slight. MITC levels in wet wood differed little with temperature, suggesting that decomposition was affected to a greater degree by moisture than temperature.

While many poles are treated during the warmer summer months, pole treatments sometimes extend into periods of inclement weather where lower temperatures could affect metham sodium decomposition. Conversely, elevated temperatures might markedly accelerate decomposition. Increased decomposition might improve the rate at which MITC moved through the wood to eliminate established decay fungi; however, the rapid release rate might also result in a more rapid loss from the wood coupled with a shorter protective period. This prospect has been investigated under tropical conditions in the Philippines, where metham sodium performance has been extremely erratic. Our laboratory results suggest that metham sodium decomposition in wood is not adversely affected by elevated temperatures. As a result, the inability of metham sodium to provide protection under more tropical regimes may reflect a more active and chemically tolerant soil flora rather than an absence of chemical in the wood.

MITC levels in both air and dry wood generally increased over the 144 hour period, although some declines were noted between 48 and 144 hours. MITC levels in wet wood tended to increase for the first 48 hours, then declined. The vials used in these studies tended to lose some MITC with time as a result of small leaks. These leaks may account for the gradual decline in MITC level between 48 and 144 hours.

Wood species exerted a major influence on decomposition efficiency in both wet and dry wood (Table I-24). A comparison of average NaMDC decomposition for each wood species at 48 hrs which combines data for all three temperatures indicated that decomposition efficiency was slightly better in hardwoods than softwoods in dry wood, but the opposite was noted in wet wood. In some instances wet wood had a marked effect on decomposition. For example, NaMDC decomposition was 6.7 % in dry Coastal Douglas-fir, but increased to 36.7 % in wet wood. It is interesting to note the low level of decomposition in Coastal Douglas-fir since this species is among the woods most commonly treated with fumigants. The relatively low decomposition rate in this species suggests that there is considerable potential for improving decomposition efficiency in this species through the use of additives.

The results indicate that temperature and wood species exert substantial influences on the efficiency of metham sodium decomposition. These effects suggest that widespread application of fumigants to woods must be preceded by preliminary testing to determine if the characteristics of that wood are amenable

to treatment. The results also suggest that there is potential for improving the efficiency of metham sodium decomposition to the theoretical level. Separate studies, for example, suggest that application of pelletized metham sodium in combination with pH 7 or 10 buffers enhances performance as measured by degree of fungal control and residual MITC level.

Further trials are underway to relate differences in metham sodium decomposition to wood characteristics such as extractive content, lignin level, and pH. These trials should help to identify conditions for optimizing metham sodium decomposition and improve the performance of this chemical as a wood fumigant.

Table 1-22. Effect of wood species and temperature on decomposition of sodium n-methylglucosaminide to MITC over a 144 hr period in dry wood.

Temperature (°C)	24 HOURS						48 HOURS						144 HOURS					
	Air MITC ng/ml	Wood MITC µg/g	MITC Air/wood ratio	Total MITC µg	% NAMDC decomp.	MITC Air ng/ml	Wood g/g	MITC Air/wood ratio	Total MITC µg	% NAMDC decomp.	MITC Air ng/ml	MITC wood µg/g	MITC Air/wood ratio	Total MITC µg	% NAMDC decomp.			
Red Alder	5	685(66)	478(171)	0.0018	2665(92.9)	4.4	498(86)	1328(175)	0.0004	684.2(88.0)	2833(804)	1178(72)	0.0025	702.5(4.5)	11.6			
	23	408(2867)	2039(951)	0.0018	1183.1(587.0)	19.6	3521(204)	1574(109)	0.0016	881.0(46.9)	3392(275)	1317(108)	0.0026	794.0(64.3)	13.2			
	32	3165(1738)	1703(416)	0.0018	978.2(248.4)	16.2	3182(1332)	2561(1013)	0.0012	1407.8(559.8)	9905(5582)	1963(220)	0.0051	1377.4(239.7)	22.0			
Alpine Fir	5	144(86)	900(346)	0.002	455.6(170.4)	7.5	444(228)	1637(204)	0.0030	836.5(102.8)	447(145)	1399(104)	0.0003	717.6(50.7)	11.9			
	23	1463(241)	1884(1131)	0.0010	10003(574.1)	16.6	4380(265)	1267(98)	0.0035	808.8(56.9)	2856(675)	1827(688)	0.0016	1077.6(371.0)	17.0			
	32	2285(178)	1421(103)	0.0016	802.1(56.1)	13.3	5978(414)	2050(307)	0.0030	1264.0(168.8)	4160(300)	2130(110)	0.0020	1231.2(66.9)	20.4			
Asplong	5	1134(266)	906(63)	0.0013	498.2(32.1)	8.3	851(300)	725(80)	0.0011	396.5(51.8)	988(338)	1258(159)	0.008	668.3(79.8)	11.1			
	23	4033(29)	971(71)	0.0042	646.7(35.0)	10.7	4280(369)	1109(34)	0.0039	722.6(19.3)	3944(70)	1050(58)	0.0038	682.8(31.8)	11.3			
	32	5376(168)	1065(82)	0.0051	747.3(46.2)	12.4	5793(247)	1291(101)	0.0045	877.2(33.7)	4200(39)	1474(62)	0.0029	904.9(31.9)	15.0			
American Beech	5	244(31)	585(131)	0.0004	302.4(66.1)	5.0	638(6)	1439(76)	0.0004	744.8(38.4)	456(91)	1909(215)	0.0002	972.8(111.2)	16.1			
	23	2601(1663)	1492(178)	0.0017	850.0(149.8)	14.1	2451(450)	1821(196)	0.0014	1008.3(80.4)	1876(150)	3073(1704)	0.0008	1611.4(649.0)	26.7			
	32	1408(322)	1234(22)	0.0011	673.2(23.7)	11.2	4634(1339)	1856(392)	0.0028	1113.6(161.10)	4005(113)	2321(414)	0.0018	1320(209.8)	21.9			
Coastal Douglas-fir	5	190(45)	760(251)	0.0003	387.6(127.2)	6.4	284(33)	672(393)	0.0006	347.4(197.1)	569(448)	857(262)	0.0007	451.3(141.0)	7.5			
	23	2335(446)	819(194)	0.0031	503.0(83.1)	8.3	1113(341)	530(51)	0.0021	309.3(39.2)	3737(515)	514(94)	0.0074	406.5(65.8)	6.7			
	32	3396(238)	606(107)	0.0066	460.4(61.4)	7.6	2146(582)	812(239)	0.0027	492.1(132.5)	5556(118)	1236(808)	0.0064	840.4(405.3)	13.9			
Sugar Maple	5	414(33)	1165(730)	0.0005	599.2(365.5)	9.9	238(109)	711(122)	0.0003	364.8(64.2)	700(104)	1056(123)	0.0007	555.9(62.3)	9.2			
	23	1697(371)	1046(158)	0.0017	590.8(65.5)	9.8	1362(270)	1093(59)	0.0012	600.8(40.5)	3831(430)	1361(73)	0.0028	833.6(24.4)	13.8			
	32	3714(1031)	1195(60)	0.0031	746.3(71.5)	12.4	2051(34)	1239(63)	0.0017	701.5(32.3)	5579(668)	1345(179)	0.0042	895.8(107.5)	14.8			
Interior Douglas-fir	5	41(4)	300(109)	0.0002	151.6(54.7)	2.5	173(21)	679(3)	0.0003	346.2(16.8)	148(13)	615(16)	0.0002	313.6(7.6)	5.2			
	23	2591(1289)	1352(981)	0.0022	779.8(542.3)	12.9	2730(380)	476(73)	0.0058	347.4(49.1)	3111(275)	981(230)	0.0034	615.0(13.7)	10.2			
	32	1910(299)	788(93)	0.0024	470.4(57.2)	7.8	5672(895)	1782(566)	0.0033	1117.7(263.2)	5694(158)	1471(206)	0.0039	963.2(108.9)	16.0			
Western Larch	5	83(1)	445(242)	0.0003	225.7(121.4)	3.7	1112(310)	1417(195)	0.0008	752.9(96.3)	826(233)	1123(64)	0.0007	594.7(50.2)	9.9			
	23	2632(524)	1304(58)	0.0020	757.2(48.0)	12.5	4315(2541)	2913(247)	0.0015	1629.3(185.9)	1402(322)	1304(175)	0.0011	707.9(92.5)	11.7			
	32	3402(837)	1280(162)	0.0026	776.3(111.4)	12.9	4539(400)	2628(308)	0.0018	1494.5(140.5)	3310(772)	944(257)	0.0036	604.4(159.4)	10.0			

