# TABLE OF CONTENTS

	MARY NOWLEDGMENTS		
	PERATORS		
PERS	ONNEL	• • • • • • • • • • • • • • • • • • • •	v
OBJE	DEVELOP SAFER CHEMICALS FOR CONTROLLING INTERNAL DECAY OF WOOD POLES	•••••	1
<b>A</b> .	EVALUATION OF PREVIOUSLY ESTABLISHED TESTS OF VOLATIL REMEDIAL INTERNAL TREATMENTS		1
	New York field test of encapsulated fumigants	Jeff	1
	Treatment of through-bored Douglas-fir poles with gelatin encapsulated MITC or chloropicrin	/ /)	2
	3. Above ground treatment with gelatin encapsulated or pelletized MITC		3
	4. Effectiveness of glass encapsulated MITC in Douglas-fir or southern pine poles	onie	4
	5. Effectiveness of MITC-FUME in ponderosa pine and Douglas-fir in California	) de la companya de l	5
	6. Effect of additives on performance of Basamid in Douglas-fir pole section	s	າ 6
1	7. Basamid treatment of Douglas-fir transmission poles	nnie	7
	8. Performance of gelled, pelletized, and liquid metham sodium as internal remedial treatments for Douglas-fir poles	Jeff?	8
В.	EVALUATE PREVIOUSLY ESTABLISHED TRIALS OF NON-VOLATION REMEDIAL INTERNAL TREATMENTS		25
<i>y</i> *	1. Ability of fused borate rods to diffuse through Douglas-fir heartwood		25
}	Performance of fused borate rods in groundline treatments of Douglas-fir poles in Owego, New York		26
. (	Performance of fused borate rods in Douglas-fir poles exposed in Corvallis, OR:	••••••	27

		4: Ability of s	sodium fluoride rods to move through Douglas-fir poles	28
	C.		EW REMEDIAL TREATMENTS FOR ARRESTING TING INTERNAL DECAY	31
		1. Effectivene	ess of basamid/metham sodium mixtures	31
	D.		UNDAMENTAL ASPECTS OF INTERNAL REMEDIAL	39
		1. Evaluation	of 40% metham sodium in small block trials	39
		2. Performan	ce of a fluoride/boron rod in laboratory trials	40
		3. Diffusion on naphthena	of copper and boron from a copper te/boron paste	40
			glycol and moisture content on diffusion of boron from on rods	41
		5. Effect of v	oids on efficacy of fumigant treatments	43
			odels which predict fumigant movement through	44
	OBJE	CTIVE II:	IDENTIFY SAFER CHEMICALS FOR PROTECTING EXPOSED WOOD SURFACES IN POLES	
`	<b>A</b> .	PENTACHLO	RY AND FIELD TRIALS OF POTENTIAL DROPHENOL REPLACEMENTS FOR PROTECTING EDCEDAR SAPWOOD FROM DECAY	53
	В.		TREATMENTS FOR PROTECTING FIELD DRILLED S	64
	OBJE	CTIVE III:	DETECT EARLY DECAY AND ESTIMATE RESIDUAL STRENG OF WOOD POLES	
	A.		BORING OF DOUGLAS-FIR POLES USING HOLE PATTERNS	65

OBJE	CTIVE IV:	EVALUATE THE POTENTIAL FOR DECAY DEVELOPMENT DURING AIR SEASONING AND IDENTIFY CONTROL STRATEGIES	71
A.		ETHODS FOR PREVENTING OR ELIMINATING FUNGAL ION IN AIR-SEASONING DOUGLAS-FIR POLES	71
		on thermal treatments to eliminate fungi from eled Douglas-fir	71
	2. Internal ter	mperature monitoring	72
	3. Boron diffi	ısion	79
ОВЈЕ	CTIVE V:	EVALUATE THE EFFICACY OF GROUNDLINE PRESERVATIVE SYSTEMS FOR WESTERN WOOD SPECIES	80
A.		NCE OF MODIFIED GROUNDLINE PRESERVATIVE I CORVALLIS, OR	80
В.	BANDAGES	NCE OF MODIFIED EXTERNAL PRESERVATIVE ON DOUGLAS-FIR, PONDEROSA PINE, AND WESTERN IN CALIFORNIA	82
C.		NCE OF GROUNDLINE BANDAGES IN SOUTHERN PINE AND EDCEDAR POLES	83
D.		HRESHOLD VALUES FOR MIXTURES OF SELECTED JE PRESERVATIVE SYSTEMS	83
OBJE	CTIVE VI:	PERFORMANCE OF COPPER NAPHTHENATE TREATED WESTERN WOOD SPECIES	89

Previously established field trials of MITC-Fume continue to show that this chemical remains in Douglas-fir and southern pine poles at fungitoxic levels 5 years after treatment. In general, increasing dosages resulted in higher chemical levels in the poles. All of the MITC-Fume treatments resulted in higher residual MITC levels than comparable metham sodium treatments. Field trials with solid basamid with and without copper sulfate continue to show the promise of this chemical. Basamid treated poles continue to contain MITC at levels which exceed those for comparable metham sodium treatments. These results, which are currently being confirmed in poles in service, indicate that this formulation can deliver fungitoxic MITC levels to wood in service, without the risk of spills associated with metham sodium.

We have completed trials with gelled and pelletized metham sodium formulations. Both of these formulations offered improved safety during application. Initial laboratory trials also suggested that the gelled formulation was more effective than comparable liquid metham sodium. Field trials, however, indicate that the formulations provided protection comparable to the liquid formulation in poles over the test period. The gelled formulation still offers the advantage of reduced risks of spills during application.

Trials are also continuing with various solid, water diffusible treatments for arresting internal decay. Trials of fused borate rods continue to show that these treatments require more moisture for effective movement in Douglas-fir poles. Field trials have also been established with borate rods with glycol as an additive to determine if glycols can accelerate diffusion in drier wood. The poles in these trials have also been sensored to monitor

internal moisture changes over time in order to better correlate boron diffusion with wood moisture content.

Trials underway with a boron/fluoride rod indicate that the boron is diffusing well from these rods, while the fluoride is moving somewhat slower. Neither chemical has approached a fungal threshold one year after treatment, but the combination of chemicals may lead to more effective fungal control.

Trials with pelletized metham sodium/basamid mixtures suggests that using ratios of these two chemicals can produce an initial rapid burst of MITC release followed by a slower MITC release with time. This combination allows for rapid control of existing fungal infestations followed by long term protection against reinvasion. These laboratory trials will be further confirmed with field trials.

The trials to evaluate the effects of voids on fumigant movement initially suggested that voids have little influence on subsequent fumigant levels on either side of the void. Sampling 8 years after treatment, however, indicates that chloropicrin levels were generally higher in poles without voids. We plan further trials of actual field poles containing voids to confirm these effects.

Trials to identify treatments for protecting the sapwood of western redcedar poles as well as wood exposed in field drilled bolt holes are continuing. Trials in western redeedar sapwood have identified a number of chemicals which can be remedially applied to protect this wood against fungal attack. At present, however, commercial pole spraying has largely ceased making further field trials difficult. Field trials to identify treatments for protecting untreated wood exposed during drilling for various pole attachments continue

to show that diffusible boron and fluoride compounds provide excellent long term protection against fungal attack. The protective effects of one diffusible treatment, Boracol, however, has begun to decline. Further sampling will be undertaken to identify the long term effectiveness of the remaining treatments.

Trials to identify enhanced patterns for through boring of Douglas-fir poles are complete. The results indicate that patterns as widely spaced as 400 mm apart longitudinally still produce a nearly completely treated pole through bored the zone. i n Pentachlorophenol levels in the through bored zone were generally above the threshold for fungal growth. Prior sampling of Douglas-fir poles in service suggest that even poles with small skips in the through bored zone contained no evidence of internal decay. These results suggest that the through boring pattern can be extended without adversely risking pole service life. A reduced through boring pattern would decrease treatment costs while minimizing impacts on pole strength.

Trials to evaluate the application of boron to freshly peeled Douglas-fir poles as a means of preventing fungal colonization using a thermal process suggest that thermal treatment failed to produce a boron loading sufficient to permit subsequent diffusion across the pole section after a 3 month diffusion period.

Evaluations of various external groundline preservative formulations continue to indicate that replacement formulations based upon copper naphthenate, boron or fluoride perform comparably to earlier formulations employing pentachlorophenol and creosote. Pentachlorophenol levels in some treatments have fallen below the threshold for fungal growth, while those in all of the replacement treatments remain above a

protective level. These results suggest that the newer groundline preservative systems should provide a reasonable level of protection against external decay. Laboratory trials to better understand the levels of combinations of chemicals required for protection in the groundline zone are continuing.

Fungal cellar evaluations of copper naphthenate treated western redcedar continue to show excellent performance at levels specified in the American Wood Preservers' Association Standards. Performance is generally better for wood which was freshly sawn prior to treatment, while wood cuts from weathered poles in service has provided slightly lower levels of protection. The weather wood apparently has higher permeability, making it more likely to lose chemical in soil contact. Further evaluations are planned.

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This research could not be performed without the active cooperation and participation of utilities, wood treaters, and suppliers as well as the staff and students. Contributions by all of these entities for success and we gratefully acknowledge the groups which have assisted us in the past year. We look forward to continued collaboration to identify solutions to problems utilities experience with their wood systems.

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- \*Central Lincoln PUD
- \*Empire State Electric Energy Research Corporation
- \*New York State Electric and Gas Corporation
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- \*ISK Biotech
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# OBJECTIVE I DEVELOP SAFER CHEMICALS FOR CONTROLLING INTERNAL DECAY OF WOOD POLES

**Improvements** in specification, treatment and inspection have combined to markedly improve the performance of wood poles in North America. Despite these steps. however, a percentage of poles in a population will eventually develop problems with decay or insect attack. In reality, this damage is no different than that which might occur with steel (which can corrode), concrete (which spalls), or any other material. Proper combinations of specification, treatment and quality control reduce the risk of such damage occurring, regardless of material, but they cannot completely prevent damage. As a result. utilities must perform regular inspections of their pole system to maintain system integrity and safety.

One of the advantages of wood for supporting overhead lines is the relative ease with which insect and fungal damage can be controlled. A wide array of treatments have been developed for remedially arresting decay and these systems have contributed, to a great measure, in the continued use of wood poles. Probably, the most important of the remedial treatments have been those designed to control internal decay of thin sapwood species. In these instances, checks through a well-treated shell of preservative permit the entry of moisture and fungal spores into the untreated wood within the pole. Eventually, decay fungi hollow out the pole near the groundline, leaving only the outer preservative treated shell to support the design load. development of fumigants for arresting this decay in the late 1960's provided one of the first widely effective methods for economically prolonging the service life of internally decay poles. As a result, nearly 90 % of utilities in North America use fumigants as part of their pole maintenance programs saving over one billion dollars per year in replacement costs.

Despite their widespread fumigants pose a challenge to users. Two of the 3 formulations registered with the U.S. Environmental Protection Agency for wood application are liquids (Table I-1), which can be spilled during application. One of these liquids, chloropicrin, is highly volatile and applicators must wear respirators when applying this chemical. In these times of heightened environmental sensitivity, the image of workers applying chemicals to poles while wearing respirators is difficult to explain to customers. The other liquid fumigant, metham sodium (32.7 % sodium nmethyldithiocarbamate), is caustic. The third fumigant registered for wood (methylisothiocyanate) is a solid at room temperature, but it too is caustic and must be contained in either aluminum or glass capsules prior to application. Despite their widespread effectiveness, the drawbacks associated with each of these chemicals has encouraged a search for safer internal remedial treatments. Under Objective I, we will present data on the currently registered fumigants along with information of formulations currently under evaluation. In addition, we will present information on the performance of various water-diffusible remedial treatments.

## A. EVALUATE PREVIOUSLY ESTABLISHED TESTS OF VOLATILE REMEDIAL INTERNAL TREATMENTS

Over the past 20 years, a variety of field trials have been established to evaluate the efficacy of various remedial treatments

(Table I-2). Many of these trials lasted only a few years, but several have been maintained for longer periods to develop data on long term performance of the more commercially important remedial treatments. Such data can be invaluable when making decisions concerning the efficacy of the various treatments. In this section, we describe results from those trials involving volatile chemicals. In last year's report (pages 5-9), we reported on the final inspections of Douglas-fir poles treated with allyl alcohol in 1977 and with methylisothiocyanate (MITC) in 1983. These trials have since been discontinued owing to the inadvertent remedial treatment of many poles by a commercial contractor. following section, we describe the results obtained from trials of non-volatile remedial treatments.

- 1. New York field test of encapsulated fumigants: The field test of gelatin encapsulated MITC established in 1983 in chromated copper arsenate treated Douglas-fir poles in the New York State Electric and Gas system was last evaluated in 1992. These poles will be the subject of an evaluation in 1996.
- 2. Treatment of through-bored Douglas-fir poles with gelatin encapsulated MITC or chloropicrin: The Douglas-fir poles treated with gelatin encapsulated chloropicrin or MITC in 1982 was last inspected in 1990. This trial will be inspected in 1997.
- 3. Above ground treatment with gelatinencapsulated or pelletized MITC: The trialevaluating gelatinencapsulated and pelletized MITC in above ground applications was last evaluated in 1990 and will be sampled in the late fall of this year to an 11 year update. Previous trials had shown that the fumigant remained well distributed around the application point and continued to prevent fungal colonization of zones around the field

drilled bolt holes in these poles.

4. Effectiveness of glass encapsulated MITC in Douglas-fir and southern pine: MITC has been found to a highly effective fumigant for arresting fungal attack of Douglas-fir, but for many years, it remained an experimental chemical owing to an inability to economically contain the caustic chemical prior to application. While field trials indicated that gelatin could effectively encapsulate MITC, the costs of this approach were considered too high to be economical. In 1987, a glass encapsulated formulation was developed by DeGussa (Fairlawn, NJ) which contained 30 g of MITC in a glass vial which plugged with combination was а polymer/aluminum cap. The cap was removed prior to application, permitting MITC vapors to diffuse from the vial into the wood.

In 1988, thirty six Douglas-fir and 36 loblolly pine poles (25 to 30 cm in diameter by 3.6 m long) were pressure treated with CCA Type C to a nominal retention of 6.4 kg/m<sup>3</sup> and then painted with an elastomeric paint to retard vapor loss. The poles were set to a depth of 0.9 m at the Corvallis test site.

Into each of six poles per wood species, a series of 2, 4, 6, or 8 holes, 1.9 cm in diameter by 20.5 cm long were 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 of 96 % MITC was added open-end down into each hole. The holes were plugged with tight fitting preservative-treated wood dowels to retard fumigant loss and prevent water collection in the treatment holes. An additional set of 6 poles per species were treated with 500 ml of metham sodium equally distributed among 3 holes drilled as described for the MITC-Fume treated poles. A final set of poles, the control group, received no chemical treatment.

MITC-Fume performance was assessed 1, 2, 3, and 5 years after treatment using a combination of bioassays and chemical analyses. For the first 3 years, a series of fungal infested dowels were placed into holes drilled at selected distances above and below the treatment zone. The dowels were removed at selected intervals after insertion and were cultured for the presence of the test fungus. which served as the measure of chemical effectiveness. Early in this process, however, it became clear that the fungus often died as the dowels dried in the poles, producing anomalous results. As a result, this procedure was not performed at the five year sampling Closed tube bioassays were point. performed on cores removed from the poles 1, 2, 3, and 5 years after treatment. Two 15 cm long increment cores were removed, 180 degrees apart, 0.3 m below the groundline and sets of 3 increment cores, 120 degrees apart, were taken from sites 0, 0.3, 0.9, and 1.5 m above the highest treatment hole. Cores were not removed from sites within the treatment zone because it was felt that high chemical levels would overwhelm the test fungus. The inner and outer 25 mm of each increment core were placed in separate test tubes containing an actively growing culture of Postia placenta. The tubes were sealed and incubated in an inverted position so that any vapors coming from the wood could move up to come in contact with the actively growing fungus. Radial growth of the fungus in the presence of wood was then measured and compared with that in similar tubes containing no wood to provide a measure of residual fungitoxicity. The middle segment of wood remaining from each close tube bioassay core was then placed onto malt extract agar in plastic petri dishes and observed for the presence of funci. Any fungi growing from the wood were examined for characteristics typical of basidiomycetes, a

group of fungi containing many important wood decayers.