Sycamore	5	1093(112)	4076(613)	0.0003	2081.6(309.4)	34.5	3678(197)	4680(208)	0.0008	2487.3(107.7)	41.2	1933(181)	3175(166)	0.0006	1664.9(89.7)	27.6
	23	5304(183)	4567(146)	0.0012	2495.8(68.8)	41.4	6280(2127)	5809(328)	0.0011	3156.0(230.8)	52.3	2323(151)	3230(339)	0.0007	1710.8(165.5)	28.3
	32	5634(153)	3933(281)	0.0014	2201.7(146.4)	36.5	6445(2193)	4065(127)	0.0016	2290.4(24.2)	38.0	2050(77)	3044(92)	0.0007	1603.8(42.8)	26.6
Tangle	5	5167(1273)	2533(2004)	0.1031	1483.2(951.2)	24.6	2776(241)	5184(1374)	0.0006	2703.1(690.4)	44.8	3572(560)	4145(772)	0.0009	2215.2(363.4)	36.7
	23	882(520)	3095(606)	0.0003	1583.0(304.4)	26.2	5998(873)	3417(580)	0.0018	1948.2(301.2)	32.3	7697(478)	3581(267)	0.0022	2098.2(152.8)	34.8
	32	2433(697)	2813(176)	0.0009	1503.9(60.0)	24.9	5633(280)	4661(620)	0.0012	2555.9(300.8)	42.4	7119(795)	2397(367)	0.0031	1483.2(155.4)	24.6
White fir	5	1252(148)	5249(1600)	0.0003	2674.6(796.7)	44.3	3916(248)	7325(532)	0.0005	3819.1(274.7)	63.3	2733(232)	4813(117)	0.0006	2516.6(63.7)	41.7
	23	4560(672)	5446(817)	0.0009	2905.4(381.7)	48.1	4828(732)	8032(317)	0.0006	4299.0(184.9)	69.7	2035(47)	4200(502)	0.0005	2181.4(252.9)	36.1
	32	5247(155d)	4733(613)	0.0011	2581.1(311.6)	42.8	4937(428)	3844(1078)	0.0014	2119.4(538.0)	35.1	1153(93)	3396(426)	0.0003	1744.2(213.6)	28.9
Bigleaf maple	5	3738(183)	3947(106)	0.0947	2123(54)	35.2	3408(811)	4436(73)	0.0768	2354(68)	39.0	1554(122)	5603(166)	0.0036	2864(79)	47.5
	23	8011(159)	4475(381)	0.0179	2558(188)	42.4	8110(990)	3682(363)	0.02203	2165(158)	35.9	2018(8782)	3024(480)	0.0041	1993(564)	33.0
	32	8805(409)	4322(73)	0.2037	2513(23)	41.6	7955(182)	3394(282)	0.0234	2015(146)	33.4	5266(1444)	2859(1488)	0.0018	1640(801)	27.2
Aplong	5	8842(6243)	5420(612)	0.1631	3064(63)	50.8	5961(930)	5859(60)	0.0509	3168(45)	52.5	2841(249)	7102(251)	0.0004	3665(123)	60.7(2.0)
	23	8189(636)	4899(183)	0.1672	2777(103)	46.0	8707(84)	4766(257)	0.0913	2731(127)	45.3	8543(448)	4188(98)	0.0204	2436(64)	40.4(1.1)
	32	8780(516)	4396(166)	0.1997	2549(80)	42.2	8337(36)	4226(257)	0.0986	2447(156)	40.5	6914(576)	3864(270)	0.1789	2209(157)	36.6(2.6)
Alpine fir	5	2834(319)	3421(54)	0.0828	1824(32)	30.2	3574(216)	4121(335)	0.0434	2203(175)	36.5	1739(302)	5965(132)	0.0003	3052(85)	50.6(1.4)
	23	7263(737)	3807(464)	0.1908	2194(222)	36.4	7096(405)	3310(220)	0.1061	1936(111)	32.1	5483(343)	2761(155)	0.0020	1600(67)	26.5(1.1)
	32	7479(590)	3808(190)	0.2342	2203(73)	36.5	6626(544)	2897(455)	0.1144	1714(207)	28.4	4824(328)	2292(825)	0.00212105	1274(303)	21.1(8.3)
White Inuan	5	6373(139)	6337(169)	0.1003	3434(87)	56.9	42.65(983)	5949(911)	0.0007	3145(480)	52.1	2024(401)	7731(375)	0.0262	3947(192)	65.4(3.2)
	23	6269(758)	4591(567)	0.1365	2546(283)	42.2	6971(1043)	3856(55)	0.0018	2207(68)	36.6	6946(817)	3979(652)	0.1746	2287(355)	37.6(3.9)
	32	9031(1392)	4863(96)	0.1857	2793(91)	46.3	8967(193)	5513(580)	0.0016	3115(296)	51.6	7612(216)	4374(1219)	0.0883	2491(614)	41.3(10.2)

Table I-24. Relative % NaMDC decomposition efficiency of selected wood species under dry on wet conditions 48 hours after treatment and incubation at 5 to 32°C.

Dry Wood		Wet Wood		
Highest efficiency	Western larch	21.4%	Alpine fir	60.8
	Red Oak	19.9%	White fir	56.0
	Bigleaf maple	19.4%	Western redcedar	45.1
	Red alder	16.4%	Sycamore	43.8
	Alpine fir	16.1%	Tangile	39.8
	American Beech	15.8	Sitka spruce	37.6
	Western hemlock	15.1	Western larch	36.8
	Tangile	14.4	Coastal Douglas-fir	36.7
	Western redcedar	14.1	Red oak	36.3
	White lauan	13.6	Bigleaf maple	36.1
	Sitka spruce	13.3	White lauan	32.9
	Sycamore	12.9	American Beech	32.9
	Southern pine	12.3	Southern pine	31.7
	Apitong	11.0	Western hemlock	31.1
	Interior Douglas-fir	10.0	Red alder	17.6
	White fir	9.3		
	Sugar maple	9.2		
	Sweetgum	8.2		
	Coastal Douglas-fir	6.7		

OBJECTIVE II

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

While we continue to make excellent progress towards the development of improved internal treatments for preventing and arresting wood decay, the application of surface treatments for control of surface decay or for protecting field-damaged surfaces of treated wood remains a problem. While most utilities employ copper naphthenate for these purposes, many linemen dislike this oily preservative. Efforts have been underway since the inception of the Cooperative to identify simple remedial treatments which would be more widely accepted by line personnel.

safety problem for utilities. Poles with deteriorated sapwood represent a climbing risk since lineman spurs may unexpectedly cut out of the decayed wood, causing the lineman to slide down the pole. Spraying with copper naphthenate at regular intervals can arrest this decay, but many utilities avoid this treatment because of fears over the potential risks associated with contamination of areas around the application site. The Cooperative has actively evaluated a variety of potential replacement compounds for spraying cedar sapwood and has established field trials to assess the performance of 25 compounds.

Deterioration of untreated sapwood in western redcedar poles poses a major

A. ACCELERATED FIELD TRIALS OF POTENTIAL PENTACHLOROPHENOL REPLACEMENTS FOR PROTECTING WESTERN REDCEDAR SAPWOOD

Trials to evaluate selected chemicals for protecting western redcedar sapwood were established on full-sized pole sections in 1982 and 1983 at Peavy Arboretum as well as on smaller blocks in 1987. These trials were not evaluated in 1991, but are all currently being evaluated by removing increment cores for *Aspergillus* bioassays and plugs for evaluation of residual decay resistance in a soil block test. These results will provide a relative measure of the residual degree of protection afforded by each treatment.

In addition to the small-scale field trials, materials have been collected for the application of selected biocides to western redcedar poles in service using the conventional commercial spray systems. These poles will be sampled before and after treatment to assess chemical loading and will then be evaluated 1, 3, 5, 7, and 10 years after treatment to determine the degree of residual protection and the retreatment cycle for each chemical.

B. EVALUATE TREATMENTS FOR PREVENTING DECAY IN FIELD-DRILLED BOLT HOLES

Preservative treatment creates an excellent barrier against fungal and insect attack, but this barrier is negated when cuts or bore holes are made beyond the depth of treatment. Exposure of untreated wood creates the potential for colonization by decay fungi. Application of preservatives to the cut surfaces can provide supplemental protection, but most utility personnel dislike the chemicals used for this purpose and therefore fail to treat the wood. The problem is particularly acute when different utilities share poles and underbuild lines on existing transmission poles. This creates an unseen, but potentially damaging problem since areas around field-drilled bolts holes can decay for many years before the damage is detected.

In 1981, the Cooperative established a field trial to evaluate potential replacements for 10% pentachlorophenol which was then the standard treatment recommended for application to field damage to treated wood. Twenty eight Douglas-fir poles (5.4 m long by 60 to 70 cm in circumference) were lightly pressure treated with pentachlorophenol in P9 Type A oil. A series of eight holes, 2.5 cm in diameter were drilled at 45 cm intervals along the length of each pole, spiraling 45 degrees around the pole for each hole. The bored region extended from 45 cm below the top to 60 cm above groundline. One of 4 chemical treatments was applied to eight holes in each of 4 poles. These treatment included 10% pentachlorophenol in diesel, an accepted standard; powdered ammonium bifluoride (ABF), powdered disodium octaborate tetrahydrate (Timbor),

and 40% boron in ethylene glycol (Boracol 40). The holes in 4 poles received no chemical treatment, but chemically impregnated washers (37.1% sodium fluoride, 12.5% potassium dichromate, 8.5% sodium pentachlorophenate, 1% sodium tetrachlorophenate, and 11% creosote) (Patox washers) were used to attach bolts to these holes. A second set of 8 poles were left untreated and served as controls. Metal gain plates were inserted in half of the holes in each pole, while plastic gain plates were inserted in the remainder. The poles were set to a depth of 1.2 m in the ground at the Peavy Arboretum test site and were watered at regular intervals for the first 6 years to the test to encourage leaching and stimulate fungal attack.

Poles with untreated bolt holes were monitored annually over the first 5 years for evidence of fungal colonization by removing increment cores from sites directly below each bolt hole gain plate on one side of the pole and from a site directly above the washer on the opposite side. These cores were cultured on nutrient media and observed for evidence of basidiomycete colonization. All poles were sampled annually in the same manner beginning 5 years after treatment.

Poles treated with water diffusible ammonium bifluoride, Boracol 40, and Timbor continue to experience low levels of colonization by both decay and non-decay fungi (Table II-1). Colonization by decay fungi was approximately half or less of that found in the untreated control poles. Colonization in samples from poles treated with Patox washers was approximately 40% higher than that found

in the controls, while treatment of bolt holes with pentachlorophenol in diesel oil provided only slight protection. The performance of the diffusible chemicals continues to be surprising, since these chemicals were applied at relatively sparse levels and had the potential to diffuse for considerable distances away from the bolt hole, where they would be of minimal value for protecting against invasion of the field damage.

The apparent lack of significant protection with pentachlorophenol treatment is interesting since this chemical was once the primary treatment for field-drilled bolt holes. While pentachlorophenol did provide some protection for the first 7 years, this protective effect was apparently lost with time. Since reapplication of pentachlorophenol to field-drilled holes is not feasible, the gradual decline in protection must be considered a major drawback to this chemical. It is unfortunate that this trial did not include copper naphthenate, the chemical now most commonly employed for treatment of cut surfaces on preservative treated wood; however, pentachlorophenol, while undergoing evaluation under the RPAR, was still considered to be an acceptable biocide. The goal of this test was to identify chemicals which could be more easily applied and which lacked the oily characteristics of pentachlorophenol in diesel. Copper naphthenate in diesel still had these same undesirable characteristics for application and was, therefore, not included.

These trials will continue to be evaluated, but they do illustrate the benefits of low toxicity, diffusible compounds for protecting wood in field-drilled holes.

Table II-1. Basidiomycetes and other fungi found in preservative-treated Douglas-fir poles 6 to 10 years after bolt holes were drilled and treated in the field, as shown by cultures from increment cores.

Field Treatment	Percentage of cores containing ...									
	Basidiomycetes					Other Fungi				
	6 yr.	7 yr.	8 yr.	9 yr.	10 yr.	6 yr.	7 yr.	8 yr.	9 yr.	10 yr.
Ammonium bifluoride (n=32)	0	2	0	2	2	5	2	16	42	9
Boracol® 40 (n=32)	0	2	0	0	3	18	27	33	66	16
Patox® washer (n=32)	5	5	8	14	13	12	22	31	66	27
Pentachlorophenol (n=32)	2	2	8	5	6	25	17	25	51	25
Timbor® (n=32)	0	0	0	2	2	11	25	25	37	14
Control (n=64)	3	9	17	9	8	30	26	46	70	33

OBJECTIVE III

DETECT EARLY DECAY AND ESTIMATE RESIDUAL STRENGTH OF POLES IN SERVICE

The early detection of decay is a major goal of utility inspection programs because fungal attack rapidly reduces wood strength, while causing minimal changes in physical appearance. Detecting incipient decay is also important because many remedial treatments seem to have lower affinities for decayed wood and therefore will be less effective on more deteriorated poles.

In previous reports, we have described methods for detecting incipient decay chemically using FT-IR

spectroscopy or by pH-sensitive indicators, physically using small scale mechanical tests, and biologically using plant-derived lectins. These methods are largely laboratory oriented and do not appear to be practical for assessing large numbers of poles in the field. As a result of our inability to reliably detect decay with these methods, culturing of increment cores remains one of the few accurate methods for assessing the presence of decay fungi in wood. We are currently using this method to detect above-ground decay.

A. ESTIMATE THE INCIDENCE OF INTERNAL DECAY ABOVE THE GROUNDLINE IN DOUGLAS-FIR POLES EXPOSED IN DIFFERENT GEOGRAPHICAL REGIONS

Many utilities now specify through-boring to completely protect the groundline zone and have instituted fumigation to control internal decay in Douglas-fir poles, but an increasing percentage of these utilities are becoming concerned about the above ground condition of these poles.

The moisture content in the above-ground portions of poles is generally

considered to be too low for decay to occur; however, poles located in coastal areas or in regions prone to wet, windy conditions have been found to have decay extending up to 6 m above the groundline.

These poles represent a major problem to utilities since there are few treatment options for arresting internal decay in this zone of the pole. Utilities are also interested in assessing the condition of these poles so they can make accurate predictions about ultimate service life of their wood system and allocate scarce resources in the best fashion.

Last year we began a project to evaluate the incidence of decay fungi above the groundline in Douglas-fir poles located throughout the Pacific Northwest. In the initial sample, poles which had been removed from service because of the presence of varying levels of internal

decay were extensively sampled by removing increment cores at 0.6 m intervals, beginning at groundline and extending upward to the first attachment. This end-point was chosen since we wanted to avoid sampling around underbuilt lines or connectors. The cores were cultured for the presence of decay fungi.

Only 3 of 58 cores were colonized by fungi, and none of these was a decay fungus. While these results imply that above ground decay is not a problem in Douglas-fir poles in the Willamette Valley, the poles in the gelatin encapsulated MITC vs. moisture level trial clearly illustrate the potential for such damage.

In the primary portion of this trial, Douglas-fir poles in service for different periods of time will be sampled along the Oregon coast, in the Puget Sound area, the Willamette Valley, and Eastern Oregon/Washington. A minimum of 20 poles per age group will be evaluated in each geographic zone by removing 3 increment cores from equidistant sites around the pole at the groundline and 2 cores 120 degrees apart 5.1 m above the groundline. The depth of preservative treatment and the presence of any visible decay on the core will be recorded and the wood will be cultured on malt extract agar for the presence of decay fungi. The poles in the Willamette Valley have already been sampled, while those along the coast are currently under evaluation. The results of these trials will provide a guide to the levels of internal decay and colonization by decay fungi in Douglas-fir poles of differing ages and environmental exposures. This information can then be used to estimate residual service life, making it easier for utilities to plan for replacement or maintenance of these

structures. Additional pole samples from different geographic areas are being sought to broaden the application these results.

OBJECTIVE IV

EVALUATE THE POTENTIAL FOR DECAY DEVELOPMENT DURING AIR-SEASONING AND IDENTIFY CONTROL STRATEGIES

The studies to identify the fungi colonizing air-seasoning Douglas-fir poles and determine the effects of these fungi on wood properties have largely been completed. These studies illustrated that relatively high rates of fungal infestation were possible throughout the range where Douglas-fir poles are typically air-seasoned. Further research has suggested

that application of either boron or sodium fluoride to freshly peeled poles delays but does not completely prevent fungal infestation. These results imply that sterilization of poles which are air-seasoned for even short periods of time should be an essential part of the treatment process.