For chemical analyses, a second set of increment cores were removed from each pole at locations adjacent to those taken for the closed tube bioassays. The outer and inner 25 mm of each increment core were placed into separate test tubes containing 5 ml of ethyl acetate. The tubes were stored for a minimum of 48 hours at room temperature and then each extract was chromatographically analyzed for **MITC** using Varian 3700 chromatograph equipped with a flame photometric detector with filters specific for MITC levels were quantified by comparison with standards.

Culturing of increment cores revealed that decay fungi were present sporadically in the various treatments. Interestingly, a number of these isolations occurred in poles treated with the highest MITC dosage (Table I-3). The reasons for these isolations are unclear. although they generally occurred above the treatment zone and may reflect invasion through checks which opened beyond the treated shell. No evidence of visible decay was noted in any treatments, including the controls. Non-decay fungi continue to be isolated at high levels from all of the poles, with the controls containing the most consistently high levels of colonization. The roles of these various fungi in the decay process or on chemical effectiveness remain poorly understood. The MITC and metham sodium treatments have apparently limited colonization by non-decay fungi, although their effects on the species composition were not investigated.

Table I-1. Characteristics of internal remedial treatments for wood poles

Trade Name	Active Ingredient	Concentration %	Toxicity (LD <sub>a</sub> )	Manufacturer
Timber Fume	Trichloronitromethane	96	205 mg/kg	Osmose Wood Preserving Great Lakes Chemical Co.
Wood Fume	Sodium n-methyldithio- carbamate	32.1	1700-1800 mg/kg	Osmose Wood Preserving
ISK	Sodium n-methyldithio- carbamate			ISK Biotech Inc.
Vorlex	20% methylisothiocyante 80% chlorinated C <sub>3</sub> hydrocarbons	99	538 mg/kg	NorAm Chemical Co.
MITC-FUME	methylisothiocyante	96	305 mg/kg	Osmose Wood Preserving
Impel Rods	boron	99		CSI Inc.
Pole Saver	sodium octaborate tetrahydrate	58.2	·	Preschem Ltd.
Rods	sodium fluoride	24.3		

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

Test Site	Chemicals Evaluated	Date Installed
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
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
Pacific Power, Corvallis	Basamid	1993
Peavy Arboretum	Boron/Fluoride Rods	1993

Closed tube bioassays of increment cores removed from the various treatments suggest that residual MITC remains in many of the poles receiving the higher MITC dosages, although the distribution has become more variable and fewer poles remain strongly fungitoxic (Table I-4). As expected, metham sodium treated poles exhibited little evidence of residual fungitoxicity, reflecting the relatively low rate of MITC production from this compound and the ephemeral nature of this formulation in wood. Similar trends were noted with the lower MITC-Fume dosages. suggesting that these low dosages should not be relied upon for long term protection against renewed fungal attack.

Chemical assays revealed that MITC levels continue to decline in all treatments. although the levels in many treatments remain above those believed to be required for fungal control (Table I-5). MITC levels in metham sodium treatments remain comparable to those found for the 60 g MITC-Fume treatment in southern pine, but the results in Douglas-fir were more variable. In several instances, the highest chemical levels were present in Douglas-fir poles treated with the lowest dosage of MITC-Fume, particularly near the treatment zone. It is likely that chemical levels in the various treatments will become increasingly variable as the poles begin to lose MITC at different rates with time.

MITC levels 0.9 and 1.5 m above the treatment zone continue to be relatively low, suggesting that the amounts of chemical diffusing upward from the treatment holes is declining. These levels of chemical may, however, remain adequate for preventing germination of invading fungal spores provided the distribution of chemical remains uniform.

The results after five years indicate that MITC-Fume continues to provide protection at dosages greater than or equal to 120 g per pole. The 60 g treatment continues to perform in a manner similar to that found with metham sodium. These poles are currently being sampled after 7 years of exposure to provide more detailed data on the rate of MITC concentration decline in the various treatments.

5. Effectiveness of MITC-Fume in ponderosa pine and Douglas-fir poles in California: In 1989 a series of Douglas-fir and ponderosa pine poles treated with pentachlorophenol in liquified petroleum gas and installed near San Francisco, CA were remedially treated with MITC-Fume. The poles were located in two sites. Half Moon Bay poles were in sand in a drier area, while the Belmont poles were set in concrete and were located closer to the coast.

The poles were treated by drilling a series of 20 mm diameter holes beginning at groundline and spiraling around the pole at 90 degree angles and upward 15 cm. A single MITC-Fume vial was applied to each hole and the holes were plugged with tight fitting, preservative treated dowels. Poles received either 90 or 120 g of MITC (3 or 4 vials). The poles were sampled 2, 4, and 5 years after treatment by removing increment cores from 3 equidistant sites 30 and 90 cm above the highest treatment hole. The outer, treated zone was discarded and the inner and outer 25 mm of each core were placed into ethyl acetate and extracted for 48 hours at room temperature. The extracts were then analyzed for residual MITC as described under Section 4. The remainder of each core was cultured on malt extract agar for the presence of basidiomycetes. A total of 7 pine and 13 Douglas-fir poles were treated at the Belmont site, while 3 pine and 7 Douglas-fir poles were treated at Half Moon Bay.

MITC levels in the inner zone were generally higher than those in the outer zone. This result follows those of previous studies and reflects the placing of the MITC-Fume vial with the opening downward in the hole towards the pole center (Table I-6). Chemical levels in the outer zone were generally more variable. MITC levels were higher in Douglas-fir poles, perhaps reflecting the lower permeability of this species. The 90 g MITC treatment of Douglas-fir contained residual chemical levels which were greater than those found with the 120 g pine treatment. MITC levels 0.9 m above the treatment zone were lower, although levels in the inner zones remained well above those necessary for wood protection. Chemical levels nearer the surface were much lower further away from the treatment zone, reflecting the tendency for most of the chemical to move vertically from the center, where the original dosage was directed.

Chemical level appeared to differ only slightly among the two test sites. These sites were chosen because they represented cool, moist coastal and drier inland exposures. However, there appears to be little difference in residual MITC levels among the sites, suggesting that environmental factors did not markedly affect fumigant performance.

6. Effect of additives on performance of Basamid in Douglas-fir pole sections: While MITC has performed well in field trials, the caustic nature of this compound requires some form of encapsulation prior to application. In an effort to identify more easily handled fumigant, we have evaluated a solid fumigant, Basamid (3,5-dimethyltetrahydro-1,3,5,2H-thiadiazine-2-thione).

This compound is a crystalline solid at room temperature and decomposes to produce MITC along with an array of other sulfur compounds. In previous studies, basamid provided limited protection against fungal attack, but did not appear to be capable of the rapid fungal control which would be necessary for a remedial treatment. Decomposition of this compound, however, can be enhanced by altering pH or by addition of bivalent metals.

In 1990, a series of 20 to 25 cm diameter by 1.6 m long untreated Douglas-fir pole stubs were air-seasoned. A series of three 22 mm diameter by 30.5 mm long holes were drilled at a 60 degree angle 70, 80 and 90 cm from one end of each stub with each hole being placed 120 degrees around from the others. Each hole received 50 g of basamid alone or amended with 1 % copper sulfate, 10 % glucose, 10 % ammonium lignin sulfonate, or 5 % sodium octaborate. Other poles received basamid with 50 ml of ethanol, acetone, methanol or water. All powdered additives were evaluated with or without 5 % powdered pH 12 buffer. The pole stubs were capped with roofing felt and placed above ground on a test fence at Peavy Arboretum. Each treatment was replicated Control stubs with no on five stubs. treatment or 150 ml of metham sodium were also established.

The poles stubs were sampled 6, 12, 24, 36, and 60 months after treatment by removing increment cores from 3 equidistant sites around the stubs, 150 mm above or below the treatment holes. Additional cores were removed from sites 450 mm above or below the treatment holes 12 to 60 months after treatment. The inner and outer halves of each core were placed into 5 ml of ethyl acetate and analyzed for MITC content as described earlier ('93 Annual Report pages

13-16).

MITC levels in all of the treatments were generally low, reflecting the slow rate of decomposition of basamid in wood (Table I-7). The levels in many treatments, however, continue to rise, even after 5 years, suggesting that the original basamid is continuing to decompose to produce MITC which can then diffuse through the wood. This characteristic provides the potential for long term controlled release of MITC. When coupled with the improved safety of this formulation in comparison with liquid fumigants, a controlled release basamid formulation would have a major advantage as a remedial wood pole treatment.

MITC levels tended to be higher in the inner zone of the pole stubs, although this trend was not always consistent. addition of alcohols to basamid had little influence on MITC production, nor did the addition of lignin markedly affect decomposition to MITC. The addition of glucose produced or boron slight improvements in MITC levels. The most dramatic effect on MITC levels was produced by the addition of copper sulfate. MITC levels were consistently higher in the presence of copper sulfate over the entire test period, confirming previous laboratory The addition of pH 12 buffer trials. enhanced MITC production over the first 3 years, but this effect has disappeared. This may reflect three years of above average rainfall at the test site which may have depleted the original solid buffer placed in the hole. Addition of pH 12 buffer did improve the release rate early in the trial and its presence may be useful for accelerating MITC production to control an existing infestation.

The results of these trials continue to demonstrate that the release rate of MITC

from basamid can be manipulated. The formulation could be routinely applied with added copper sulfate to control existing infestations much in the same way as metham sodium, but without the risk of chemical spills. Alternatively, unamended basamid could be employed to protect new poles which are not colonized by decay fungi and are therefore not in immediate need of chemical protection.

Further field trials of basamid in poles in service are underway to confirm the results of these small scale trials.

7. Basamid treatment of Douglas-fir transmission poles: The results of the small scale Basamid additive trial suggested that the decomposition of this fumigant to MITC could be markedly enhanced by addition of These trials, however, were performed in untreated pole sections exposed out of ground contact. In 1993, 30 Douglas-fir transmission poles located near Corvallis, OR were treated with Basamid (200 or 400 g), Basamid plus 1 % copper sulfate (200 or 400 g), or 500 ml metham sodium applied to three steeply sloping holes drilled at 120 degree intervals around the pole beginning 30 cm above the through bored zone and moving upward at 15 cm intervals. The holes were then plugged with tight fitting dowels to retard fumigant loss. Each treatment was replicated on 6 poles.

The poles were sampled for MITC content one year after treatment by removing increment cores from 2 sites 120 degrees around from the highest treatment hole, as well as three cores each from sites located 1, 2, and 3 m above the highest treatment hole. The outer preservative treated shell was discarded, and the inner and outer 25 mm of the remaining core were individually placed into test tubes containing 5 ml of ethyl acetate. The ethyl acetate extracts were

analyzed for residual MITC as described in earlier sections. Although it was not done in 1994, future inspections will also involve culturing the remaining increment core segment for the presence of basidiomycetes.

MITC levels in the poles one year after treatment were generally low, even with the metham sodium treatment (Table I-8). Metham sodium typically decomposes rapidly, albeit inefficiently, after treatment, leaving a large residual concentration which then dissipates over a 2 to 3 year period. The MITC levels noted in the metham sodium poles herein are similar to those found for similarly treated poles in the initial basamid study (Section 6). MITC levels in the Basamid treated poles were generally lower than those found with the metham sodium treatment, although the differences were sometimes slight. The addition of copper markedly enhanced MITC levels at both dosages, confirming the results found in the small pole sections. MITC was not detected consistently 2 and 3 m from the treatment zone, suggesting that the rate of Basamid decomposition was inadequate to provide protection at these distances from the treatment site. As a result, some modification of the fumigant application pattern may be necessary in order to ensure complete protection of the pole.

The results indicate that basamid is decomposing at rates approaching those of metham sodium under field conditions. Further evaluations of these tests are planned.

8. Performance of gelled, pelletized, and liquid metham sodium as internal remedial treatments for Douglas-fir poles: Fumigants are widely used in North America for arresting and controlling internal decay in utility poles, pilings, and bridge timbers. Of the currently registered fumigants, liquid

metham sodium (32.7% sodium n-methyl-dithiocarbamate) is the most widely used because of its relatively low toxicity to humans and minimal volatility. Metham sodium is, however, caustic, and many workers experience skin burns after use. It is also highly toxic to fish. These handling properties have encouraged a search for formulations with improved properties.

Metham sodium can be applied as a relatively pure sodium salt, but this approach has attracted little commercial interest. Recently, metham sodium has been formulated as a gel with 40 percent active ingredient (A.I.) and in pellets with 25 percent A.I. (ICI, Richmond, CA). Both formulations reduce the chance of spills during application, but their efficacy as wood fumigants remains unknown. Metham sodium must decompose to become effective, and the effects of formulation modifications on decomposition are unclear. In this report, we describe laboratory and field trials to evaluate these new formulations.

Laboratory trials were conducted with a previously described small block test in which 25-X 25- x 100-mm-long Douglas-fir heartwood blocks were inoculated at each end with Antrodia carbonica, an important decayer of Douglas-fir poles. The blocks were incubated for a minimum of 6 weeks to permit complete fungal colonization; then 50, 100, 250, 400, or 500 mg of liquid or gelled 40 percent metham sodium was added to each block through a single hole (9 mm in diameter by 20 mm long) drilled at the center of the block. The hole was then plugged with a tight-fitting serum cap. and the blocks were incubated in humidified containers for 1, 3, 5, 7, 10, 14, or 28 days at 23° to 25°C. One set of 56 blocks was treated with a single dosage (250 mg) of liquid or gelled metham sodium for periodic sampling over 28 days. A second set of 40 blocks was treated with liquid or gelled metham sodium and incubated for 7 days prior to sampling. Each treatment was replicated on 12 blocks.

At each timepoint, four blocks per treatment were sampled by cutting three 5-mm-thick sections from each end. The outermost sections were discarded, and the remaining two sections were cut into 16 equally sized squares. The inner four squares from the center sections were placed on petri dishes containing 1.5 percent malt extract agar amended with 10 ppm benomyl and observed for growth of the test fungus. Fungal survival served as a measure of fumigant effectiveness.

The inner four squares from the innermost sections were placed in 5 mL of ethyl acetate and stored for 48 hours at room temperature (23° to 25°C). The ethyl acetate extracts were then analyzed by gas chromatography for methylisothiocyanate (MITC), the presumed primary fungitoxic product formed by the decomposition of metham sodium.

The effects of gelling on MITC decomposition were further investigated in a series of test tube trials. Douglas-fir heartwood was ground to pass a screen with 2-mm square mesh and air-dried to 7 to 9 percent moisture content. Five-hundred mg of sawdust were added to each of 72 40-mL borosilicate vials, and 10 or 25 mg of gelled or liquid metham sodium, respectively, was added to each vial. The vials were sealed with plastic caps equipped Teflon<sup>®</sup>-lined septa. The vials were incubated at one of three temperatures (5,

21, or 32°C) for one of four time periods (24, 48, 72, or 144 hours). At each time period, three vials per treatment were sampled. A headspace sample was removed and injected into the gas chromatograph as previously described. The caps were then removed, and 3 mL of ethyl acetate were added to each vial. The samples were extracted for 15 minutes, then analyzed for MITC with the gas chromatograph. MITC levels were determined by comparisons with prepared standards. These values were combined to provide MITC levels/vial.

In field trials, Douglas-fir pole sections (250 to 300 cm in diameter by 3.6 m long) were treated with ammoniacal copper zinc arsenate prior to being set to a depth of 0.6 m at a site 10 km north of Corvallis, OR. Gelled metham sodium was applied at dosages of 100, 200, 300, 500, or 750 g/pole, while pelletized metham sodium was evaluated at 100, 200, or 300 For each formulation, 5 g/pole. poles/dosage were evaluated. At each application, the chemical was equally distributed among three steeply angled holes, 19 mm in diameter and of a sufficient length to accommodate the given dosage, drilled at equidistant points around the groundline. Each hole was plugged with a tightly fitting dowel to retard fumigant loss.

Fumigant levels in the poles were assessed after 6, 12, 24, and 36 months by removing increment cores from three equidistant sites around the pole at heights of 0.3, 0.9, and 1.5 m above groundline. The outer preservative-treated zone was discarded, and the inner and outer 25 mm of the remaining cores were extracted in 5 mL of ethyl acetate and analyzed for residual MITC content as described above. The remainder of each core was evaluated

for residual fumigant with a closed-tube bioassay in which the core was placed in a glass test tube under an inverted slant of 1.5 percent malt extract agar previously inoculated with Postia placenta. With this bioassay, any fumigant present in the wood volatilizes and moves upward where it can inhibit growth of the test fungus. Percentage of inhibition of fungal growth in tubes without wood provides a comparative ofresidual measure fungitoxicity. This method is sensitive to very low levels of MITC.