A. IDENTIFY METHODS FOR PREVENTING COLONIZATION OR FOR ELIMINATING DECAY FUNGI FROM AIR-SEASONING DOUGLAS-FIR POLES

Studies to assess the use of boron or fluoride treatments for limiting colonization of Douglas-fir poles during air-seasoning are now complete. Both treatments slowed, but did not prevent colonization. There were considerable concerns expressed by treaters over the potential for leaching of fluoride from the air-seasoning poles and these concerns would largely limit the use of this chemical. Treaters were less concerned by the use of boron, although many questioned the need for application of a chemical treatment which did not completely arrest fungal colonization, given the need to include a later sterilization period in the treatment process. While this comment has merit, it is important to note that such preventative treatments provide added insurance against the survival of fungi through a shorter treating process.

In addition to the pretreatments to limit fungal colonization, extensive tests have been performed to determine the treatment times required for sterilization. In earlier trials, internal temperatures were monitored in Douglas-fir poles during treatment with AZCA, pentachlorophenol in oil and pentachlorophenol in liquified petroleum gas. The results of these studies have appeared in previous reports and were used to prepare heating curves to predict treatment times required to achieve sterilization. This past year, we have extended this study to kiln-drying.

Green Douglas-fir pole sections (25 to 35 cm in diameter by 2.4 m long) were obtained from McCormick and Baxter Creosoting Co. These pole sections were stored under a sprinkler to retain moisture until needed. The poles were end-sealed with an elastomeric paint and six holes

0.95 cm in diameter were drilled perpendicular to the grain to depths of 7.5, 12.5, or 20.5 cm along the upper surface of each pole at least 60 cm from the ends. Each pole received 2 holes of a given depth. Copper constantin thermocouples were threaded through the center of a 2.5 cm dowel and the tip was inserted in a lengthwise notch in a 2.5 cm long dowel and this dowel was driven to the bottom of the hole. The holes were then filled with Dow Corning silicone rubber to within 3.75 cm of the surface, then the 2.5 cm long dowel was driven into the wood and the remainder of the hole was filled with a two-part epoxy sealant and allowed to cure for a minimum of 24 hours. The poles were then included in a kiln charge of freshly peeled Douglas-fir poles and temperatures at the different depths were monitored and collected over the kiln cycle using a 21X microdata logger. The resulting files were then transferred to an IBM PC for further manipulation. A total of 12 logs in 6 kiln charges were evaluated in this manner. The kiln cycles varied in length from 100 to 120 hours and temperatures began at approximately 50°C and increased to 75°C over the cycle.

Sterilization is typically considered achieved when the wood has been heated to 67°C at the center for a minimum of 75 minutes. While these values were originally developed by M. Chidester in the 1930s using fungi common to southern pine, subsequent studies have shown that this value is also applicable to the fungi colonizing Douglas-fir.

The results of these trials indicate that the desired temperature for sterilization was achieved at all depths in the poles in all 6 charges. Furthermore,

the poles remained well above 60°C for 20 to 30 hours. Previous trials have shown that these time-temperature conditions are lethal to most important decay fungi colonizing air-seasoning Douglas-fir. These results indicate that kiln-dried poles do not require an additional sterilization period during the pressure treatment cycle provided there is not a long delay between drying and treating. The exact limitations on this delay between drying and treating are difficult to quantify since most studies evaluating colonization by air-seasoning fungi have examined poles only after 3 months of exposure. It is doubtful that kiln-dried wood would remain untreated for this period of time. Furthermore, the kiln-dried poles would be drier and therefore less suitable for fungal colonization.

The data from these studies will be manipulated to develop heating rate curves for various kiln conditions to provide guidance for utilities and treaters developing sterilization requirements for wood poles. The research will be performed in cooperation with scientists in the OSU Department of Chemical Engineering.

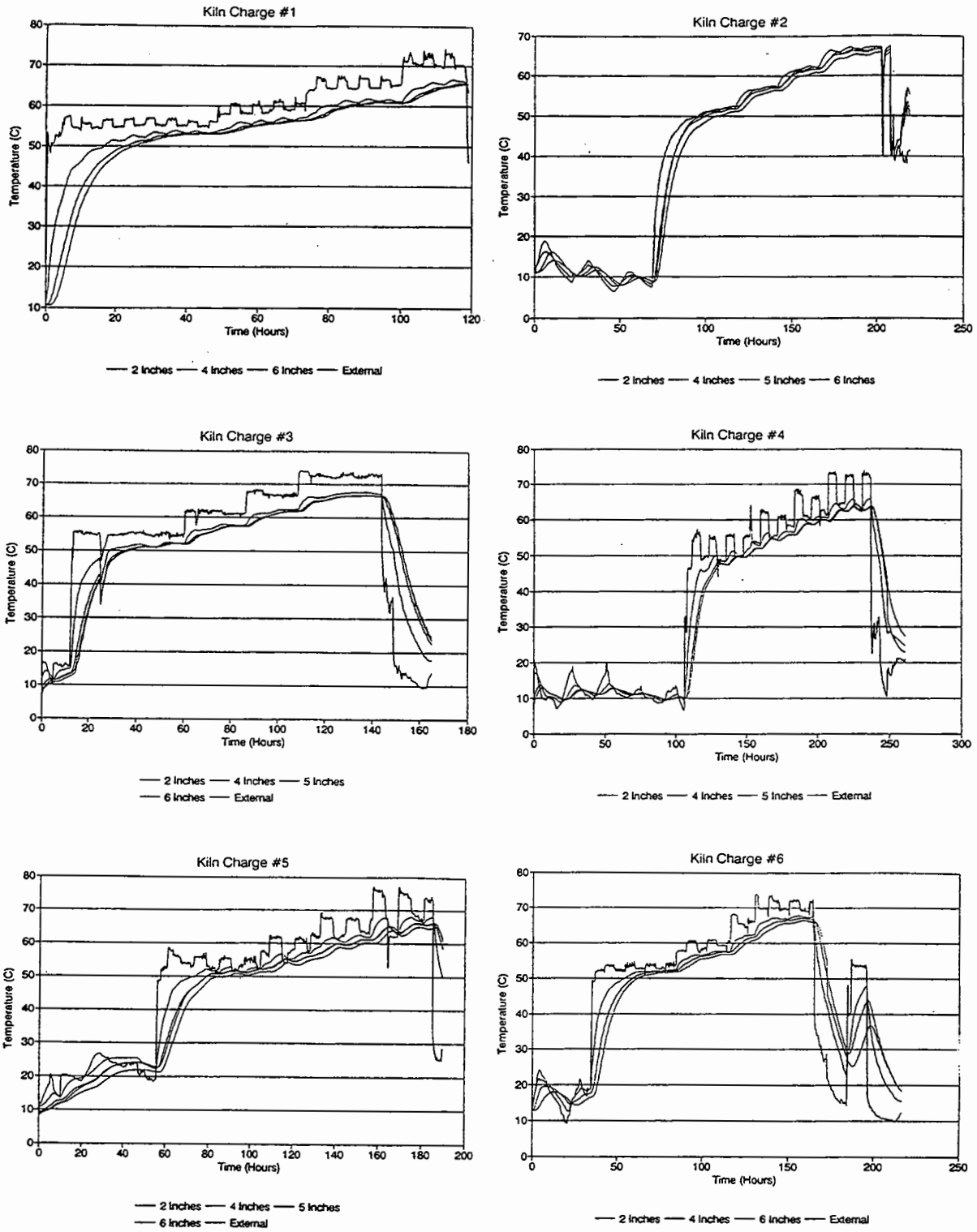


Figure IV-1. Internal temperature development during kiln-drying of Douglas-fir pole sections in 6 different kiln charges.

OBJECTIVE V

EVALUATE THE EFFICACY OF GROUNDLINE PRESERVATIVE SYSTEMS FOR WESTERN WOOD SPECIES.

A. PERFORMANCE OF MODIFIED GROUNDLINE PRESERVATIVE SYSTEMS

Pressure treatment with preservatives creates an excellent barrier against fungal and insect attack; however, the effectiveness of this barrier can sometimes decline with length of service. As the barrier declines, preservative tolerant soft rot fungi invade the wood, drastically reducing strength in the affected zone. External decay is considered a common problem with southern pine but may also occur with other species when the wood is treated with pentachlorophenol in liquified petroleum gas, when treated wood is buried in concrete or when poles are moved to a different site and reset.