After a 7-day incubation, gelled metham sodium appeared to be slightly more effective then the liquid formulation in terms of both fungal survival and residual MITC (Table I-9). MITC levels tended to rise with increasing dosage, although the rates of increase were not directly proportional. After incubations of 1 to 4 weeks, MITC levels tended to decline. reflecting rapid a initial decomposition of metham sodium to MITC followed by a slower diffusion from the wood (Table I-10). MITC levels were generally higher in the blocks treated with gelled metham sodium, perhaps reflecting the ability of the gel to retard decomposition to MITC or to delay MITC release into the wood after application. Moisture and contact with the wood appear to be critical for the decomposition of metham sodium. The ability of the gel to hold moisture would be an important added benefit of using this system, while the gel could retard movement of metham sodium into the surrounding wood, where it would interact to decompose, thus decreasing the rate of MITC release.

Fungal survival after treatment followed trends that were inverse to those found with MITC concentration,

decreasing with increased dosage (Table I-9). Liquid metham sodium eliminated the test fungus at the highest dosage tested, while results with the gelled formulation were more variable. Fungal survival in blocks treated with gelled metham sodium is of some concern, but the chemical levels present in this study suggest that the fungi would be eliminated upon prolonged incubation.

Samples removed from blocks treated with 250 mg of gelled or liquid metham sodium and exposed for up to 28 days suggested that residual MITC in these two series of blocks followed similar trends. with high initial MITC levels that declined 5 to 7 days after treatment (Table I-10). These results confirm the observation that metham sodium is a relatively ephemeral treatment. Fungal survival proved more variable: some survival was noted in both treatments davs after chemical 14 application. In both instances, however, fungal levels were declining, suggesting that both treatments would ultimately be effective.

Measurements made of MITC levels in test tubes containing Douglas-fir sawdust to which gelled or liquid metham sodium was applied varied quite widely with temperature, formulation, and dosage (Table I-11). Conversion rates of metham sodium to MITC were also low (<40%), but these values were within the ranges of previous studies. Levels in the tubes also tended to decline with time, suggesting that the MITC decomposed with time or that the tubes leaked. Despite these losses, the overall trends provide useful information concerning the relative decomposition rates of the two formulations. For example, MITC levels tended to decrease between 5° and 32°C with the liquid formulation, but increased with the gelled system. The was gelled formulation developed specifically for application to soils in Conventional liquid warmer climates. metham sodium performs poorly in these environments because it tends to lose moisture so quickly that decomposition does not occur. The remainder of the treatments did not consistently differ with time or temperature with the two formulations. These results imply that, for practical purposes, the formulations differ little in their ability to decompose to produce MITC.

The inconsistencies in MITC levels at various time points in the trial made comparisons difficult. For this reason, MITC concentrations were averaged for the four sampling times each for dosage-temperature combination. Average MITC levels in gelled treatments tended to steadily increase with temperature; they were more variable with the liquid formulation (Fig. I-1). MITC levels increased slightly between 5° and 21°C, then declined at 32°C for the low dosage liquid formulation. MITC levels at the higher liquid dosage were initially high, but declined with temperature. trends reflect the characteristics of the two The liquid formulation formulations. should rapidly sorb to the wood, where it can interact to decompose to produce MITC. Eventually, however, moisture in the sawdust would limit decomposition. The gelled formulation moves into the wood more slowly, producing lower initial MITC levels, but maintaining production for longer periods of time. characteristic might be useful for extending the protective period afforded by metham sodium.

These results suggest that more MITC

is produced in the gel treatments when they are incubated at higher temperatures. This feature could be extremely useful for producing rapid control of existing fungal infestations during warmer periods of the vear when chemicals would be released more rapidly. The effect of slower chemical release at cooler temperatures on the performance of gelled metham sodium is difficult to predict. The effect would be minimal if the gel remained in the wood during the cold period and was activated as temperatures rose. However, in all likelihood the gel would dry during the cold period, resulting in a marked sodium reduction metham in decomposition. Consequently, the long-term protective effect of fumigant treatment might be reduced.

Results of the laboratory trials indicate that gelled metham sodium was slightly better than the liquid formulation for decomposition to **MITC** comparable for eliminating fungi established in Douglas-fir heartwood. Residual MITC was detected at the lowest sampling zone of the test poles within 6 months after treatment for all but the outer zone of cores from poles receiving 300 mg of pelletized metham sodium (Table I-12). MITC levels 0.9 and 1.5 m above the groundline were minimal for both gelled and pelletized treatments, suggesting that MITC decomposition and movement were inadequate to protect areas removed from MITC levels were the treatment zone. generally lower than those found previously with liquid metham sodium.

Chemical levels tended to be highest in the inner zone, reflecting the fact that the fumigant was directed toward the center through the use of downward-sloping holes that exposed a high proportion of the pole cross-section to the treatment. The differences between chemical levels in inner and outer zones, however, were slight and tended to lessen with time, suggesting that diffusion had evened out the fumigant distribution. Nevertheless, in all poles fumigant levels tended to decline sharply by 36 months to levels far below those previously reported for liquid metham sodium. The reasons for these low levels are unclear, especially in view of the improved laboratory performance of these formulations.

Closed-tube bioassays of cores revealed considerable residual fungitoxicity in both gelled and pelletized metham sodium 6 months after application (Table I-13). These levels of inhibition improved at 12 and 24 months. Residual fungitoxicity was present at both 0.9 and 1.5 m above the groundline, a finding that contradicts the chemical assays in this study. Metham sodium decomposes to a variety of fungitoxic compounds besides MITC; other decomposition products not sampled in the chemical analysis may account for the residual protection up to 2 years after treatment. Samples removed 3 years after treatment, however, indicated that little volatile residual fungitoxic protection remained in the wood.

typically is Metham sodium considered a short-term treatment in which volatile fungicidal components remain detectable for 2 to 4 years and fungi typically do not reinvade the wood at high levels for 5 to 10 years after treatment. With regard to residual fungitoxicity, the gelled and pelletized formulations appear to be slightly less effective than conventional liquid metham sodium. This slight decrease may be acceptable in view of the improved handling characteristics of these systems, especially the pelletized formulation, which was far easier to apply The gelled formulation, than liquids. although it reduced the risk of spills, was difficult to apply accurately because the gels tended to adhere to the application tool. Special applicators would probably be necessary for commercial use of the gelled formulation in wood.

While gelled and pelletized metham sodium performed well in laboratory trials, their performance in field trials was slightly lower than that of conventional liquid metham sodium. These systems, however, may still be useful for improving the safety of application during internal remedial treatments of wood poles and structures.

Table I-3. Incidence of decay and nondecay fungi in southern pine and Douglas-fir poles 6, 12, 24, 36, and 60 months after treatment with MITC-Fume® or metham-sodium.®

Composition	0 (33)	6(6)	0 (100)	0 (33)	0 (39)	28 (50)	8 (100)	8 (33)	17 (44)	28 (50)	25 (100)	0 (50)	0 (25)	42 (67)	(100)	0 (100)	0 (25)	33 (75)	33 (100)	:	Control
	0 (53)	0 (0)	10 (80)			13(7)	10 (80)	10 (50)	0 (33)		—	0 (40)		-	0 (40)	0 (60)	0 (30)	0 (40)	0(60)	500	Metham-sodium
	0(0)	0 (13)	0 (100)	25 (75)	0(17)	0 (0)	0 (100)	0(8)	0 (22)	0(8)		_	0(17)	0(0)	0(17)	0 (29)	0(8)	0 (33)	0 (33)	240	
	0 (28)	0 (22)				0 (17)		0 (75)	0(11)	0(10)	_	0 (58)	0(0)	0(8)	0 (17)	0(16)	0(9)	0(17)	0 (50)	180	
Company   Comp	0 (22)		(001)0	10 (40)		0 (10)	7 (100)	0 (64)	0 (11)			0 (71)	0(8)	0(0)	0 (29)	0 (29)	0(8)	0(17)	0 (57)	120	
Column   C	0 (22)		0 (100)	0 (100)	0(17)		0 (100)	0 (50)	0 (11)	0(0)	_	0 (33)	0(8)	⊢	_	0 (25)	0(0)	0 (42)	0(0)	8	MITC-Fume®
Column   C														AS-FIR	Doug						
Column   C	6 (61)	0 (83)	0 (100)	0 (100)	0 (72)	0 (89)		0 (100)	0 (72)	0 (83)	0 (100)		0 (50)			0 (100)	0 (25)	0 (92)	0 (100)	:	Control
Percentage of cores contaming decay (nondecay) Fange   Percentage of cores   Percentag	8 (53)	0 (87)	0 (100)	0 (100)		0 (93)	0 (100)	0 (100)	0 (33)			0 (100)	0 (20)		0 (40)	0 (40)	0 (30)	0 (70)	0 (40)	500	Metham-sodium
Control   Cont	6 (94)	0 (94)	0 (100)	0 (100)	6 (33)	0 (94)		0 (100)	6 (28)	_		0 (100)	0 (8)	0(17)	0(0)	0 (50)	0 (33)	0 (58)	0(0)	240	
	0 (50)	0 (52)	0 (100)		0 (56)	0 (52)		0 (100)	0 (33)				⊢	<u> </u>	0(57)	0 (30)	0 (25)	0 (57)	0 (28)	180	
Percentage of cores containing decay (nondecay) funge	0 (39)	0 (56)	0 (100)	0 (100)		0 (56)	0 (100)	0 (100)	5 (28)		_	_	8 (17)	<del>-</del>	0(17)	0 (83)	0 (33)	0 (42)	0 (50)	120	
Percentage of cores containing decay (nondecay) fungr <sup>b</sup>	0 (61)	0 (88)	0 (100)	0 (100)		0 (83)	0 (100)	0 (100)	6 (22)		0 (100)	_	-	0 (17)	9	0(67)	0 (50)	0 (67)	0 (50)	8	MITC-Fume®
Percentage of cores containing decay (nondecay) fungs*														RN PINE	South						
Percentage of cores containing decay (nondecay) fungs*  0.0 m 0.3 m 0.9 m	60 mo	******	********	12 mo.	60 mo.	36 mo	24 mo	12 mo	60 ma		*****	12 mo	60 ma.		24 mo	12 то.	60 mo	36 ma	24 mo	Dosage *	n eamiem
Percentage of cores containing decay (nondecay) fungs		m	1.5			m	0.5			3 m	0.			0 m	0			m*	-0.3		Chemical
									fung) <sup>b</sup>	ndecay)	decay (no	taining.	cores coa	ntage of	Perce						

Core were removed from selected locations at different vertical distances above and below the treatment zone. The middle segment of cores was used for this analysis.
 Values reflect an average of 15 total cores per dosage/position. Figures in parentheses represent nondecay fungi isolated from the same cores.

Table I-4. Incidence of fungal growth, as measured by closed-tube bioassays of increment core segments, in southern pine and Douglas-fir poles 12, 24, 36 and 60 months after treatment with MITC-Fume® or metham-sodium.

Vertical						Funç	al growth (as	% of contr	ol)°			
distance from	Core	Months			Southern :	pine				Douglas-	fir	
treatment	segment tested	after treatent		MITC	-Fume®		Metham- sodium		MITC-	Fume®		Metham- sodium
	asaca		60 g	120 g	180 g	240 g	500 ml	60 g	120 g	180 g	240 g	500 mi
-0.3 m	Outer	12	12	0	0	0	23	34	25	4	0	77
		24	17	0	20	0	100	16	6	20	0	20
<b>]</b>		36	55	41	33	32	78	25	21	20	22	82
1		60	74	99	71	79	73	90	79	74	91	80
l f	Inner	12	0	0	0	0	14	0	12	0	0	49
i		24	0	0	0	0	0	0	0	0	0	16
i		36	14	1	3	0	7	1	14	13	16	69
L		60	51	28	52	1	28	71	45	53	61	57
0.0 m	Outer	12	16	3	11	0	40	0	0	0	0	10
		24	0	7	30	0	100	16	0	0	0	12
		36	38	12	24	10	69	19	21	26	21	76
		60	76	82	87	72	90	85	47	75	77	58
[ ]	Inner	12	0	0	0	0	0	0	0	0	0	0
		24	0	0	0	0	0	0	10	0	0	0
		36	13	3	7	3	5	8	2	1	0	82
		60	47	53	36	1	26	73	46	66	47	46
0.3 m	Outer	12	80	0	21	41	63	65	32	4	0	67
		24	83	36	33	33	100	40	23	0	0	0
		36	51	25	28	27	67	24	19	15	7	91
		60	79	96	85	68	89	94	91	74	69	48
	Inner	12	40	0	0	0	45	16	12	0	0	15
1 1		24	0	0	13	0	13	16	13	0	0	33
		36	5	6	19	1	23	8	20	14	3	84
	0.1	60	76	66	83	33	67	92	75	71	62	75
0.9 m	Outer	12	100	73	95	100	90	79	64	27	19	70
<b></b>		24	90	77	94	100	100	43	43	23		60
1 1		36	101	77	63	85	84	37	31 82	69	77	83 68
)	7	12	96 60	102 33	92	100	86	27	26	22	8	39
	Inner	24	57	63	35	48	60	20	0	16	0	33
		36	78	49	43	36	50	38	54	41	15	90
∦ `		60	89	99	89	79	86	79	103	80	82	79
1.5 m	Outer	12	100	100	100	100	100	63	100	62	48	86
1.711	Outer	24	97	100	100	100	87	53	47	60	100	100
		36	88	91	89	85	93	74	71	72	86	92
		60	98	99	108	90	98	93	102	93	90	54
	Inner	12	100	100	100	50	97	95	100	68	50	84
		24	100	94	80	57	70	77	43	30	67	67
		36	99	83	74	61	57	76	74	75	77	102
		60	97	93	95	76	86	76	107	75	93	73
L		<u> </u>									<u> </u>	

<sup>\*</sup> Core were removed from selected locations at different vertical distances above and below the treatment site.

Values 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.

<sup>°</sup> Outer - 2.5 cm from pole surface; Inner - 12.5 to 15.0 cm from pole surface.

TABLE I-5. Residual MITC content, as measured by gas chromattographic analysis of increment cores, in southern pine and Douglas-fir poles 6, 12, 24, 36, and 60 months after treatment with MITC-Fume® or metham-sodium.\*

Vertical						Resd	iual MITC ()	ug/g of we	od)			
distance					Southern	pine				Dougla	s-fir	
from treatment	Core segment	Months after		MIT	C-Fume®	-	Metham-		MITC	-Fume®		Metham-
zone	tested	treatent					sodium					sodium
			60 g	120 g	180 g	240 g	500 ml	60 g	120 g	180 g	240 g	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
		60	14	70	86	61	56	58	65	24	18	26
	Inner	12	369	1534	1282	1644	147	292	270	1327	441	
		24	203	1996	2028	1754	535	1322	154	2161	1240	143
		36	536	368	284	277	257	186	219	182	127	44
		60	187	120	188	854	212	68	58	95	36	26
0.0 m	Outer	12	93	147	169	275	85	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
1		60	10	107	92	235	15	99	36	44	37	18
Ī	Inner	12	2031	2777	3009	3425	1986	2525	2879	3745	3985	978
		24	2054	1798	2033	2381	310	1191	1928	1600	1242	34
		36	675	673	736	1332	227	418	223	260	251	68
		60	137	131	330	1085	93	267	70	135	46	64
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
ŀ		24	T	40	33	13	T	46	94	177	311	22
		36	21	42	34	36	2	37	48	63	99	8
Į Į		60	9	17	46	37	13	51	31	26	56	30
	Inner	6	1	14	12	6	2	132	296	534	624	352
	i	12	239	316	212	184	96	128	349	1052	262	105
		24	285	353	322	281	54	256	459	363	554	306
		·36	77	139	91	135	19	92	142	108	107	24
		60	51	48	47	112	10	29	30	18	28	10
0.9 m	Outer	6	0	0	0	0	. 0	0	2	0	0	0
ı		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
		60	6	6	5	15	8	21	30	18	28	10
	Inner	6	0	0	0	0	0	2	115	4	2	2
ĺ		12	T	12	9	Т	0	24	198	26	31	102
1		24	T	T	T	46	0	149	117	92	165	49
		36	2	12	12	8	T	34	26	28	48	8
		60	8	7	15	15	8	12	22	12	16	15
1.5 m	Outer	6	0	0	0	0	0	0	0	0	0	0
		12	0	0	0	0	0	5	Т	T	Т	T
		24	0	0	0	0	0	Т	Т	T	49	0
		36	0	· T	T	2	T	3	3	Т	4	T
Ļ		60	7	24	3.	11 .	7	9	15	7	16	16
	Inner	6	0	0	0	0	0	0	0	0	0	0
		12	0	0	0	0	0	Т	T	Т	21	0
		24	0	0	0	0	0	T	T	Т	120	0
		36	0	T	Т	2	T	3	6	3	2	T
<u>l</u>		60	5	4	4	12	9	9	9	7	12	14

Core were removed from selected locations at different vertical distances above and below the treatment site.
 T -- trace amount of MITC present but not quantifiable.
 Outer - 2.5 cm from pole surface; Inner - 12.5 to 15.0 cm from pole surface.

TABLE I-6. Residual MITC in Douglas-fir and southern pine poles at Belmont, CA or Half Moon Bay, CA, 2, 3, or 5 years after receiving 90 or 120 g of MITC-Fume®.

					Resid	ual MITCO	(ug/g oven	dry wood)			
					Dougl	as-fir			Po	nderosa Pi	ше
	Distance			90 g MITC			120 g MITC		1	20 g MIT	С
Test Location	Above Treatment (m)	Core Position	2 yrs.	3 yrs.	5 yrs.	2 yrs.	3 yrs.	5 yrs.	2 yrs.	3 yrs.	5 yrs.
Half Moon	0.3	inner	81	255	306	938	568	706	210	69	92
Bay	İ	outer	30	54	22	60	276	30	63	8	3
	0.9	inner	3	174	114	165	267	32	25	20	30
		outer	-	93	4	3	204	27	19	14	1
Belmont	0.3	inner	138	174	146	171	245	222	184	28	92
		outer	56	7	24	8	49	36	89	10	14
	0.9	inner	1	70	12	15	108	72	8	39	16
	L	outer	3	9	-	1	20	4	1	9	3

Values reflect means of 7 pine poles and 13 Douglas-fir poles at Belmont and 3 pine and 7 Douglas-fir poles at Half Moon

TABLE I-8. Residual MITC in pentachlorophenol treated Douglas-fir transmission poles 1 year after internal treatment with 200 or 400g. of basamid alone or amended with 1% (wt.) of copper sulfate as compared with similar poles receiving 500 ml of metham-sodium.

				1	Residual M	ITTC (ug/g	oven drie	ed wood)*		
					Distano	e above tre	atment zo	ae (m)		
Chemical	Copper	Dosage		0	1	m	2	<b>19</b> 1	3	100
	Sulfate Added	(g)	inner	outer	inner	outer	inner	outer	imer	outer
Metham-sodium	-	500	21	30	57	38	1	-	1	-
Basamid	-	400	4	22	16	56	1	-	-	1
	+	400	25	24	31	64	•	-	-	1
Basamid	-	200	3	7	3	16	-	-	1	-
	+	200	12	14	26	42	-	1	2	

<sup>\*</sup>Values reflect means of 18 samples per position. Core positions reflect inner and outer 25 mm of each increment core, (-) signifies no MITC detected

TABLE I-7. MITC distribution in Douglas-fir pole pole sections (n - 15 core segments) 1 to 5 years after internal treatment with metham-sodium or Basamid amended with amended additives.

						ug MITC/g	wood (over	idry) '			
			Dist	ance Above	Treatment	Zone	D	istance Belo	w Treatment	Zone	
		Time since treatment	45	cm	15	cm	15	cm	45	cm	All Measurements
Treatment	pH 12°	(mo)	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	(n = 120)
Metham-sodium	-	6	-	•	113.3	195.6	173.4	104.2	-	-	147
	•	12	9.6	79.1	29.9	80.4	19.8	54.5	12.2	34.5	40
	•	24	8.4	15.7	5.0	21.3	15 ner Cuter 5.6 173.4 0.4 19.8 1.3 5.3 0.6 4.3 0.0 0.0 6.6 12.9 0.8 5.9 1 6.1 0.0 15.3 1.9 13.4 1.6 16.4 3.5 11.0 2 3.6 1.9 24.9 5.5 10.7 5.9 10.2 5.7 13.5 7/1 11.7 4.9 43.1 7.3 27.2 3.1 90.5 0.8 21.4 0.9 99.7	14.3	2,3	5.0	10
	•	36	1.7	3.7	5.3	10.6	4.3	3.5	2.5	3.1	4
	-	60	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.7	0
Basamid Alone	•	6	-	-	9.5	16.6	12.9	19.9	-	-	14
	•	12	5.2	13.7	9.7	10.8	5.9	26.5	1.1	5.6	10
	•	24	2.6	3.7	4.1	8.1	6.1	7.7	3.8	3.1	5
	-	36	11.6	14.8	6.0	20.0	15.3	60.7	9.7	12.4	18
	•	60	1.2	6.9	29	21.9	13.4	87.9	16.6	13.5	21
	+	6	-		9.3	14.6	16.4	100.5	-	-	44
	÷	12	0.0	5.7	0.2	13.5	11.0	44.8	0.1	10.8	11
	+	24	0.0	0.6	0.0	7.2	3.6	32.5	1.7	8.3	7
	+	36	3.1	5.8	10.9	21.9	24.9	49.0	9.3	16.6	18
	+	60	0.0	3.8	12.7	15.5	10.7	43.3	6.8	23.1	15
Basamid plus	-	6	•	-	15.9	45.9	10.2	39.1	-	-	27
copper sulfate	-	12	20.8	17.8	11.2	45.7	13.5	Section   Course   Course	3.9	20	
	-	24	5.9	9.1	10.3	47/1	11.7	66.7	12.2     34.5       2.3     5.0       2.5     3.1       0.0     1.7       -     -       1.1     5.6       3.8     3.1       9.7     12.4       16.6     13.5       3     -       0.1     10.8       1.7     8.3       9.3     16.6       6.8     23.1       -     -       0.0     3.9       0.4     6.8       14.5     5.4       9     6.8     25.3       -     -       4     6.7     64.3       95.8     124.5	20	
	-	36	3.4	12.7	34.1	104.9	43.1	95.2	14.5	5.4	39
	-	60	4.1	24.7	19.6	87.3	27.2	106.9	6.8	25.3	38
	+	6	-		55.3	58.1	90.5	95.4	-	-	75
	+	12	8.2	76.3	22.0	120.8	21.4	203.1	6.7	64.3	65
	+	24	49.2	47.6	69.9	63.9	99.7	96.5	95.8	124.5	81
	+	36	50.1	48.5	60.7	59.4	72.1	69.6	79.9	78.9	65
	+	60	3.4	15.7	13.8	44.3	17.5	62.5	12.0	46.1	27

									Basamid plus boron										Basamid plus lignin									glucose	Basamid plus
+	+	+	+	+	•		•	•	•	+	+	+	.+	+		•			•	+	+	+	+	+	•	•			•
60	36	24	12	6	60	36	24	12	6	60	36	24	12	6	60	36	24	12	6	60	36	24	12	6	60	36	24	12	6
2.9	29.2	0.2	0.0	•	2.3	0.3	0.6	0.4	•	0.0	2.1	0.0	3.2	•	4.9	2.3	1.5	1.4	•	2.2	1.2	0.6	1.8	-	2.4	2.2	0.0	0.5	•
2.3	54.5	1.1	11.8	•	5.6	0.3	1.6	11.3	•	8.5	1.6	1.6	17.4	•	4.8	6.6	2.5	2.8	•	4.2	3.9	1.9	20.0	-	13.1	7.8	0.0	0.2	-
2.0	8.8	3.5	7.7	7.0	13.4	7.6	4.5	6.6	9.5	6.9	19.3	1.2	7.0	3.3	3.6	8.7	4.0	2.9	0.2	10.4	9.3	9.0	6.8	16.6	7.9	33.2	2.7	1.7	7.6
9.3	17.7	13.0	24.2	11.6	20.7	17.9	12.7	30.8	17.9	46.8	13.5	26.4	63.6	27.0	6.0	20.8	17.8	24.9	5.5	18.4	29.4	33.5	76.9	37.1	57.6	62.1	13.8	17.1	13.2
8.0	66.5	9.2	17.2	8.0	31.9	21.6	5.8	15.0	18.9	5.6	35.3	7.7	16.1	4.2	9.7	16.0	15.5	4.8	1.3 ·	27.5	48.7	21.2	81.7	17.6	30.3	35.2	7.8	4.8	1.3
38.8	33.8	29.3	33.5	30.4	55.4	27.1	25.5	49.6	33.1	52.7	28.9	50.7	79.6	41.3	30.7	33.0	52.1	93.1	23.2	62.0	91.8	54.5	14.2	62.8	84.7	112.4	30.9	32.8	20.5
1.6	11.3	2.0	1.0	•	4.1	2.6	1.2	0.1		4.3	3.1	0.0	5.5		1.6	3.7	3.1	2.1		29	9.0	2.3	33.1	•	11.5	160	0.0	2.6	•
11.9	49,1	5.8	5.6	•	17.5	2.6	2.9	5.2		10.8	9.2	9.8	3.0	•	8.3	5.8	18.7	14.0		25	23.9	5.0	21.6	-	28.5	30.0	3.5	3.7	
10	34	8	13	14	19	10	7	15	20	17	14	12	24	19	9	12	14	18	<b>∞</b>	16	27	16	32	33	30	8	7	<b>∞</b>	11

Basamid plus		6		•	3.0	6.0	0.1	12.0		•	5
ethanol		12	0.0	2.1	0.4	15.3	0.2	7.3	0.0	0.0	3
		24	0.0	0.5	1.8	4.7	1.8	6.3	0.4	0.2	2
		36	0.1	8.0	1.0	8.4	3.0	12.5	0.7	1.4	4
		60	6.7	4.7	8.3	23.9	14.2	24.1	2.3	7.1	11
Basamid plus		6		•	1.2	4.4	1.0	8.2	•	•	4
acetone	٠	12	4.3	18.3	9.3	17.0	15.2	26.1	15.6	12.9	15
		24	0.0	0.0	2.8	8.3	7.2	16.0	0.9	1.3	3
		36	2.0	4.2	9.3	27.3	14.0	38.2	7.0	15.3	14
		60	0.0	0.0	2.4	25.8	14.4	181.2	10.1	18.1	32
Basamid plus		6		-	2.8	7.2	0.8	16.0		•	8
methanol	•	12	0.0	0.1	0.0	3.7	0.2	9.5	0.3	0.6	. 2
		24	0.0	0.5	0.8	3.3	2.6	8.6	0.0	0.1	2
	•	36	0.2	0.9	9.6	11.6	19.0	28.7	7.2	5.0	10
	•	60	0.0	0.0	0.9	7.0	0.0	44.1	2.0	4.4	7
Basamid plus water		6		-	1.0	3.0	1.6	14.8		•	5
	. 1	12	0.0	1.2	0.0	2.3	0.4	8.3	0.0	0.0	2
		24	0.3	2.0	1.5	7.3	5.1	22.1	2.6	7.7	6
	٠	36	0.0	0.2	1.6	6.0	9.6	79.8	6.2	5.5	14
		60	3.3	8.1	3.4	14.6	11.3	80.7	2.6	7.0	16

<sup>• --</sup> indicates no core was taken

• + indicates the addition of powdered pH 12 buffer (5% by weight) to Basamid.

Table I-9. Residual MITC levels and percentage of fungal survival in Douglas-fir heartwood blocks treated with selected dosages of 40% gelled and liquid metham sodium and incubated for 7 days."

Dosage	Gel	led	Liqu	nid
	Fungal survival	MITC level	Fungal Survival	MITC level
(mg)	(%)	(μg/g wood)	(%)	(μg/g wood)
50	17	b	38	50(41)
100	8	417(100)	29	61(8)
250	8	164(55)	38	98(38)
400	29	618(399)	4	361(248)
500	13	757(293)	0	342(145)

<sup>\*</sup> Values are based upon four blocks per dosage. Values in parentheses represent one standard deviation.

Table I-10. Residual MITC levels and percentage of 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	Gel	led	Liq	uid
(days)	Fungal Survival	MITC level (µg/g wood)	Fungal survival	MITC level (μg/g wood)
1	92	415(240)	67	543(275)
3	58	489(221)	17	485(426)
5	500	519(268)	29	321(426)
7	8	218(166)	0	109(108)
10	13	10(5)	4	22(13)
14	38	0	13	0
28	0	0	0	0

<sup>\*</sup>Values reflect means of four blocks per time point. Values in parentheses represent one standard deviation. Fungal survival for untreated controls ranged from 30 to 78% over the exposure period. These samples received an equivalent amount of water and were incubated separately to minimize the risk of chemical contamination.

b Not tested.

Table I-11. Effect of dosage, temperature, and time on decomposition of gelled and liquid metham sodium (applied to Douglas-fir sawdust) to MITC as measured by GC.\*

Dosage	Temp.	Time	Total MITC	recovered
(mg)	(°C)	(hr)	Gelled	Liquid
			(µgt)	vîal)
10	5	24	334(143)	474(56)
		48	72(20.7)	197(75)
		72	28(37)	228(36)
		144	339(87)	241(17)
	21	24	266(300)	459(209)
	ĺ	48	119(56)	368(99)
		72	284(263)	390(120)
		144	382(139)	297(183)
	32	24	604(115)	121(24)
		48	597(579)	272(110)
		72	781(336)	205(136)
		144	248(79)	3(0)
25	5	24	574(191)	919(110)
		48	575(356)	1238(742)
		72	311(329)	1072(137)
		144	479(424)	655(463)
·	21	24	1278(929)	613(120)
		48	1509(847)	1028(484)
		72	1383(842)	241(134)
		144	440(419)	587(413)
	32	24	1486743)	251(-)
		48	2248(651)	375(81)
		72	5054(1263)	274(110)
		144	930(672)	-

<sup>\*</sup> Values represent means of three replicates; values in parentheses represent on standard deviation. MITC levels reflect total chemical in the wood and air in a given vial.

Table I-13. Growth of Postia placenta in a closed-tube bioassay of wood samples removed from Douglas-fir poles at various heights and times after treatment with gelled or pelletized metham sodium.

Metham	Dosage		0.3	0,3 пин			5.0	0.9 m			1.5	l 5 m	
sodium	(3)	6 шо	12 mo	24 mo	36 то	6 то	12 mo	24 mo	36 то	6 то	12 mo	24 то	36 mo
40%	100	48(46)	18(13)	22(12)	93(28)	62(46)	20(13)	20(12)	86(28)	58(48)	21(14)	21(14)	85(37)
gelled	200	46(39)	15(11)	13(12)	78(29)	60(44)	14(11)	18(15)	81(34)	41(41)	13(13)	12(13)	65(41)
	300	17(24)	16(15)	13(15)	62(32)	39(38)	17(16)	17(16)	67(27)	27(34)	13(14)	12(14)	73(28)
	500	30(29)	15(13)	15(12)	79(20)	58(42)	23(12)	23(12)	96(10)	36(43)	21(12)	21(12)	100(21)
	750	37(12)	ŀ	37(12)	101(14)	29(11)	;	19(11)	92(29)	27(11)		27(11)	105(20)
25%	100	29(37)	10(12)	10(12)	69(24)	44(42)	23(13)	23(13)	77(25)	20(39)	10(13)	10(13)	66(28)
pelletized	200	17(32)	12(12)	12(12)	81(25)	37(41)	22(8)	22(8)	93(23)	33(47)	15(9)	15(9)	89(30)
	300	50(45)	15(12)	15(12)	103(22)	81(44)	20(10)	20(10)	.99(17)	37(52)	16(13)	16(13)	110(20)

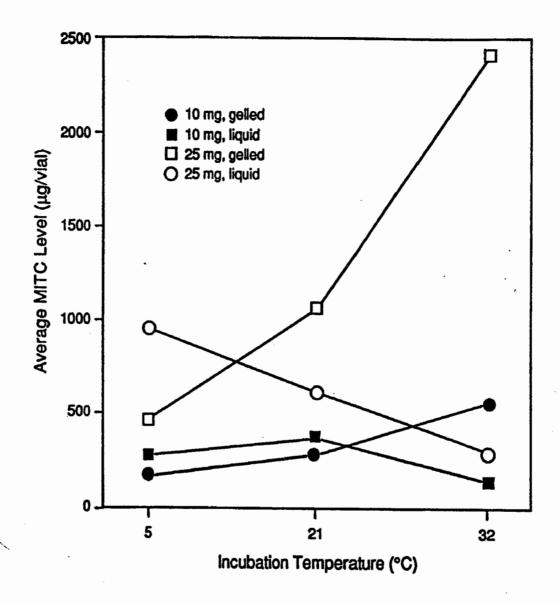
Values represent means of 15 replicates. Those in parentheses represent one standard deviation.