Surface decay can be controlled by application of external preservative formulations containing mixtures of oil and waterborne preservatives. The oilborne component is presumed to remain close to the wood surface where it supplements the existing preservative to prevent renewed invasion by soft rot fungi. The waterborne component is believed to migrate further into the wood to eliminate any established fungi. For many years, external preservative formulations contained highly effective mixtures of creosote, pentachlorophenol, sodium fluoride, sodium dichromate, and dinitrophenol. The efficacy of these formulations has been demonstrated through their widespread commercial use as well as several carefully controlled studies. Recently, however, concerns about the

safety and the environmental effects of these mixtures has encouraged extensive substitution of components to improve applicator safety and reduce the need for licensing of lineman. As a result, the majority of groundline preservative formulations used in the United States now contain mixtures of copper naphthenate, sodium fluoride, or sodium tetraborate decahydrate. The fungicidal capabilities of each of these chemicals is well known, but their ability to effectively arrest external soft rot attack remains to be demonstrated. In this paper, we compare the diffusion of copper naphthenate, sodium fluoride, and sodium tetraborate based formulations with conventional pentachlorophenol and creosote based compounds in untreated Douglas-fir posts over a 30-month period.

Freshly peeled Douglas-fir posts (25 to 30 cm in diameter by 1.8 m long) were stored for 6 months undercover to permit some surface drying to occur. Five pole sections each were treated with one of the following preservative formulations:

1. CUNAP WRAP (Tenino Wood Preservatives Inc.) containing 2% copper naphthenate (as Cu) on an absorbent pad with a plastic barrier.

2. Cu-RAP 20 (Chapman Chemical Co.) a paste containing 18.16% amine based copper naphthenate and 40% sodium tetraborate decahydrate.

3. Pole Nu 15-15 (Chapman Chemical Co.) a grease containing 12.9% pentachloro-phenol, 15% creosote and 1.5% chlorinated phenols to serve as an accepted standard.

4. Pole-Nu (Chapman Chemical Co.) a grease containing 10.2% pentachlorophenol.

5. COP-R-NAP (Osmose Wood Preserving, Inc) a paste containing 19.25% copper naphthenate.

6. CRP-82631 (Osmose Wood Preserving, Inc) a paste containing 19.25% copper naphthenate and 45% sodium fluoride.

The pastes were applied according to manufacturer instructions and, with the exception of the self-contained CUNAP WRAP, all were covered with polyethylene wrap. The posts were capped on the top with roofing felt prior to being set in the ground to a depth of 45 cm at the OSU Peavy Arboretum test site.

The test site receives 105 cm of rainfall per year, with 81% falling between October and March when average monthly temperatures range from 3.9 to 11.7°C. The remaining months are dry with temperatures rarely falling below 0 or rising above 30°C. The soil is Olympic silty-clay and slightly acidic (pH 5.4). During the winter months, the water table rises to within 15 cm of the surface, creating an extreme environment for preservative performance.

The migration of each preservative from the paste or grease into the wood was assessed 18 and 30 months after treatment by removing either 1 cm diameter plugs or

increment cores from 3 equidistant points around each pole section 15 cm below the groundline. The samples were cut using a razor blade into segments corresponding to 0 to 4, 4 to 10, 10 to 16, and 16 to 25 mm from the wood surface. Segments from the same zone of plugs from each pole were combined and the wood was ground to pass a 20 mesh screen. The ground wood was first analyzed for copper or pentachlorophenol using an Asoma 8620 X-ray fluorescence (XRF) analyzer. Previous laboratory trials have shown a high correlation between copper level as determined by XRF and that determined using atomic absorption spectroscopy.

Borate analysis was performed by ashing samples, adding 3 drops of 6 N HCl to the residue and washing the acidified residue into a beaker with hot water. The resulting residue was stirred for 5 minutes, then filtered through Whatman #4 filter paper. The filter paper was washed 3 times with 10 ml of hot water and the resulting solution was diluted to 250 ml in a volumetric flask. One ml of this solution was pipetted into a 1 cm cuvette along with 1 ml of ammonium acetate buffer. One ml of Azomethine-H reagent was added and absorbance of the resulting solution was measured at 420 nm 30 minutes later. Boron concentration was calculated by comparison with results obtained with standard solutions. Subsequent trials in our laboratory have shown that this method averaged >90% boron recovery from treated wood.

Fluoride analysis was performed by R. Ziobro (Osmose Wood Preserving Inc.) on a blind sample basis using AWWA Standard A2 Method 7 wherein ground

wood is washed in sodium carbonate, and the fluoride trapped in the sodium salt is released and converted to hydrofluoric acid by adding sulfuric acid. The HF forms an azeotrope with water which is distilled off into a beaker containing sodium hydroxide which converts the HF to sodium fluoride. Total fluoride was determined using a specific ion electrode. This method recovers an estimated 80% of fluoride present in the wood.

Untreated control poles had begun to experience considerable surface decay 18 months after installation and were too heavily decayed to be sampled below ground 30 months after installation. These results clearly demonstrate the biological severity of the site. All of the external preservative treated posts were sound 30 months after installation. In many instances, upward preservative migration was evident on the wood surface, however, this rarely extended more than 5 to 10 cm above the groundline.

As expected, chemical levels below the groundline declined rapidly from the surface inward (Table V-1). Pentachlorophenol was detected to a depth of 10 mm with Pol-Nu 15-15 and 16 mm for Pol-Nu; however, the levels detected at these zones were far below those reported as thresholds for this chemical. Levels in the surface zone were at or above the threshold for this chemical 18 months after installation. Sampling 30 months after installation indicated that penta levels in both treatments had declined 28 to 31% in the outer zone of the penta based formulations, while levels further in the wood also declined. These results suggest that preservative is being lost to the

surrounding soil or is diffusing further into the wood.

Evaluation of the copper naphthenate based formulations indicated similar trends with this chemical. For practical purposes, copper naphthenate was not detected beyond 10 mm from the wood surface, even with the amine based, water-soluble formulation in Cu-RAP 20. The lack of extensive diffusion in this formulation may reflect volatilization of amine, which would precipitate the copper naphthenate and prevent further inward migration. Copper levels declined 17 to 37.5% between 18 and 30 months after installation. Cop R Nap experienced the lowest decline in copper concentration, while the other formulations experienced slightly higher rates of copper loss. Copper levels in the outer zones of all treatments remained above the threshold for non-copper tolerant fungi; however, the rapid loss of copper naphthenate with the CUNAP WRAP is of some concern since this formulation contains no other supplemental preservative.

As with the oilborne components, the water-based sodium fluoride and boron both showed substantial concentration gradients inward from the surface 18 months after installation. Both components were detectable at the deepest zone sampled (25 mm from the surface) indicating that they were capable of significant migration from the wood surface. In both cases, chemical levels in the inner sampling zone were far above the toxic thresholds for each chemical, suggesting that they would be capable of eliminating established fungi from the wood. This elimination may be quite important in long-term performance of

Table V-1. Chemical content of Douglas-fir posts 18 or 30 months after treatment with selected groundline bandage systems.

Average Chemical Level ^a																		
Chemical Treatment	Exposure Period (Mos)	COPPER				PENTA				BORON				SODIUM FLUORIDE				
		(kg/m ³)				(kg/m ³)				(% BAE)				(% wt/wt)				
		0-4mm	4-10mm	10-16mm	16-25mm	0-4mm	4-10mm	10-16mm	16-25mm	0-4mm	4-10mm	10-16mm	16-25mm	0-4mm	4-10mm	10-16mm	16-25mm	
Cunap wrap	18	2.56	1.60	0.80	0.32	-	-	-	-	-	-	-	-	-	-	-	-	
	30	1.60	1.28	0.64	0.16	-	-	-	-	-	-	-	-	-	-	-	-	
Cop-R-Rap	18	2.72	0.64	0.32	0	-	-	-	-	-	-	-	-	-	-	-	-	
	30	2.24	0.64	0.32	0	-	-	-	-	-	-	-	-	-	-	-	-	
CuRap 20	18	3.36	0.80	0.16	0	-	-	-	-	1.75	1.41	0.87	0.51	-	-	-	-	
	30	2.40	0.48	0.16	0	-	-	-	-	0.27	0.27	0.28	0.23	-	-	-	-	
CRP-82631	18	3.84	1.12	0.48	0.16	-	-	-	-	-	-	-	-	2.38	1.21	0.55	0.35	
	30	2.88	0.64	0.32	0.16	-	-	-	-	-	-	-	-	2.38	1.23	0.81	0.55	
Pol-Nu 15-15	18	-	-	-	-	3.36	1.44	0.48	0.16	-	-	-	-	-	-	-	-	-
	30	-	-	-	-	2.40	0.96	0.32	0.16	-	-	-	-	-	-	-	-	-
Pol-Nu	18	-	-	-	-	6.24	2.56	0.80	0.16	-	-	-	-	-	-	-	-	-
	30	-	-	-	-	4.32	1.76	0.64	0.16	-	-	-	-	-	-	-	-	-

^aBy distance (mm) from wood surface.

these formulations, particularly in light of the seemingly rapid loss of chemical near that boron levels had declined near the surface and that there was no longer a concentration gradient away from the surface, while the fluoride levels continued to increase between 18 and 30 months. Chemical levels were generally lower than those previously found with scots pine poles 28 months after treatment, but these differences may reflect variations in wood permeability as well as exposure conditions. Boron levels in our trials were approximately 40% above the estimated threshold 30 months after installation, but had declined substantially near the wood surface. Surface depletion reflects inward diffusion as well as some loss into the surrounding soil. These results must be viewed with some caution; however, since the test posts lacked an oil-treated shell. Field trials using pentachlorophenol in oil-treated test poles are now underway to confirm these results.