Table I-12. Residual MITC levels in Douglas-fir poles at various heights and times after treatment with gelled or pelletized metham sodium.

	0	0				Ü	,	mile to to the 18 of the second and the second seco	Semperal B	mini northern and medamon mine		****	1	
	(g)	(mm)		0.3 m	=			0.9 m	3			15 m	3	
			6 mo	12 mo	24 mo	36 mo	6 mo	12 mo	24 mo	36 mo	6 mo	12 mo	24 mo	36 mo
40% gelled	100	0-25	1(3)	1(2)	1(2)	0(0)	1(2)	0(0)	0(0)	0(0)	0(0)	0(0)	0(0)	0(0)
	·	50-75	6(11)	3(6)	3(6)	1(2)	4(10)	3(6)	0(0)	0(0)	0(0)	0(0)	0(0)	0(0)
	200	0-25	1(4)	0(0)	0(0)	0(0)	1(3)	0(0)	0(0)	0(0)	0(0)	0(O)	0 (0)	0(0)
		50-75	3(8)	3(5)	3(5)	<b>6</b>	00	2(2)	2(2)	0(0)	0(0)	0(0)	0 (0)	0(0)
	300	0-25	4(6)	5(9)	5(9)	4(14)	0(0)	0(0)	0(0)	0(0)	0(0)	0(0)	9	0 (0)
		50-75	17(30)	11(14)	11(14)	5(9)	<b>0</b> (0)	1(3)	1(3)	0(0)	0(0)	0(0)	0(0)	0(0)
	500	0-25	9(14)	18(19)	18(19)	2(8)	3(5)	0(0)	0(0)	0(0)	2(5)	0(0)	0(0)	0(0)
		50-75	12(5)	16(16)	16(16)	12(12)	2(4)	0(0)	0(0)	0(0)	(0)0	0(0)	0(0)	0(0)
	750	0-25	9(12)		9(12)	0(0)	0(0)	1	0(0)	0(0)	1(1)	. 1	1(1)	0(0)
		50-75	6(12)	-	6(12)	8(11)	4(8)	ı	4(8)	0(0)	1(2)	-	1(2)	0(0)
25% pelletized	100	0-25	7(11)	5(8)	5(8)	0(0)	0(0)	1(0)	1(1)	0(0)	0(0)	0(0)	0(0)	0(0)
		50-75	4(5)	4(5)	4(5)	1(3)	0(0)	0(0)	0(0)	0(0)	(0)0	0(0)	0(0)	0(0)
	200	0-25	20(21)	5(9)	5(9)	0(0)	3(6)	1(2)	1(2)	0(0)	(0)0	0(0)	0(0)	0(0)
		50-75	19(20)	14(19)	14(19)	4(6)	2(4)	1(2)	1(2)	0(0)	(0)0	0(0)	0(0)	0(0)
Į	300	0-25	0(0)	6(13)	6(13)	0(0)	0(0)	1(1)	1(1)	0(0)	(0)0	1(1)	1(1)	0(0)
		۲۵ 7۲	22(34)	13(15)	13(15)	4(5)	3(5)	0(0)	0(0)	0(0)	5(10)	0(0)	0(0)	0(0)

Values represent means of 15 replicates. Values in parentheses represent one standard deviation.

Figure I-1. Effects of dosage and temperature on MITC levels in Douglas-fir heartwood sawdust treated with gelled or liquid 40% metham sodium. Values represent means of 24-, 48-, 72-, and 144-hour samples for each treatment.



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

While fumigants have worked well for rapidly arresting fungal attack of wood poles, many users object to the volatile nature of the liquid formulations as well as the restricted nature of the solid formulation. These concerns have stimulated development of alternative internal remedial treatments, primarily based upon boron or fluoride as active ingredients. Both of these chemicals move with moisture through wood and have long histories as fungicides, particularly in Europe and Australasia. As a result of the increased interest in these compounds in North America we have initiated a number of projects to evaluate these systems in U.S. wood species.

- 1. Ability of fluoride/boron rods to move through Douglas-fir poles: The fluoride and boron rod formulation evaluated in these trials was produced by Preschem Ltd. (Cheltenham, Victoria, Australia) and each 23. 5 g rod contained 24.3 % sodium fluoride and 58.2 % sodium octaborate tetrahydrate. Twenty pentachlorophenol treated Douglas-fir poles (250-350 mm in diameter by 2 m long) were set to a depth of 0.6 m at the Peavy Arboretum test site. Steep angled holes were drilled into sets of five poles using the following drilling patterns:
  - 1. 3 holes beginning at groundline and spiraling upward at 120 ° intervals and 0.3 m increments (70.5 g rod)
  - 2. 3 holes beginning at groundline and spiraling upward at 90° intervals and 0.3 m increments (70.5 g rod)
  - 3. 6 holes beginning at groundline and spiraling upward at 120° intervals and 0.15 m increments (141 g rod)

4. 6 holes beginning at groundline and spiraling upward at 90 ° intervals and 0.15 m increments (141 g rod)

Each hole received a single rod, then the holes were plugged with tight fitting dowels.

Fluoride/boron movement in the poles was assessed 12 months after treatment by removing 3 increment cores equidistantly spaced around the pole from sites 150 mm below the lowest treatment hole, from the middle of the treated zone, and 150 mm above the highest treatment hole. The outer treated zone was discarded and the remaining segment was equally divided into inner and outer zones. Segments from a respective zone for cores from given height were combined for the five poles per treatment group. These segments were ground to pass a 20 mesh screen prior to analysis. The ground samples were thoroughly mixed, oven-dried (54 C), and divided in half.

One half of the wood was extracted for 30 minutes in boiling water; the water was then filtered and analyzed for residual boron using the Azomethine H method as described in American Wood Preservers' Association Standard A2 method 15.

Fluoride was analyzed by placing 0.15 g of ground wood into a 25 ml glass tube and adding 15 ml of 0.1 M HClO<sub>4</sub>. The tubes were sonicated for 3 hours, then left to stand for an additional 2 hours at room temperature (21 to 25 C). A portion of the extract (10 to 12.5 ml) was added to 30 ml of water, then 2 % NaOH was added to the bottle dropwise until the pH was between 5 and 6, then the solution was adjusted to 50 g with deionized water. Five ml of Orion TISAB III solution was added, and the amount of fluoride in the resulting mixture was measured using an Orion fluoride electrode. Values were compared with similarly prepared standard fluoride solutions.

Fluoride and boron levels were generally

uniformly low above the treatment zone, reflecting the inability of either compound to diffuse upward at significant levels one year after treatment (Table I-14). Within the treatment zone and below the ground, boron tended to be present at higher levels than fluoride. This trend reflects, in part, the higher boron content of the rods; however, the boron to fluoride ratio was far higher in the wood than in the original rod, suggesting that boron moved to a greater extent from the rods.

Fluoride levels in the inner sampling zone tended to be slightly higher than those in the outer zone, although the differences were sometimes slight. The threshold for fluoride is reported to be approximately 0.2 % (wt/wt), far greater than the values detected in the wood at any location one year after treatment.

These results indicate that fluoride is not yet present in the wood at levels which would protect against fungal attack. Previous trials with ammonium bifluoride in Douglas-fir suggest that relatively low levels of chemical will exclude fungi, but the levels required for eliminating existing infestations in this species are not known.

Boron levels in the samples tended to vary more widely than fluoride with no consistent trends in chemical levels between the inner and outer zone, or between below ground and within the treatment zone samples. Boron levels in a number of samples were above those reported as the threshold for decay fungi, suggesting that the rod treatment would effectively inhibit fungal growth in and slightly below the treatment zone.

Treatment dosage differences produced surprising results. While higher dosages would be expected to increase the resulting chemical levels, analyses revealed an opposite effect in some instances. The reasons for the inverse relationship between dosage and resulting chemical level in the wood are unclear. One possible cause for this effect could be sorption of excess moisture by the second rod in a treatment hole. If moisture

was limiting near the treatment hole, then moisture sorbed from the wood by the second rod would reduce the amount available for subsequent diffusion. A moisture/rod dosage interaction might slow the initial rate of chemical movement at higher chemical loadings, but should ameliorate with time.

One aspect of the performance of the fluoride/boron rod which could not be determined in this analysis was the effect of mixtures of boron and fluoride on protection. In several instances, sublethal levels of each compound were present; however, it is possible that sublethal combinations of boron and fluoride could provide protection and further studies are suggested to better understand the interactions of these biocides.

These poles will continued to be sampled on an annual basis for the next two years to better delineate the movement of both chemicals.

2. Performance of fused borate rods in Owego, New York: Fused borate rods have been extensively used in Europe for controlling fungal attack of a variety of large dimension wood products. In general, the boron diffuses wherever free moisture is present (wood moisture contents above 30 % by weight). The advantages of borate rods are their safety, ease of handling and high level of active ingredient per unit area. However, there is little data supporting the use of these chemicals in North America and the following trial was established to more fully understand the performance of borate rods in Douglas-fir poles.

Pentachlorophenol treated Douglas-fir poles in a line located near Owego, New York, were presampled by removing increment cores from sites near the groundline and culturing the cores on malt extract agar for the presence of decay fungi. The poles were then allocated so that the 6 poles in each of the four treatment groups had approximately the same level of fungal infestation.

Three holes (20 mm in diameter by 200 mm long) were drilled beginning at the groundline and spiraling 120° and upward 150 mm with each hole. The poles received either 3 or 6 fused borate rods or 120 and 240 g of rod, respectively. Holes in one half of the poles receiving each borate dosage also received 150 ml of water equally distributed among the three holes, while the remainder were left dry to evaluate the benefits of supplemental moisture on borate release.

Borate movement was assessed one and three years after treatment by removing 3 increment cores from 3 equidistant sites around the pole at groundline and 300 or 900 mm above the groundline. The outer, treated zone was discarded and the remaining segment was divided into inner and outer zones. Respective zones from a given height and treatment were combined, then the wood was ground to pass a 20 mesh screen. The ground wood was extracted in hot water as described above and analyzed for boron by Ion-Coupled Plasma Spectroscopy (ICP).

Boron levels one year after treatment were generally at the limit of the assay method employed suggesting that moisture levels in the wood were inadequate for breakdown of the rods or for diffusion (Table I-15). Application of supplemental moisture at the time of treatment had little effect on boron levels, nor did the application of more rod per treatment hole. The limited boron diffusion one year after treatment was surprising since many of the poles were located in low-lying areas where the soil moisture contents would tend to be higher.

Samples removed 3 years after treatment indicated that boron had begun to move through the poles at levels which would confer protection against fungal attack. Boron levels 900 mm above the groundline were negligible regardless of dosage or moisture addition, indicating that little upward movement of

boron occurred. Boron levels 300 mm above the groundline were generally higher, although they tended to vary widely among the treatments. The addition of moisture or more boron rods had little consistent effect on subsequent boron levels. Moisture can vary widely within large wood members, and it is likely that inherent variations in moisture distribution within the poles produced an associated variation in boron levels.

Boron levels in samples removed from the groundline zone 3 years after borate rod application were all above those required for inhibition of fungal attack. Boron levels again did not follow consistent trends with moisture or dosage. For example, boron levels were higher in the inner zone of poles receiving 120 g of rod plus water than they were in the 240 g treatment with moisture. Boron levels near the groundline also tended to increase from the outer to inner zone, suggesting that the steep slope of the original treatment holes tended to direct boron towards the center of the pole.

3. Performance of fused borate rods in Douglas-fir poles exposed in Corvallis, OR: Thirty Douglas-fir pole sections (250 to 300 mm in diameter by 2 m long) were pressure-treated with pentachlorophenol in diesel oil. The pole sections were treated with 180 or 360 g of fused borate rod applied to 3 holes drilled perpendicular to the grain direction beginning at groundline and moving upward at 150 mm intervals and spiraling around the pole 120°. Each treatment was replicated on 10 poles. The poles were stored outside for 2 months before being set to a depth of 60 cm at a test site located near Corvallis, Oregon.

The poles were sampled one year after treatment by removing increment cores from sites 75, 225, 450, and 600 mm above the highest treatment site as well as 150 mm below the groundline. The outer treated zone of each core was discarded and the remainder of each core was divided into equal outer and inner

zones. Respective zones for a given height in each treatment group were combined and ground to pass a 20 mesh screen prior to analysis for boron by ICP as described above. In addition to the boron sampling, wood moisture content at the time of sampling was assessed using a resistance type moisture meter with 75 mm long pins. Moisture readings were taken to a depth of 62.5 mm at 3 locations around each pole at groundline and 150 mm below groundline.

Boron levels in poles 1 year after treatment again varied widely among the sampling locations (Table I-16). Boron levels were generally higher in the inner zone, although the differences were sometimes slight. Boron levels were lowest below the groundline, a finding which contradicts the need for moisture for diffusion. Boron levels seemed to be negatively correlated with dosage.

Boron levels in the low dosage poles were greatest 75 to 225 mm above the highest treatment zone. These results again contradict those found in the earlier New York trial. The reasons for the substantial upward diffusion in this study are unclear, however, the poles in this test were stored in a horizontal position for 2 months prior to installation and it is possible that some lateral diffusion occurred during this time. Boron levels above the threshold for fungal growth were present 150 mm below ground as well as 75 to 450 mm above the treatment zone. This zone of protection was markedly greater than that found in previous tests with Douglas-fir.

Boron levels in the higher dosage poles were consistently lower than those found with the lower dosage. Boron levels above the threshold for fungal growth were present in only three sample zones (inner and outer 75 mm above the treatment zone and inner 225 mm above). The presence of lower boron levels in poles receiving more chemical is perplexing; however, wood moisture variations may have adversely affected distribution. This initial difference should

disappear with time.

Moisture is critical for boron movement from the rods Limited sampling with a resistance type moisture meter indicated that moisture levels 62.5 mm from the pole surface were consistently below the fiber saturation point (Table I-17). Moisture levels below groundline were 23.8 and 22.6 % for the 180 and 360 g treatments, respectively, while those below groundline were 19.4 and 19.6 % at the same dosages. These readings were taken in July, following several weeks of dry weather. Low moisture readings over the summer months would be expected at this test site owing to the low rainfall during this period. Further studies are now underway to better delineate the seasonal variations in wood moisture content throughout a pole cross These data should help to better understand the variations in chemical content which seem inherent in boron tests.

Fused borate rods are capable of moving through Douglas-fir heartwood. Variation in boron distribution, as shown by analysis of the wood samples, however, remains high. The more limited diffusion range of these materials in the wood, coupled with their tendency to require more time than fumigants to effectively eliminate established decay fungi suggest that considerable caution must be exercised with diffusible systems as replacements fumigants. Further sampling of the field trials are planned to more completely delineate the protective period afforded by each treatment. Trials are also underway to better establish internal moisture distribution in larger wood members in soil contact.

4. Ability of sodium fluoride rods to move through Douglas-fir poles: Fluoride has long been used as a remedial treatment for railroad ties, but there is little data on the efficacy of this treatment for protecting larger utility poles. This past year, we installed 20 pentachlorophenol treated Douglas-fir poles (25-30 cm by 2.4 m long) to a depth of 0.6 m at the Peavy Arboretum test site.

A series of 3 holes were drilled in a spiral pattern beginning at groundline and moving upward at 15 cm and 120 degree intervals around the pole. Each hole received 1 or 2 sodium fluoride rods. The holes were then plugged with tight fitting wood dowels. Each treatment was assessed on 10 poles. Fluoride movement will be assessed 1, 2, and 3 years after treatment by removing increment cores from 3 sites around each pole 15 cm below groundline, 22.5 cm above groundline and 15 cm above the highest treatment hole.

The outer, preservative treated shell will be discarded, and the remainder of the wood will be divided into inner and outer halves. The samples will be ground and extracted prior to fluoride analysis using a specific ion electrode. In addition, 3 poles will be dissected using a chainsaw three years after installation and sprayed with fluoride indicator to visually assess fluoride movement across the pole section. In addition, 3 poles will be dissected using a chainsaw, three years after installation to visually assess fluoride movement across the pole section.

Table I-14. Residual boron and fluoride at selected locations above or below the groundline in Douglas-fir poles one year after treatment with fluoride/boron rods.

						Res	dual Chen	ncal (%F	or BAE) b				
						Di	stance from	n Treatme	nt Zone				
Dosgae (g)	Application Pattern		-300	mm			300	mm			600	mm	
	(Degrees) *	O.	iter	lr	ner	0	ater	In	ier	Ou	iter	Int	IET
		F	BAE	F	BAE	F	BAE	F	BAE	F	BAE	F	BAE
70.5	90	0.02	0.10	0.11	0.63	0.08	0.54	0.11	0.51	<0.01	0.03	0.01	0.02
	120	0.01	0.06	0.03	0.26	0.02	0.09	0.06	0.49	<0.01	0.04	<0.01	0.05
141.0	90	0.01	0.28	0.07	0.06	0.02	0.07	0.07	0.36	0.01	0.03	0.01	0.05
	120	0.04	0.09	0.12	0.67	0.03	0.10	0.04	0.20	0.01	0.04	0.01	0.05
0	-	-	0.01	-	0.08		0.04		0.01		0.01	-	0.01

Application patterns were holes at 90 or 120° intervals around the pole.

b Values represent composite analyses of 5 poles/treatment. BAE represents boric acid equivalent.

Table I-15. Residual boric acid equivalent (BAE) at selected locations in Douglas-fir poles 1 or 3 years after treatment with borate rods with and without supplemental moisture.

					Residual	l Boron C	Concentra	tion (%B	AE) by p	osition*			
Borate	Water		Groui	ndline		300	mm abo	ve Gound	lline	900	mm abov	e Groun	dline
Dosage (%)	Added	Oi	iter	lnı	ner	Ot	iter	In	ier	Ou	tter	ln	ner
		Year 1	Year 3	Year 1	Year 3	Year 1	Year 3	Year l	Year 3	Year 1	Year 3	Year 1	Year3
120	•	0.02	0.17	0.02	0.34	ND	0.20	ND	0.32	ND	0.02	ND	0.02
	+	0.02	0.49	0.02	0.72	ND	0.11	ND	0.16	ND	0.03	ND	0.04
240	•	0.02	0.45	0.02	0.75	ND	0.13	0.02	0.10	ND	0.05	ND	0.04
	+	0.01	0.38	0.02	0.54	ND	0.14	ND	0.22	ND	0.03	ND	0.04

<sup>&</sup>lt;sup>a</sup> Values represent composite analyss of 5 pole sections. ND signifies boron levels <0.01% BAE.

Table I-16. Residual boron (as % boric acid equivalent) in Douglas-fir poles 1 year after treatment with 180 or 360 g of fused borate rod.

Borate Dosage	Distance from Treated Zone	Boric Acid Ed	unvalent (%)
(g)	(mm)	Inner Zone	Outer Zone
180	-150	0.38	0.24
	+75	2.82	0.65
	+225	0.89	0.98
	+450	0.54	0.22
	600	0.18	0.14
360	-150	0.09	0.07
	+75	0.96	0.59
	+225	0.48	0.13
	+450	0.04	0.02
	+600	0.05	0.02

Table I-17. Wood moisture contents 62.5 mm below the surface at the groundline and 150 mm below groundline of Douglas-fir poles 1 year after treatment with 180 or 360 g of fused borate rod as measured using a resistance type moisture meter.

Borate Dosage	Average Wood Mo	nisture Content (%)
(g)	150 mm below GL	Groundline
180	23.8 (7.0)	19.4 (7.5)
360	22.6 (6.4)	19.6 (4.1)

Values represent means of 45 measurements at each site, while those in parenthesis represent one standard deviation

## C. IDENTIFY NEW REMEDIAL TREATMENTS FOR ARRESTING OR PREVENTING INTERNAL DECAY

Over the past decade, we have identified a wide array of compounds for arresting and preventing internal decay in large wood members. There is, however, a continuing need for eversafer products which provide comparable efficacy. The goal of this section is to continue to identify suitable alternatives to existing internal treatment formulations.

1. Effectiveness of basamid/metham sodium mixtures: Two potential replacements for liquid fumigents are Basamid (3,5-dimethyl-(2 H)-tetrahydro-1,3,5-thiadizine-2-thione) and solid metham sodium (sodium n-methyl-dithiocarbamate or NaMDC). Both chemicals decompose to produce a variety of fungitoxic compounds, of which methylisothiocyanate (MITC) is the most active, but their decomposition rates differ markedly.

Basamid is a crystalline solid that has been used to treat soil for a variety of crops. This compound decomposes too slowly to arrest active fungal attack, but its slow release rate can be used to provide long-term protection against renewed fungal attack.

Metham sodium is the most widely used chemical for internal treatment of wood, but its

caustic nature can cause worker injuries. Furthermore, this chemical is extremely toxic to aquatic life and must be used carefully near surface The problems associated with liquid metham sodium can be mitigated through the use of pelletized formulations. Pelletized metham sodium can be formulated to approximately 25% active ingredient, which is somewhat lower than the 32.7% active ingredient typically used with the liquid formulation; the decrease in active ingredient, however, is balanced by the increase in safety. Field tests with pelletized metham sodium suggest that it performs similarly to liquid formulations, with both providing relatively short protection (5 to 7 years) in Douglas-fir poles. The relatively short protective period reflects the rapid and fairly inefficient rate of decomposition to MITC.

Preliminary studies suggested that the decomposition rates of Basamid and metham sodium could be exploited to produce a formulation that would provide a high initial level of MITC to kill existing fungal infestations, then a steady release of MITC to prevent renewed attack. In this report, we describe laboratory trials of such mixtures on Douglas-fir and southern pine blocks and sawdust at selected temperatures and wood moisture contents (MC).

Small block trials: We used a small block technique to perform tests on Douglas-fir

heartwood and southern pine sapwood blocks (25 x 25 x 100 mm long) were soaked to approximately 80-100% MC. A hole was drilled at the center of one flat face of each block and the desired amount of Basamid, metham sodium, or mixtures of both were weighed into the holes. Additional blocks were left untreated or received 300 mg of 32.7% metham sodium in water to serve as controls. The holes were plugged with tight-fitting rubber serum caps and the blocks were then incubated for either 1, 4, or 8 weeks at room temperature (23 to 25°C). At each time point, 3 blocks per treatment were sampled by cutting three 5-mm thick slices from each end of the The outer slice from each end was blocks. discarded. The remaining four slices were each cut into 16 equal-size cubes and the center 4 cubes from each slice were placed into 5 ml of ethyl acetate and extracted for 48 hours at room temperature. The extracts were injected into a Varian 3700 gas chromatograph equipped with a flame photometric detector with filters specific for sulfur to determine residual MITC. Operating conditions were: injector temperature, 150°C; oven temperature, 100°C; detector temperature 240°C; carrier gas, nitrogen. A glass column (2 m x 2 mm inner diameter) packed with 10% carbowax 20M on 80/100 supelcoport solid support was used to separate elements of interest.

Sawdust Trials: The block trials suggested that Basamid/metham sodium mixtures could be more effective than equivalent amounts of either chemical alone, but the testing method made it difficult to assess the many variables that might affect decomposition. We used conditioned sawdust to evaluate those variables.

Douglas-fir heartwood and southern pine sapwood were ground to pass a 20-mesh screen; the MC of the dry sawdust was 6.4 and 6.3%, respectively. Selected samples were then wetted to raise the MC to 40 or 80% (weight basis). The wet sawdust was then placed in glass jars and equilibrated for 2 months at 5°C.

For each condition, 0.5 g (oven-dry basis) of wood was placed into a 40-ml borosilicate vial equipped with a Teflon®-lined septum in a screw

cap (Table I-19). The vials were treated with 30 mg of Basamid and metham sodium in ratios of 1:0, 0:1, 1:1, 1:2, and 1:5. In addition, the Basamid alone, metham sodium alone, and 1:1 Basamid:metham sodium treatments were repeated with the addition of 5 mg of copper sulfate, since this compound had previously been shown to encourage decomposition of both fumigants. Each treatment was replicated in 3 vials per time/temperature condition. Following treatment, the vials were sealed and incubated at 5, 25, or 32°C for 6, 24, or 48 hours.

MITC levels in the air in 3 vials per treatment were assessed at each time point by removing headspace samples through the septa and analyzing them by gas chromatography as described above. Headspace sample sizes depended upon the quantity of MITC present. MITC levels were quantified by comparison with prepared standards.

Small Block Tests: Residual levels of MITC were consistently higher in Douglas-fir than in southern pine blocks, regardless of treatment (Table I-18). In addition, MITC appeared to be lost more quickly from the pine. This reflects the higher permeability of southern pine compared to the more refractory Douglas-fir. In previous field trials, liquid metham sodium and chloropicrin provided far shorter protective periods to southern pine than to Douglas-fir. These differences appear to be primarily related to permeability since metham sodium appears to decompose at similar rates in both species.

As expected, the Basamid-only treatment produced the lowest MITC levels 1 week after treatment, reflecting the slow decomposition rate of this chemical. Over the 8-week test period, however, the MITC levels in Douglas-fir increased slightly while those in the other treatments declined. MITC levels in southern pine treated with Basamid alone were uniformly low, suggesting that the higher permeability of this species permitted MITC to diffuse out prior to the initial 7-day sampling.

Increasing the ratio of metham sodium in the Basamid produced corresponding increases in

residual MITC 1 week after treatment and ultimately resulted in MITC levels that both exceeded those found with solid metham sodium alone, and approached those found with liquid metham sodium. These results suggest that Basamid and metham sodium interact in a manner that enhances decomposition to MITC. Both compounds tend to decompose more efficiently at higher MC and in the presence of organic compounds, but the enhancement was unexpected. Both compounds can decompose into a wide array of sulfur compounds, which may then react to produce additional MITC.

Sawdust Trials: The results of the small block test suggest that Basamid-metham sodium interactions enhanced MITC production, but because the test is a relatively crude method for assessing furnigant movement, the conclusions that can be drawn from it are limited. The sawdust trials were initiated to further explore the effects of selected variables on the production of MITC over time

Unlike in the small block trials, MITC levels in both types of sawdust with mixtures of Basamid and metham sodium did not consistently exceed those in the metham sodium alone (Tables I-19, 20). Increasing the levels of metham sodium consistently increased MITC levels, and the presence of some metham sodium with Basamid markedly increased MITC levels compared to Basamid alone. MITC levels appeared to be slightly higher in Douglas-fir heartwood, but the differences were inconsistent and may reflect minor measurement differences rather than any real wood-induced effect. In both Douglas-fir and southern pine, MITC levels rose over the first 24 hours of the trials, then either stabilized or decreased slightly.

Increasing either temperature or wood MC induced marked changes in MITC levels at the lower ends of the change. For example, increasing MC from 6 to 40% produced near 100-fold increases in MITC levels in the air, while increasing MC to 80% produced a more variable

effect on MITC levels (Tables I-19, 20). The presence of excess moisture can result in MITC degradation, although whether this degradation could have adversely influenced MITC levels in the short time periods employed in the current experiment is questionable. The results do illustrate the critical need for moisture with both chemicals.

Low temperatures produced only minimal decomposition to MITC, while incubation at room temperature markedly increased MITC levels, particularly in the presence of moisture (i.e. 40 and 80% MC). MITC levels were slightly higher in southern pine incubated at lower temperatures, which is consistent with previous findings. Increasing the temperature from 25 to 32°C produced only marginal changes in MITC content within a given treatment, suggesting that this small change in temperature had little influence on decomposition.

The addition of copper sulfate produced substantial increases in MITC levels, particularly with Basamid alone and with all treatments at the earliest sampling point. Bivalent metals have been previously shown to enhance decomposition of both Basamid and metham sodium to MITC; our results indicate that this effect also occurs when the two fumigants are combined. The ability of copper to enhance decomposition, particularly at lower MC and temperatures, may be especially useful for improving the efficacy of these mixtures when applied to wood poles under suboptimal field conditions. While a treatment may be applied to a dry zone of a pole, MC across wood members in soil contact is rarely uniform. As a result, conditions may be suitable for decay development away from the site of remedial treatment. The production of MITC under these conditions may permit rapid control of the infestation before more substantial damage occurs. Its decomposition rate has limited the use of Basamid for remedial internal decay control. The addition of small amounts of copper and metham sodium may represent an attractive method for providing

both short and long-term protection against fungal attack.

Mixtures of pelletized Basamid and metham sodium in combination with copper sulfate appear to enhance MITC

production under a wide array of conditions. A relatively safe formulation with the ability to provide broad-spectrum control regardless of environmental conditions has important implications for wood maintenance.

Table I-18. Residual levels of MITC in Douglas-fir and Southern pne blocks 1, 4, and 8 weeks after treatment with varying levels of pelletized Basamid and metham sodium(NaMDC).

	treatment		MIT	°C (µgMITC/g ox	ven-dried woo	d)*	
Basamid	NaMDC	l w	reek	4 wee	ks	8 we	eks
		Douglas-fir	Southern pine	Douglas-fir	Southern pine	Douglas-fir	Southern pine
300	-	51.4(5.1)	1.1(1.9)	75.0(6.0)	ND	88.3(3.8)	ND
-	300	170.3(72.5)	64.3(24.6)	38.1(5.0)	ND	8.6(0.7)	ND
270	30	141.5(53.9)	11.6(10.5)	90.9(7.7)	ND	61.1(8.1)	ND
240	60	152.4(39.4)	18.(13.4)	100.3(15.8)	ND	61.1(8.1)	ND
210	90	157.3(19.2)	74.2(32.6)	116.7(34.0)	ND	46.2(37.1)	ND
180	120	193.2(37.1)	75.6(18.3)	156.6(29.3)	ND	24.1(5.1)	ND
120	180	19.0(56.7)	143.0(22.6)	160.6(9.8)	ND	11.4(3.5)	ND
-	300 liquid	254.3(62.2)	149.4(43.5)	19.4(9.8)	ND	ND	ND

<sup>\*</sup> Values represent the average of 6 replicates while figures in parentheses represent one standard deviation (ND=not detected).

Table I-19. Effect of temperature and wood moisture content (MC) on MITC released from mixtures of Basamid, metham sodium (NaMDC) and copper sulfate (CuSO<sub>4</sub>) in Douglas-fir heartwood sawdust.

						_		40.0									6.4		MC (%)	
15	•	30	5	10	15	-	30	-	15	•	30	5	10	15	•	30			Basamid (mg)	W.
15	30	•	25	20	15	30	•	•	15	30	•	25	20	15	30	•			NaMDC (mg)	Wood
5	5	5	•	•	•	•	_	•	5	5	5	•	•	•	•	•	•	(mg)	Cuso.	
18.3(16.3)	71.8(23.5)	11.4(3.6)	2.0(0.5)	1.1(0.1)	0.5(0.2)	2.6(0.5)	0.2(0.1)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5°		
95.6(87.2)	133.3(47.6)	21.2(4.4)	18.8(1.6)	7.9(4.0)	10.9(3.1)	21.2(4.4)	0.3(0.1)	ND	0.5(0.1)	ND	0.9(0.1)	ND	ND	ND	ND	ND	ND	25°	6 hours	
273.4(63.4)	313.0(19.9)	33.6(14.3)	22.2(0.7)	20.9(2.5)	17.2(7.4)	45.9(9.3)	2.4(0.4)	ND	1.4(0.5)	0.3(0.1)	4.3(1.3)	0.3(0.1)	ND	0.1(0.2)	ND	ND	ND	32°		
84.4(33.7)	81.6(17.8)	24.5(1.4)	11.2(3.7)	6.7(3.8)	6.3(1.5)	7.9(1.3)	0.2(0.1)	ND	ND	ND	DN	ND	ND	ďΝ	UD	ND	ND	5°		ľ
271.4(22.1)	246.3(45.2)	24.1(5.8)	40.1(13.7)	64.2(19.8)	53.8(15.0)	82.9(69.8)	3.3(0.2)	ND	0.7(0.1)	ND	1.2(0.4)	ND	ND	ND	ND	· ND	ND	25°	24 hours	MITC (µg/gwood)
314.2(45.3)	303.9(15.6)	81.6(12.9)	169.9(88.5)	111.2(85.7)	142.8(65.9)	353.3(15.3)	17.2(2.3)	ND	2.5(0.9)	0.4(0.1)	13.5(3.0)	0.4(0.1)	0.4(0.2)	0.2(0.2)	0.1(0.2)	0.2(0.3)	ND	32°		•
286.1(14.7)	229.6(76.8)	22.5(5.8)	20.5(1.8)	17.1(1.4)	8.5(3.5)	20.9(10.2)	0.2(0.1)	ND	2.1(0.3)	ND	2.4(0.6)	ND	ND	ND	ND	ND	ND	30		
371.0(52.3)	394.8(149.7)	51.0(2.1)	149.0(44.1)	148.7(101.1)	112.3(37.6)	279.0(38.8)	8.8(0.9)	ND	3.3(0.3)	ND	3.1(1.2)	ND	ND	ND	ND	ND	ND	25°	48 hours	
393.7(84.9)	343.9(33.0)	113.8(31.2)	547.8(56.2)	86.1(11.0)	189.5(14.3)	396.5(12.2)	20.5(2.1)	ND	16.7(2.1)	1.7(0.5)	28.4(5.9)	1.4(0.3)	0.7(0.2)	0.7(0.2)	0.5(0.1)	0.5(0.2)	ND	32°		