In all instances, the formulations appear to be performing as expected in the untreated Douglas-fir posts 30 months after installation. Chemicals levels remain above the toxic threshold near the surface

B. PERFORMANCE OF GROUNDLINE PRESERVATIVE SYSTEMS IN DOUGLAS-FIR, WESTERN REDCEDAR AND PONDEROSA PINE UTILITY POLES

The Peavy Arboretum evaluation of groundline preservatives was designed to evaluate preservative migration in the absence of existing preservative treatments. This test will provide comparative data without the complication of existing treatments; however, many utilities have asked for additional trials using preservative treated wood in service.

and the wood is sound. One facet of performance that remains to be investigated is the toxic threshold of mixtures of preservatives against common soil inhabiting organisms. Previous efforts to determine toxic thresholds of earlier formulations used soil block tests; however, even these tests might not accurately reflect the levels of chemical required to control more chemically tolerant soil flora. Trials to determine these levels are now underway as a means of more accurately determining when preservative levels have declined below the protective level. In addition, the field trials will continue to be evaluated over the coming years to determine when retreatment is advisable.

At present, the four external preservative formulations evaluated appear to be performing at levels which are comparable to those obtained with pentachlorophenol and creosote-based formulations. Further comparative trials of the copper naphthenate based formulations are underway on ponderosa pine, Douglas-fir and western redcedar poles near Merced, CA, to confirm performance under in-service conditions.

Last year (11th Annual Report, pages 113-115) we described the establishment of a second field trial evaluating 3 groundline preservative systems: amine copper naphthenate/boron, copper naphthenate alone, and sodium fluoride alone.

Douglas-fir, western redcedar and ponderosa pine poles in a Pacific Gas and

Electric Co. line located near Merced, California were initially sampled by removing increment cores from three sites around the groundline. These cores were ground and analyzed for residual preservative retention. The results were used to divide the poles into three groups of nine poles per species with approximately equivalent preservative distributions.

The poles were then treated with CUNAP Wrap (Tenino Wood Preservatives Inc.), CURAP 20 (ISK Biotech) or Patox II (Osrose Wood Preserving Inc.). The composition of the first two formulations can be found in section A of this Objective. Patox II contains 70.3% sodium fluoride. Wraps were applied from a zone extending 8 cm above the groundline to 45 cm below the groundline and the soil was replaced around the pole.

One year after treatment, one third of the poles in each treatment group were sampled by removing increment cores from sites 15 cm below the groundline. The cores were divided into zones corresponding to 0-4, 4-10, 10-16, and 16-25 mm from the wood surface. These zones were then combined for cores from a given pole and ground to pass a 20 meshscreen. The ground wood was

analyzed for copper by x-ray fluorescence spectroscopy (XRF) using the CCA mode and corrected for copper content using a standard curve prepared by dual analysis by XRF and atomic absorption spectroscopy. The samples were then analyzed for boron or sodium fluoride content as described in section A of this Objective.

The results indicate that all components of the preservative systems are moving into the wood (Table V-2). In general, copper naphthenate declined to the greatest degree with increasing wood depth, reflecting the less mobile nature of this chemical. Copper levels were generally highest with the amine based copper formulation in CuRap 20. This formulation is water soluble and may be capable of greater initial movement; however, mobility should decline with time of treatment since loss of the amine component reduces solubility.

Boron and fluoride levels were generally comparable with the two systems, suggesting that each was capable of readily moving through the wood. In the Peavy Arboretum tests, boron levels declined substantially between 18 and 30 months and it will be interesting to see if this same trend occurs at the drier Merced site.

C. DIFFUSION OF COPPER AND BORON FROM A GROUNDLINE WRAP FORMULATION THROUGH DOUGLAS-FIR HEARTWOOD

Although pressure treatment greatly increases the service life of utility poles, specific types of decay may still decrease pole longevity. Many naturally occurring micro-fungi, usually soft rotters, can cause significant below-ground decay that presents a serious problem in utility pole applications. The fungi are often tolerant

of preservative components such as copper or pentachlorophenol, or are able to take advantage of preservative depletion over years of leaching. Occasionally, genetic selection within a fungal population may allow for an "acquired" preservative tolerance.

Table V-2. Residual copper naphthenate, boron or sodium fluoride content of wood removed from ponderosa pine, Douglas-fir, or western redcedar poles one year after treatment with selected external preservative systems.

Treatment	Chemical Level ^a											
	Copper Naphthenate (kg/m ³ as Cu)						Boron (% BAE)			Fluoride (% NaF)		
	0-4 mm	4-10 mm	10-16 mm	16-25 mm	0-4	4-10	10-16	16-25	0-4	4-10	10-16	16-25
CuRap 20	3.84	1.76	0.32	0	2.17	1.51	0.85	0.38	-	-	-	-
Cunap	0.96	0.64	0.32	0.32	-	-	-	-	-	-	-	-
Patox II	-	-	-	-	-	-	-	-	1.90	1.11	0.80	0.44

^aZones correspond to depths from the wood surface. Values reflect means of 3 increment core from each of 9 poles.

One recently developed paste containing copper naphthenate and boron was shown in field tests to diffuse readily, both radially and longitudinally, when applied as a groundline wrap on unseasoned pole stubs of southern pine, but no controlled studies of diffusion of the components have been reported. Here we describe the movement of components of this paste formulation through Douglas-fir heartwood at two moisture contents under laboratory conditions.

Douglas-fir heartwood cubes (10 by 10 by 10 cm) were pressure-soaked with water and air-equilibrated to either 30% or 60% moisture content (MC). The equilibrated blocks were triple-coated with paraffin to retard further moisture loss. A flat-bottomed treatment hole 2.5 cm in diameter by 3 mm deep was drilled into the center of either the transverse or the tangential face of each block, and 5g of a paste containing 18.16% amine-solubilized copper naphthenate and 40% sodium tetraborate decahydrate (POL-NU CuRAP 20, ISK Biotech, Memphis, TN) was placed in the hole, which was covered with heavy-duty tape and sealed with molten paraffin. The blocks were maintained at room temperature (22° to 25°C) and oriented with the grain running vertically to provide gravitational force for perpendicular radial diffusion and parallel longitudinal diffusion downward. Selected blocks were destructively sampled 1, 2, 3, 6, and 12 months after treatment.

After each exposure time, a 2.5-cm² square was taken from each of five blocks per treatment directly beneath and parallel to the treatment hole. Each square was divided into five assay zones: 0-6 mm, 6-13 mm, 13-25 mm, 25-38 mm,

and 38-64 mm. The samples were oven-dried over night, ground in a Wiley mill through a 20-mesh screen, and analyzed for copper and boron content.

The percentage, by weight, of copper in the wood was determined with an ASOMA 8620 X-ray fluorescence analyzer (Asoma Inc., Austin, Texas) configured for chromated copper arsenate analysis. Selected samples were later digested in boiling nitric acid and analyzed by atomic absorption spectroscopy to confirm ASOMA results. A standard regression line ($R^2 = 0.997$) was used for final copper calculations.

The percentage, by weight, of boron as boric acid equivalent (BAE) in the wood was determined by ashing 1g (to nearest 0.0001g) of each sample at 500°C for 16 hours. Upon cooling, three drops of 6N HCl were added to each crucible, and the acidified residue was washed four times with 5 ml hot, distilled water into a small beaker that was shaken on a wrist shaker for 5 minutes. The samples were filtered through Whatman #4 filter paper, washed three times with 10 ml hot, distilled water, and diluted to 250 ml with distilled water. One ml of the diluted extract was placed in a cuvette of 1 cm path length. One ml of a buffer solution (250g ammonium acetate, 400 ml distilled water, 15g disodium EDTA, 125 ml acetic acid) was added to the cuvette and mixed before 1 ml of an azomethine-H reagent (0.45g azomethine-H dissolved in 100 ml of 1% ascorbic acid) was added and mixed. Absorbance of the resulting yellow solution was measured after 30 minutes on a Spectronic 301 spectrophotometer at 420 nm. Samples that had absorbencies beyond the instrument range were diluted

further with distilled water and reassayed. Boron concentrations were determined by comparing the absorbencies of test samples to those of boric acid standards and a distilled water blank. Previous analyses of boron-treated wood with this assay have resulted in 93.5% boron recovery. All boron values reported here have been adjusted accordingly.

Chemical analyses indicated that both paste components moved into the wood in radial and longitudinal directions at both 30% and 60% MC (Figs. V-1, 2), but orientation affected diffusion more than MC. Chemical gradients were generally steep at first and then gradually leveled as the reservoir of chemical on the surface was depleted.

Effect of moisture content: Both boron and copper were more mobile in wet (60% MC) than in dry (30% MC) samples. Samples with low MC were characterized by high surface loading and a steep decline in chemical concentration further into the wood. Wet samples had more shallow chemical gradients that flattened with time. This was particularly evident in blocks with 60% MC that were longitudinally oriented. Although the wet samples showed more effective diffusion, drier samples still allowed some chemical migration (e.g., radial diffusion in samples with 30% MC). By 12 months, the chemical had begun to move out of the assay portion of all blocks as they equilibrated.

Effect of orientation: As expected, chemical movement was greatest in the longitudinal direction. Boron completely penetrated the sampling zone longitudinally in all samples within 1 month. Chemical

levels declined in the outer zones and increased further within the blocks as diffusion proceeded.

Boron and copper movement: Boron is a highly diffusible chemical that moves along moisture gradients. Water-soluble amine-based copper naphthenate in the formulation was also expected to move into the wood; however, boron diffusion always exceeded that of copper. Complete longitudinal boron penetration of the assay zone was achieved in 1 month, while complete copper penetration never occurred. The slower movement of copper may reflect its dependence on amine for water solubility; evaporation of the amine component would render copper naphthenate water insoluble and may have reduced diffusion. Copper also has been shown to react with cellulose and may be selectively adsorbed and so depleted as the formulation progresses further from the application site. Such depletion may reduce the potential for internal fungal control, but copper/wood interactions near the surface may still provide a barrier against renewed microbial attack from the surrounding soil. Boron has little reactivity with wood, therefore less depletion occurred during diffusion.

Copper naphthenate and boron in the paste evaluated in this study moved in both longitudinal and radial directions at 30% and 60% MC. As expected, movement was greatest in the longitudinal direction and at the higher MC. Direction of movement seems to affect diffusion more than MC. The diffusion of both paste components through Douglas-fir heartwood suggests that they should diffuse through against decay; however, the levels required for effective protection remain to be

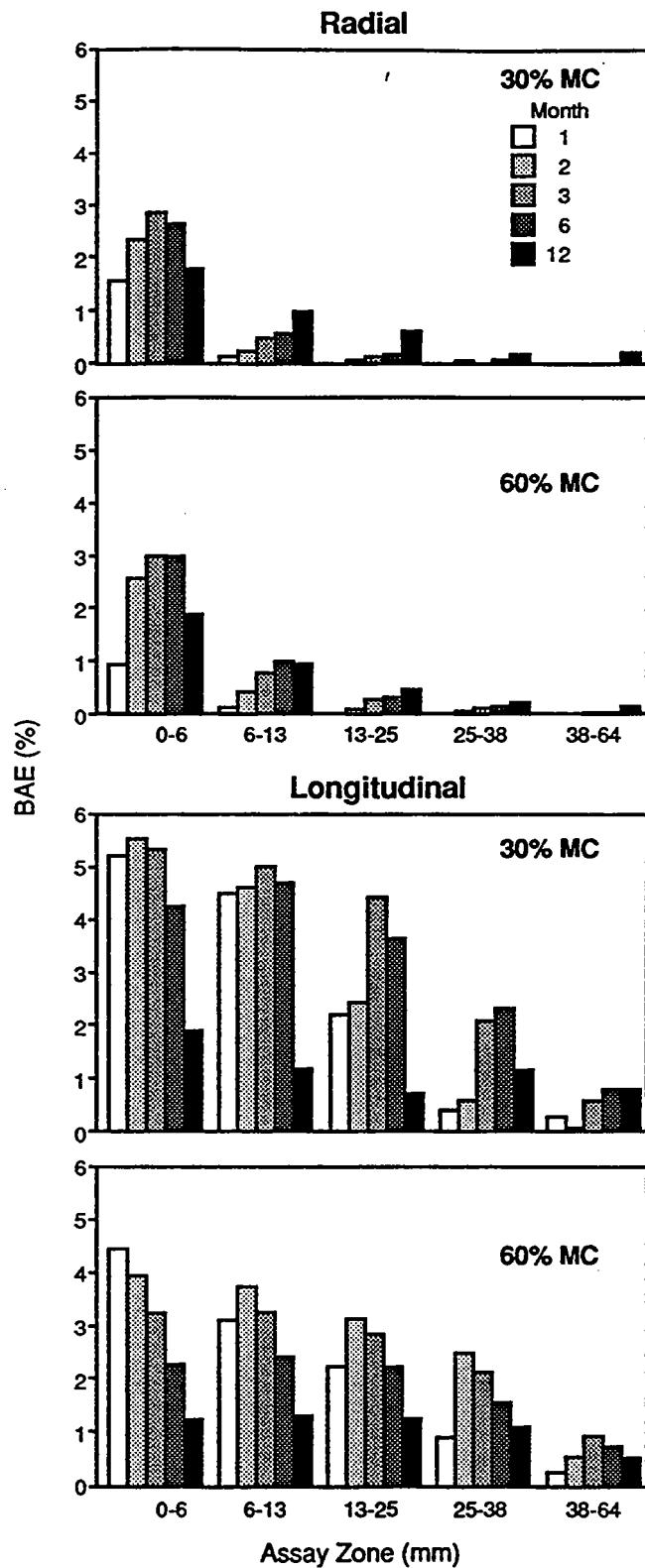


Figure V-1. Boron concentration, expressed as boric acid equivalent (BAE), measured over 1 year at radial or longitudinal depths and at 30% or 60% moisture content (MC) in Douglas-fir heartwood blocks after treatment with 5g of copper naphthenate and borate paste.