740.9(84.3)	473.2(44.8)	297.6(21.0)	479.9(24.7)	2/3.0(9.3)	(0.51)0.012	202.0(27.0)	(Oct.) Care 1 (O					17.1
	100.0(10.0)	7 (000)		776 0/0 3	216 4/10 4)	232 3(19 0)	111.2(13.3)	22.4(3.7)	5	15	15	
-	703 3/70 6)	545 2/68 5)	352.4(17.4)	384(35.5)	211.2(10.0)	308.7(64.5)	142.1(19.8)	26.1(7.4)	۰	30		
-	111.8(6.1)	13.3(4.8)	14.1(6.8)	64.0(7.3)	9.0(5.1)	37.1(1.0)	25.4(5.7)	0./(0.8)				
_	156.8(37.4)	10.1(1.6)	106.1(13.6)	48.4(8.5)	6.5(0.3)	28.2(1.4)	16.5(3.2)	(0.0)0.1			30	
_	103.8(21.)	9.5(1.6)	90.2(19.0)	32.6(4.3)	47(1.1)	2.2(5.3)	11.0(1.3)	0.0(0.1)		25	5	
-	58.7(4.9)	5.2(3.2)	71.2(20.6)	32.1(7.3)	2.2(1.6)	22.8(1.1)	10.1(2.2)	0.8(0.1)		20	10	
602.7(136.6)	546.4(160.2)	25.3(3.8)	482.8(74.4)	2//.5(105.1)	10.1(3.7)	20.0(3.3)	10 102 0	0 4/0 1)		15	15	
-	(c.1)0.62	0.2(0.1)			16 1/2 7	25.65.20	21.3/6.3)	5.3(0.6)	•	30	•	
-	26 9/1 6	0 2/0 1)	29.5(5.8)	14.3(0.7)	0.2(0.0)	4.3(0.5)	0.7(0.1)	ND			۶	
_	ğ	ND	ND	ND	ND	ğ	3	2			30	
	25°	50	32°	25°	5"	32		N. C.		-		80
	48 hours			Sinon			260	ŝ	(gm)			
<b>1</b> 00				345			6 hours		CuSO,	NaMDC (mg)	Basamid (mg)   NaMDC (mg)	MC (%)
				MITC (µg/gwood)	, and					34.000	31	Ī
								CONTRACTOR (CONTRACTOR (CONTRA				

and a represent means of unce replicates while those in parentheses represent one standard deviation (ND = not detected).

Table I-20. Effect of temperature and wood moisture content (MC) on MITC released from mixtures of Basamid, metham sodium (NaMDC) and copper sulfate (CuSO<sub>4</sub>) in southern pine sapwood sawdust.

	Wood	8 XXXXI						MITC (ug/gwood)	od) •			
MC (%)	Basamid	NaMDC	CuSO <sub>4</sub>		6 hours			24 hours			48 hours	(8888)
	(mg)	(mg)	(gm)	5°	25°	32°	- 50	25"	, ZE	- 5°	25°	
6.3	•	•	•	N)	ND N	Ą	Ą	Ŋ	ND	ND	ND	
	30	•	-	ND	ND	Ą	AD	N	0.2(0.1)	ND	UN	
	•	30	•	ND	Ą	0.9(0.3)	AD	0.6(0.1)	1.2(0.1)	0.2(0.1)	0.5(0.1)	$\neg$
	15	15	•	ND	ND	0.7(0.2)	AD.	0.4(0.1)	0.9(0.2)	0.1(0.1)	0.4(0.1)	
	10	20	•	AN D	0.1(0.1)	0.7(0.2)	Ä	0.1(0.1)	1.2(0.1)	0.1(0.1)	0.5(0.1)	
	5	25	•	ND	0.3(0.1)	0.7(0.1)	ND	0.2(0.1)	1.3(0.1)	0.2(0.0)	0.5(0.1)	
	30		5	ND	1.8(0.9)	2.4(0.7)	0.2(0.1)	2.4(0.2)	8.1(0.5)	0.2(0.1)	5.1(0.3)	
	•	30	5	ND	0.4(0.1)	2.0(0.1)	ND	1.1(0.2)	4.5(0.1)	ND	2.0(0.3)	
	15	15	5	ND	0.8(0.2)	2.4(0.6)	0.2(0.1)	2.2(0.5)	5.8(0.7)	0.3(0.1)	2.5(0.2)	
40.0	•	•		ND	ND	ND	ND	ND	ND	ND	ND	
	. 30	•		ND	ND	1.0(0.0)	ND	2.3(0.5)	11.8(0.3)	ND	4.6(0.1)	
	•	30	•	6.9(0.1)	50.0(10.5)	65.3(12.4)	9.8(0.6)	260.5(7.0)	418.7(6.8)	20.9(3.1)	477.3(37,2)	543.2(51.0)
	15	15	•	2.7(0.5)	40.2(2.0)	98.3(12.6)	2.1(0.4)	87.2(19.4)	359.9(22.3)	4.9(0.1)	187.2(15.2)	294.3(9.7)
	10	20	•	5.0(1.3)	44.6(10.1)	102.4(11.1)	5.0(0.6)	219.3(20.3)	402.4(21.7)	6.9(2.2)	310.8(12.5)	337.0(58.5)
	5	25	•	7.2(1.1)	49.5(1.8)	144.8(36.4)	7.6(0.1)	243.0(14.7)	493.6(31.6)	13.0(1.1)	355.7(13.6)	407.4(52.9)
	30	•	5	5.7(1.9)	20.2(8.6)	24.6(10.6)	10.1(2.2)	35.7(4.9)	43.8(11.1)	21.3(1.9)	37.3(26.2)	129.2(21.5)
	•	30	5	18.5(3.9)	71.9(57.2)	216.7(69.2)	11.2(0.4)	310.1(49.9)	378.3(37.0)	319.4(48.4)	386.2(26.2)	234.8(22.9)
	15	15	5	25.1(12.3)	163.0(44.0)	283.1(15.8)	37.1(87.1)	183.8(11.4)	268.2(27.9)	188.5(32.0)	247.9(18.3)	332.3(48.4)

Ī	Wood	ä		Α,				MITC (//g/gwood)	od) t			
MC(%)	Basamid	NaMDC	CuSO,		6 hours			74 5 00	64)			
	(mg)	(mg)	(gm)	60	STOTE			24 hours			48 hours	
8					63	32	50	25°	32°	Lig.	25°	32°
8				Ą	Ą	Ą	ND	Ŋ	ND	N)	Ŋ	N N
	30	•	•	N	1.8(0.2)	18.8(0.5)	¥	10 7/0 5)	(0.0176.08	0 4/0 1)	10000	
	•	30		12 3/4 7	16417000			(3.2)	07:2(10:0)	0.4(0.1)	40.0(0.7)	233.8(11.6)
	;			12.5(4.7)	134.1(20.2)	263.3(39.9)	62.6(14.9)	340.3(14.1)	504.5(29.9)	323.6(37.4)	565.9(47.3)	558.1(33.2)
	5	10		2.2(0.5)	32.5(2.5)	80.3(19.9)	7.9(8.0)	208.4(5.2)	386.4(8.4)	128.5(18.2)	382 7(18.6)	310 8/73 11
	10	20		5.0(0.2)	36.7(8.9)	82 9/11 6	37 1/13 /	3170 0116	***************************************			
	\$	25		5 400 00	20.1(0.2)	02.5(11.0)	27.1(12.4)	3/3.8(13.6)	5/6.1(261.9)	233.1(3.3)	404.8(19.1)	574.8(27)
	3			3.4(0.6)	31.4(8.4)	166.3(46.9)	47.2(11.9)	343.4(52.7)	542.9(68.7)	274.9(6.7)	575.6(98.6)	808.4(213.3)
	٤			9.6(2.0)	20.4(4.1)	58.3(8.1)	11.8(2.9)	26.4(3.9)	112.8(21.5)	18.2(5.8)	54.4(17.4)	250.2(27.1)
		30	5	24.3(1.4)	237.3(85.1)	336.9(40.9)	179.1(24.8)	396.5(41.8)	384.9(2.6)	304.3(19.0)	350 2/48 8)	387 1/0 1)
	15	15	v	20.7(43.4)	201.2(43.4)	264.8(37.3)	163 4(3.6)			200 0/20 4		( )
W					7Ł		100.1(0.0)	721.0(27.0)	311.0(27.0)	234.0(50.7)	254.0(50.7)	230.5(17.6)

Values represent means of three replicates while those in parentheses represent one standard deviation (ND = not detected).

## D. EXPLORE FUNDAMENTAL ASPECTS OF INTERNAL REMEDIAL TREATMENTS

1. Evaluation of 40 % metham sodium in small block trials: Metham sodium remains widely used in North America. formulation is typically used as a 32.7 % solution of the sodium salt. Recent changes transportation regulations encouraged a number of companies to consider using a more concentrated metham sodium. While the difference concentration should not markedly affect performance, we elected to identify any Potential effects on performance using our small block test.

Douglas-fir heartwood blocks (25 by 25 by 100 mm long) were pressure soaked before being autoclaved for 25 minutes at 100 C. The ends of each block were taped. then the blocks were dipped in molten wax. The tape was removed and an agar square cut from a plate containing actively growing mycelium of Antrodia carbonica (a common decay fungus of Douglas-fir poles) was placed on the exposed surface. A 25 by 25 by 12.5 mm long Douglas-fir block was placed on each end of the block and the entire assembly was held in place with a rubber band. The assembled blocks were incubated for 4 to 6 weeks at room temperature. A single 13 mm diameter hole was drilled in the center face of each block and 50, 100, 150, 200 or 250 mg of 40% metham sodium was added. The holes were plugged with tight fitting rubber serum caps and the blocks were incubated in aerated chambers for 2, 4, or 6 weeks at room temperature.

At each time point, a series of three 5 mm thick sections were cut from each end of

4 blocks per chemical dosage. The outer section on each end was discarded, while the two inner sections were cut into 16 equal sized squares. The inner four squares from the second section from the surface were placed on malt extract agar and observed for evidence of regrowth of the test fungus. Fungal survival was used as a measure of chemical effectiveness. The inner four squares from the inner most section were placed into 5 ml of ethyl acetate and stored for 48 hours at room temperature prior to analysis for residual methylisothiocyanate was described earlier under this Objective.

MITC levels ranged from 53 to 114 ug/g of oven dried wood 2 weeks after treatment, but declined rapidly over the remaining 6 weeks of the trial (Table I-21). These results are typical of those found with the 32.7 % metham sodium which produces a rapid release of MITC followed by rapid loss of chemical with time. This chemical loss reflects both the poor rate of metham sodium conversion to MITC as well as the relatively high surface to volume ratio of the test blocks. These results, however, differ little from those found with previous trials of 32.7 % metham sodium.

The effect of metham sodium on fungal survival was relatively uneven 2 weeks after application. Fungal survival declined in most dosages over the remaining 6 weeks of incubation, although it appeared to increase at 4 weeks at 150 mg and 8 weeks at 200 mg. The reasons for these anomalies are unclear, although they may reflect variations in decomposition efficiency, wood defects, or moisture content variations. Despite these deviations, the 40 % metham sodium appears to provide protection similar to that previously found with the less concentrated formulation and has the advantage of

reduced transportation cost for a given level of active ingredient.

2. Performance of a fluoride/boron rod in laboratory trials: We have already established field trials of the fluoride/boron rod (Preschem), but had no comparable laboratory information on this formulation. The rods were tested under laboratory conditions using the small block procedure described in the previous section. Douglasfir heartwood blocks prepared as described above receive 50, 100 or 200 mg of fluoride/boron rod. The blocks were then incubated for 4 or 8 weeks at room temperature before being cut for analysis as described above. Fluoride levels were assessed by extraction and analysis of the extract using a specific ion electode, while the boron levels were determined using the Azomethine H method

Fluoride levels tended to increase with increasing dosage at both time points, although the fluoride levels tended to be lower after 8 weeks (Table I-22). While this appears odd, it may reflect diffusion to produce a more even distribution along the block. It may also represent the presence of a small checks in the wood which encouraged diffusion of large quantities of chemical in a short time. This would produce elevated levels in the assay zone shortly after treatment. Continued diffusion would decrease the concentration differences across the blocks. Unlike fluoride, boron levels 2 weeks after rod application were fairly variable among the 3 dosages, again suggesting that minor variations in the blocks produced marked differences in the rate of chemical movement. Boron levels 8 weeks after treatment followed a more orderly pattern with increased dosage.

Fungal survival at both time points was

low at all dosages tested, with fungal survival occurring only at the lowest dosage 4 weeks after treatment. The results indicate that the fluoride/boron rod has excellent fungal control potential once it diffuses from the point of application.

3. Diffusion of copper and boron from a copper naphthenate/boron paste: While boron and fluoride rods have received extensive attention as potential internal remedial treatments, other diffusible formulations may also prove useful for this Among these is a copper application. naphthenate/boron paste which is typically used as a supplemental groundline preservative (CuRAP 20, ISK Biotech). In 1989, a series of Douglas-fir pole stubs (25-30 cm in diameter by 2.0 m long) were set to a depth of 0.6 m and treated with 150 or 300 g of the copper naphthenate/boron paste through a series of three 21 mm diameter holes drilled at a 45 degree angle beginning at groundline and moving upward 15 cm and around the pole 120 degrees. Ten poles each received 150 or 300 g of a paste containing 18.16 % amine based copper naphthenate and 40 % sodium tetraborate decahydrate. The chemical was applied using a grease gun and the holes were plugged with tight fitting wooden dowels.

Chemical movement was assessed 3 and 5 years after treatment by removing increment cores from 3 equidistant sites around the pole 8 cm below the groundline as well as 8, 16, 24, and 32 cm above groundline. The cores were divided into inner and outer halves and each was ground to pass a 20 mesh screen. Copper content was determined using an ASOMA 8620 x-ray fluorescence analyzer (XRF), while boron content was determined using American Wood Preservers' Association

Standard A2 (Azomethine H method).

Analyses of cores removed 3 years after treatment revealed that boron was present at levels ranging from 0.06 to 1.15 % boric acid equivalent (BAE), while copper levels ranged from 0.01 to 0.54 kg/m³ (Table I-23). Chemical levels were generally higher at or slightly above the groundline, reflecting the application pattern. Chemical levels were generally higher in the inner zones of the poles, again reflecting the application pattern. As expected, chemical levels also increased with increased dosage and decreased with increasing distance away from the groundline.

The two years since the 3 year sampling have been characterized by above average rainfall. Under these conditions, the water table at the test site comes very close to the surface during the wetter winter months. The wetness of the site was demonstrated by the dramatic decrease in levels of both copper and boron in poles sampled 5 years after treatment. Levels of either chemical were virtually at background levels, suggesting that the intervening wet period has markedly accelerated depletion. Further trials are planned with these poles to confirm the results, but the current analyses indicate that the internal treatments provided only short term protection to the poles at the dosages tested.

4. Effect of glycol and moisture content on diffusion of boron from fused boron rods: Although we have established a variety of boron rod field trials, the results from these tests have indicated that boron movement through Douglas-fir appears to be slower than through other wood species. While the reasons for these differences remain unknown, it is clear that methods must be identified for accelerating boron movement

through this wood species. One approach to enhancing movement is the addition of glycol to the boron at the time of application. Previous trials in Europe suggest that glycol enhances boron diffusion through drier wood, thereby producing more effective control under moisture regimes which would normally not be conducive to this treatment.

To study these effects, two trials have been established. In the first, 38 by 88 by 150 mm long blocks were pressure soaked with water and conditioned to one of three moisture contents (15, 30, or 60 %). The blocks were then dipped in molten wax to retard further changes in MC and the wood was stored for an additional 4 weeks at 5 C to encourage more even distribution of moisture.

A single 9.5 or 11.1 mm by 60 mm long hole was drilled at the midpoint of the 38 mm wide face of each block and a measured amount of boron alone or with Boracol 20, Boracol 40, Boracare (diluted 1:1 with water), 10 % Timbor, or glycol was added to each hole. The holes were plugged with rubber serum caps and incubated at room temperature for 4, 8 or 16 weeks.