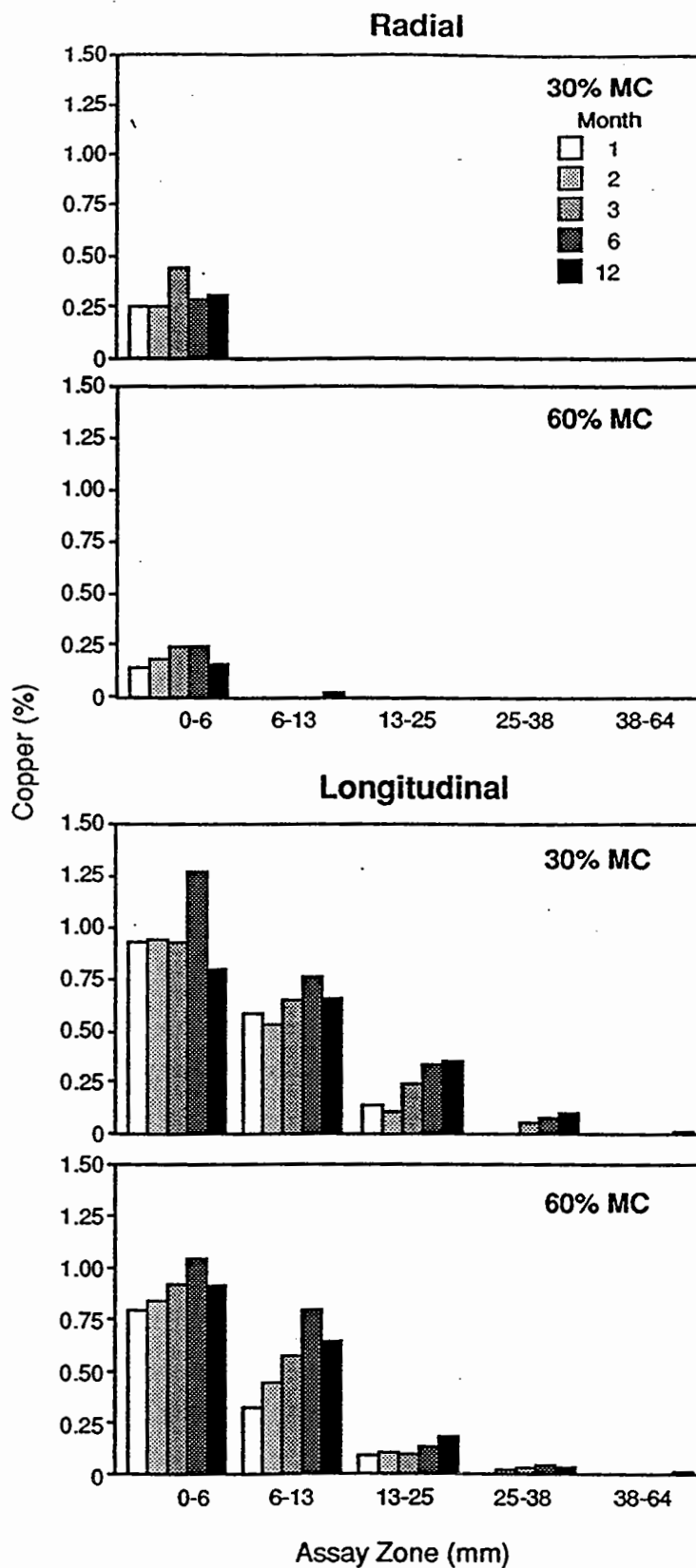


Figure V-2. Copper concentration, measured over 1 year at selected radial or longitudinal depths and at 30% or 60% moisture content (MC) in Douglas-fir most refractory woods to provide some internal as well as surface protection

determined. Field trials of this formulation have been established to evaluate more fully the rate of diffusion in

western redcedar, Douglas-fir, and ponderosa pine.

D. THRESHOLD VALUES FOR BIOCIDES EMPLOYED IN GROUNDLINE PRESERVATIVE SYSTEMS

As we continue to develop data on the levels of various biocides in the wood following application of external preservative systems, it becomes increasingly clear that we also need to develop data on the levels of the various components which are required to adequately protect wood from decay fungi. This poses a challenge since components of formulated products will move at dissimilar rates into the wood, providing varying degrees of protection. Earlier tests to determine thresholds were performed with creosote, pentachlorophenol and sodium fluoride based external preservative systems by Falhstrom and others; however, there is little or no data on the performance of the newer formulations.

To develop this information, we have assembled components for each of the three most commonly employed preservative systems. Ponderosa pine sapwood blocks (1 cm cubes) will be oven-dried (54°C) and weighed to the nearest 0.01 g. The blocks will then be treated with solutions of varying concentrations of the components to produce retentions of copper naphthenate (amine, Osmose oil, or Tenino oil) of 0.08, 0.16, 0.32, 0.96, 1.60, or 2.40 pcf (as copper). The Tenino blocks will then be reweighed and stored. The blocks treated with the amine copper will then be treated to retentions of 0,

0.20, 0.40, 0.80, or 2.40 pcf with sodium tetraborate decahydrate while the Osmose copper naphthenate treated blocks will be treated to the same retentions with sodium fluoride.

The treated blocks will be conditioned and weighed to determine initial starting weight, then sterilized by gamma irradiation. The durability of the sterile blocks will be evaluated in a modified soil burial test in which the blocks will be buried 16 to 24 weeks in moist, non-sterile soil at 32°C. At the end of the test period, the blocks will be removed, scraped clean of adhering debris and weighed to determine wood moisture content. The blocks will then be oven-dried and weighed to determine wood weight loss over the exposure period. Selected blocks will then be ground and analyzed for residual chemical content as described in previous sections of this Objective. The results should provide guidance concerning the degree of protection afforded by the presence of remedial treatment chemicals. Since the wood used in this test will not incorporate the presence of an initial preservative in the wood, the results should represent the maximum degree of protection which can be expected from a given combination of preservative components.

OBJECTIVE VI

PERFORMANCE OF COPPER NAPHTHENATE-TREATED WESTERN WOOD SPECIES

Copper naphthenate is increasingly used for initial treatment of utility poles, but there is little data on the performance of this chemical on western wood species. The poles currently being installed

throughout the western United States present an excellent opportunity to begin tracking service life of poles treated using this preservative system.

A. DECAY RESISTANCE OF COPPER NAPHTHENATE TREATED WESTERN REDCEDAR SAPWOOD IN A FUNGUS CELLAR EXPOSURE

Western redcedar contains a high percentage of naturally durable heartwood, but the outer, non-durable sapwood must still be preservative treated to provide optimum service life. The potential performance of copper naphthenate in this species was evaluated in western redcedar sapwood stakes (1.25 by 2.5 by 15 cm long) cut from freshly sawn western redcedar sapwood as well as from the above ground portion of poles which had been exposed for approximately 15 years in service. The stakes were conditioned and treated with copper naphthenate diluted in diesel oil to target retentions of 0.8, 1.6, 2.4, 3.2 and 4.0 kg/m³ (as copper). Fifteen stakes of each wood type were treated to each target retention, and then five stakes in each group were randomly selected and analyzed for copper content to determine actual retention.

The remaining stakes were then exposed at 28°C and 80% relative humidity in a forest loam soil. The soil was regularly watered, but was allow to

cycle between wet and dry. The stakes were regularly assessed for degree of fungal attack on a scale from 0 to 10 where 0 represents complete failure and 10 represents no evidence of attack.

The results indicate that preservative treated, freshly sawn western redcedar continues to outperform similarly treated, but weathered material (Table VI-1). All of the copper naphthenate treated, weathered groups continue to decline slightly 26 months after treatment, although the effect is most noticeable at the lowest retention evaluated (0.8 kg/m³ copper). Freshly sawn wood treated with copper naphthenate continues to perform similarly regardless of retention, suggesting that certain initial, cosmetic damage occurs at an early stage, but does not proceed to a significant extent in the first 2 years of fungus cellar exposure. The presence of diesel solvent also continues to provide a significant degree of protection in comparison to the untreated

controls, although the condition of these stakes continue to decline.

At present, the results indicate that copper naphthenate is performing well in western redcedar stakes treated to the recommended retention levels. While

there are differences in performance when weathered poles are retreated, these effects are slight at the higher retentions which are commercially employed. Further evaluations are planned of these samples.

B. EVALUATION OF COPPER NAPHTHENATE TREATED DOUGLAS-FIR POLES IN CALIFORNIA AND OREGON

As copper naphthenate treated poles of western wood species are installed, we have begun to collect data on the rate of microbial colonization. These trials are in cooperation with OMG. Each pole has been sampled by removing duplicate increment cores from sites located at groundline and 1.65 m above the groundline. The cores are placed into plastic drinking straws for return to the laboratory where they are placed on the surface of malt extract agar in petri dishes and observed for evidence of fungal growth. The duplicate core from each site has been segmented into zones corresponding to 0-1.25, 1.25-2.50, 2.50-3.75, 3.75-5.00, 5.00-6.25, 6.25-7.50, and 7.50-10.00 cm for analysis of residual copper content by OMG personnel. The goal of this study is to develop chemical depletion data in concert with fungal colonization levels at various sites. At present, poles at sites in California and near Eugene, Oregon have been evaluated. Poles at the Eugene site were also sampled at one location 15 cm below the groundline. Poles from the California site contained no viable fungi 1 year after treatment, while cores from the Eugene site are now being evaluated.

Table VI-1. Condition of western redcedar sapwood stakes treated to selected retentions with copper naphthenate in diesel oil and exposed in a soil bed for 6 to 26 months.

Target Retention ¹ (kg/m ³)	Weathered Samples						New Samples		
	Actual Retention (Kg/m ³)	Average Decay Rating ²			Actual Retention (Kg/m ³)	Average Decay Rating ²			
		6 mths.	14 mths.	26 mths.		6 mths.	14 mths.	26 mths.	
control	-	4.7	0.9	0.4	-	6.6	3.2	1.3	
diesel	-	8.5	6.8	5.3	-	9.9	8.4	8.0	
0.8	1.6	9.0	8.0	7.5	0.6	10.0	9.6	9.4	
1.6	1.4	9.5	8.9	8.8	1.3	10.0	9.4	9.3	
2.4	2.1	9.6	9.2	9.1	1.9	10.0	9.4	9.4	
3.2	2.7	9.6	9.1	9.0	2.6	10.0	9.2	9.2	
4.0	4.0	9.9	9.2	9.1	3.4	10.0	9.5	9.4	

¹Retentions measured as kg/m³ (as copper).

²Values represent averages of 10 replicates per treatment, where 0 signifies completely destroyed and 10 signifies no fungal attack.