At each time point, four blocks per chemical treatment/moisture content combination were sampled by cutting a series of 5 mm thick sections 10, 25, 45, and 60 mm from the original treatment hole. These sections were oven dried overnight (54 C), sanded lightly to remove any possible boron carry over from sawing, and sprayed with a curcumin/salicylic acid indicator specific for boron.

The laboratory trials are still in progress and results are only available for three treatments at the selected moisture levels (2.1 g of rod plus 1.1, 2.2, or 3.3 g of

ethylene glycol). The results confirm the need for some moisture for boron movement, even in the presence of glycol (Table I-24). Boron distribution was extremely poor in blocks conditioned to 15 % MC prior to treatment, and improved steadily at 30 and 60 % MC. penetration was nearly complete on blocks conditioned to 60 % MC. Increased glycol level produced only a slight improvement in boron distribution and this effect was inconsistent among the various treatments and sampling sites, suggesting that the wood moisture content had a more substantial effect on diffusion which could not be overcome by glycol addition.

The indicator provides only a qualitative guide to boron distribution and further analyses are planned to more fully delineate the differences between the various treatments. The remainder of chemical combinations will be tested over the next few months.

In addition to the laboratory trials, a limited number of boron rod/glycol combinations have been evaluated in field trials. Thirty 25 to 30 cm diameter by 3.6 m long pentachlorophenol treated Douglas-fir poles were set to a depth of 0.6 m. Three 17.5 mm diameter by 267 mm long holes were drilled at a 45 degree angle around each pole 75 mm above the groundline. The poles received one of 6 treatment combinations as follows:

- 1. Six boron rods (152 g rod)
- 2. Six boron rods (152 g) plus 140 g ethylene glycol
- 3. Three boron rods (91 g) plus 199 g Boracol 40
- 4. Three boron rods (125 g) plus 183 g Boracol 20
- 5. Three boron rods (125 g) plus 177 g Boracare (1:1 in water)

# 6. Six boron rods (140 g) plus 170 g 10 % Timbor

The holes were then plugged with tight fitting wood dowels. The treatment delivered a total of 220 to 224 g of boric acid equivalent to each pole. Each treatment was replicated on five poles. These poles were treated this past winter and will be sampled at the one year point to determine boron levels -300, 0, 300, 400, and 500 mm away from the groundline. Samples from the 0 and 300 mm locations will be removed 120 degrees around from the original treatment holes, while the remainder will be taken from three equidistant locations around the pole.

In addition to the monitoring for boron distribution, these poles will also be used to establish seasonal changes in internal moisture content. Previous trials have shown the importance of moisture in boron diffusion, but there is relatively little information on internal moisture contents of poles in service. While removing increment cores at selected time points which are then segmented and oven dried to determine moisture content can be used to assess moisture distribution, this process is destructive and disrupts the wood integrity. Portable moisture meters can also be used, but these meters support pins to a maximum depth of 75 mm. We elected to produce stainless steel probes which could be permanently placed into the poles to desired depths and to monitor changes in both current and resistance between two adjacent probes on a monthly basis.

A series of pointed stainless steel probes (6 mm in diameter by 75, 125, and 175 mm long) were fabricated. Each probe was coated along the length with shrinkable plastic tubing so that only the tip of each probe remained exposed.

A series of 2.5 mm diameter holes were drilled 60 mm apart vertically to depths of 23, 73, and 148 mm at 150 mm below the groundline as well as 0, 150, and 300 mm above the groundline. The probes were driven into each predrilled hole to the desired depth (25, 75, or 150 mm) and the edge around each rod was sealed with an epoxy resin to retard moisture movement along the metal. A rubber cap was placed over the exposed end of each probe to protect the metal from the elements.

The pins were sampled monthly by attaching clips and measuring resistance using a 30 volt AC power supply across each electrode pair. In addition, a limited number of trials were performed in which a conventional resistance type moisture meter was used to obtain a moisture measurement immediately adjacent to the permanent sampling site in 8 pins set to 25 or 75 mm. The correlation between the conventional and permanent pin approaches was 0.53 at 25 mm and 0.90 at 75 mm (Table I-25). The reasons for the improved correlation between the two methods at the deeper depth is unclear, although there may be slightly better contact with the more deeply driven pins. These preliminary samplings suggest that the permanent pins should prove at least as reliable as conventional moisture meter pins, but have the added advantage of permitting rapid repeated sampling to depths not attainable with the conventional pins. In addition, the results suggest that our readings can be translated directly to moisture contents within the moisture range for which the conventional meter is accurate.

Measurements of pins in all 12 poles indicate that resistance declines with increasing distance above ground, reflecting

the lower moisture levels farther away from the soil (Table I-26). Resistance and current both declined over the first 2 months, probably as a result of the poles drying out following the winter wet season. These results, however, are preliminary and further trials are planned to assess resistance changes seasonally and to develop more precise correlations between our measurements and the actual wood moisture content.

5. Effect of voids on efficacy of fumigant treatments: The presence of voids in the groundline poses a dilemma to the inspector. First, from a strength standpoint, large voids leave too little shell to support the design load. There are, however, simple tables to assist the inspector in reaching a strength decision. The other dilemma concerns the subsequent course of treatment should the pole be deemed sound. While there are an array of potential treatments for arresting internal decay, there is considerable debate concerning the ability of these treatments to move around voids to control fungal attack across the groundline zone. To help answer these questions, twelve Douglas-fir pole sections were cut in half and a 5 cm diameter by 15 cm long hole was cut into each cut end of the pole. The poles were reassembled and the edge between the two cut ends was sealed using an elastomeric paint to retard fumigant movement from the void. The poles were then treated with 80 or 160 g of either metham sodium or chloropicrin applied to holes drilled above the void. Each treatment was applied to 3 poles. A similar number of poles without voids were treated in the same manner and all poles were exposed outdoors at the Forest Research Laboratory.

Fumigant movement was assessed

periodically 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 inner and outer 25 mm of each core were placed into hexane (for chloropicrin) or ethyl acetate (for metham sodium). The cores were extracted for 48 hours at room temperature, then the extracts were analyzed for chloropicrin or MITC by gas chromatography as previously described.

Because of logistical problems. chloropicrin treated poles were only analyzed 4 and 8 years after treatment. The results of these analyses indicated that high levels of chloropicrin remain in the area immediately adjacent to the treatment zone 4 years after chemical application (Table I-27). While chemical levels were much lower 8 years after treatment, although they were still generally above the levels required for long term fungal control. The presence of voids in the poles initially had little effect on chloropicrin distribution, but analyses 8 vears after treatment show marked differences in fumigant levels in poles receiving voids. These differences imply that voids do diminish the long term effectiveness of this fumigant.

Analysis of metham sodium treated poles were performed more frequently. For the purposes of simplicity, only the 3, 5, 6 and 8 year results are reported (Table I-28). Unlike the chloropicrin assays, MITC levels have remained relatively low over the course of the trial. These lower levels most likely reflect the inefficiency of metham sodium decomposition to MITC in wood. Fumigant levels have also varied more widely with time in these treatments, perhaps reflecting sampling variations. Unlike the chloropicrin treated poles, however, there appears to be little difference between residual MITC levels in poles with and without voids. The

absence of a void effect may reflect differences in how these two chemicals interact with the wood. Chloropicrin can be readily removed from wood by aeration, suggesting that it has only minimal interactions with the wood. It is generally difficult to remove all MITC from wood by aeration, suggesting more substantive chemical or physical interactions. Given these properties, a void would provide an opportunity for the less strongly bound chloropicrin to migrate from the pole, while the MITC may be less strongly affected by the void.

6. Develop models which predict fumigant movement through wood poles: Last year, we reported on the first trials with a model for predicting the movement of MITC through Douglas-fir poles using a finite element modeling program called ANSYS. This past year, we have hired a graduate student in Electrical Engineering to continue this work. One problem which we face with these models is a concern about the validity of our diffusion coefficients and sorption/desorption values for each of the fumigants on the various wood species. This past year, we began a small project to refine our data on these areas. This information will be critical for refining the accuracy of the model.

The development ofsorption/desorption values has been undertaken by conditioning Douglas-fir heartwood blocks of selected dimensions to varying moisture contents by storing over salt solutions. The moisture regimes evaluated were 0, 7, 10, 30, and 40 % moisture content. One half of the conditioned blocks were exposed to saturated atmospheres of chloropicrin for 4 to 6 weeks. A fumigated block was then placed in glass jars with teflon lined caps along with another block conditioned at the moisture content but without chloropicrin. The jars were incubated at room temperature for 5 and 10 days, then the blocks were removed and separately extracted in hexane for 24 hours prior to analysis for chloropicrin using a Shimadzu Gas Chromatograph equipped with an electron capture detector. The amounts of fumigant in the two blocks was used to develop a desorption/sorption ratio using the chloropicrin levels of the original fumigated block which was desorbing chemical and the non-fumigant-treated block which was sorbing chemical. The percentage of fumigant-treated wood was varied in the chambers. Each moisture level/fumigated wood ratio was replicated on 3 chambers per time point.

The results indicate that the fumigant was more strong retained by the desorbing block at lower moisture contents 5 days after initiation of the experiment (Table I-29). This effect was greatest when lower percentages of fumigated wood were present in the chambers. Exposure of blocks for an additional 5 days resulted in nearly complete desorption of chloropicrin from the fumigated blocks, suggesting that the chloropicrin levels were nearing equilibrium (Table I-30). Levels were most similar in treatments with the lowest amounts of fumigant treated wood in the chambers. This effect was not expected since the eventually equilibrium should result in a desorption/sorption ratio which reflects the volumes of fumigated and non-fumigated wood present. The low ratios after 10 days imply that some fumigant is being lost over time possibly as a result of sorption to the glass in the jars. Further trials will be required to more closely refine the values.

An equilibrium desorption of zero would be expected for a chemical such as chloropicrin which has minimal wood interactions if the amounts of fumigated and non-fumigated wood were the same in a chamber. The fumigant should rapidly move from the higher concentration in the original fumigated block to the surrounding air and into the non-fumigated wood. Previous studies have shown a tendency for fumigants to move into wood at higher concentrations than might be expected from those present in the air, implying a selective sorption.

Additional trials with blocks exposed for longer periods and with other wood species are underway. The results of these trials, along with those for the model will be reported in the next Annual Report.

Table I-21. Residual MITC content and fungal survival in Douglas-fir heartwood blocks 2, 4 and 8 weeks after treatment with 0 to 250 mg of 40% metham sodium.

Dosage (mg)	Residual MII	C concentration wood)	(µg/g ovendry	Fungal	survival (as % of	control)
	2 weeks	4 weeks	8 weeks	2 weeks	4 weeks	8 weeks
0	0	0	0	100		100
50	53	7	0	16	0	0
100	43	12	1	53	5	. 0
150	107	8	3	11	42	4
200	134	16	6	5	0	31
250	114	27	10	16	0	0

Table I-22. Residual boron or fluoride vs. fungal survival in Douglas-fir heartwood blocks. \* TRESHEM

Dosage	Residual fluoric	le (% NaF)	Residual bor	on (%BAE)	Fungal sur	vival (%)
(mg)	4 weeks	8 weeks	4 weeks	8 weeks	4 weeks	8 weeks
0	0	0	0	0	59.1	46.9
50	0.007	0.002	0.97 097	0.04	3.1	0
100	0.016	0.004	0.14	0.16	0	0
200	0.081	0.009	0.23	0.32	0	0

Values represent means of 4 analyses for chemical assays and 32 samples for fungal survival.

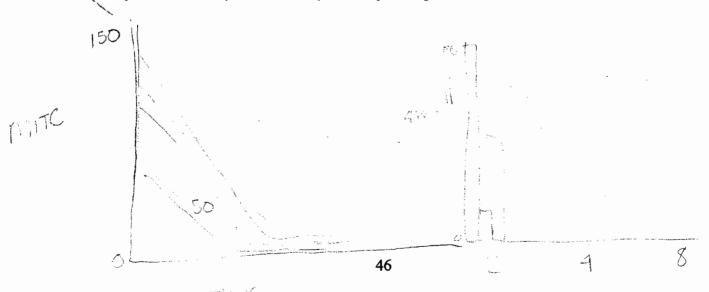


Table I-23. Residual boron and copper retentions in Douglas-fir posts 3 or 5 years after internal treatment with a copper naphthenate/boron paste.

_	т	<del></del>	***************************************
300	150	0	Dosage
0.10	0.13	0.07	-8cm *
1.02	0.48	0.05	8cm
1.15 0.61 0.11 0.01	0.43	1	Boron Retent 3 years 16cm 24cm 32cm
0.61	0.50	1	Boi 24cm
0.11	0.04	;	Boron Retention (%BAE)  32cm -8cm
$\overline{}$	0.01< 0.01< 0.01< 0.01< 0.01< 0.04	0.01	# 5 years  -\$cm   8cm   16cm   24cm   32cm
0.01	0.01<	0.01	E)
0.01<	0.01<		5 years
0.01<	0.01<	'	24cm
0.01 0.01< 0.01< 0.01< 0.02	0.01<	1	32am
	L	0.01	-8am
0.51	0.21	0.01	8 <i>c</i> m
0.54	0.26	1	3 years 16cm
0.25	0.26 0.01	-	Co 24am
0.03	0.01	ı	pper Reter
0.54 0.25 0.03 0.01< 0.01< 0.01< 0.01< 0.01< 0.01<	0.01<	0.01	
0.01<	0.01<	0.01	
0.01<	0.01< 0.01< 0.01< 0.01< 0.01<	1	5 years 16cm 24cm 32cm
0.01<	0.01<	1	24cm
>10.0	>10.0		32cm

<sup>\*</sup>Distance away from the groundline.

Table I-24. Effect of moisture content and glycol on boron penetration in Douglas-fir blocks four weeks after treatment with 2.1 g of fused borate rod as measured using curcumen/salicylic acid indicator.

<del></del>			
3.3	2.2	1.1	Glycol treatment (g)
30.0	18.5	4.1	01
6.0	1.0	0.5	159
0.9	0	0.4	15%MC
0.1	0	0.3	60
92.5	88.8	85.0	Av Dist
70.0	73.8	70.6	verage Boro 309 tance from t
40.6	45.4	21.5	Average Boron Penetration (%)*  30% MC  Distance from treatment hole (mm)  25 43 66
25.6	35.6	10.9	e (mm)
100	100	100	10
98.8	100	100	60%
96.3	100	100	60% MC
95.0	98.8	98.8	60

Values represent the mean of eight samples.

Table I-25. Comparison between resistance measurements obtained from fabricated stainless steel pins and a commercial resistance type moisture meter 25 and 75 mm from the wood surface.

			Distance from	surface (mm)	
Pole#	Distance from groundline	25.1	nm	75	mm
	(mm)		Resistance (	mega ohms)	
		Conventional	Experimental	Conventional	Experimental
1741	-150	16.5	18.6	20.7	19.0
	0	16.7	16.6	18.5	16.5
	150	16.7	15.5	17.3	15.5
	300	14.9	14.6	17.5	15.9
1751	-150	18.8	18.3	24.3	22.8
	0	16.9	16.5	24.0	22.1
	150	17.0	16.6	25.6	22.7
L	300	15.5	15.4	21.8	22.7

Table I-26. Resistance measurements at selected depths in pentachlorophenol treated Douglas-fir poles remedially treated with combinations of boron rods and glycol solutions.<sup>a</sup>

Sampling depth	Distance from	Volta	ge (V)	Curren	nt (µA)	Resistance (	mega-ohms)
(mm)	the groundline (mm)	2 months	3 months	2 months	3 months	2 months	3 months
25	150	30.2	29.9	27.5	10.3	1.2	7.5
	0	30.2	29.9	24.9	7.4	1.8	12.0
	150	30.2	29.9	11.0	2.0	3.1	15.4
	300	30.2	29.9	10.5	8.1	3.3	14.0
75	-150	30.2	29.9	45.4	14.2	1.0	3.2
	0	30.2	29.9	38.4	8.8	1.1	5.3
``.	150	30.2	29.9	28.5	6.8	1.5	9.8
	300	30.2	29.9	28.3	23.6	1.3	9.7
150	-150	30.2	29.9	141.6	111.0	0.4	0.5
	0	30.2	29.9	204.8	125.3	0.3	0.6
	150	30.2	29.9	235.4	152.3	0.3	1.5
	300	30.2	29.9	123.4	52.3	0.4	1.2

<sup>&</sup>lt;sup>a</sup> Values represent means of samples from 12 poles per time period.

Table I-27. Residual chloropicrin at various sites above or below Douglas-fir poles 4 or 8 years after treatment with selected dosages of chloropicrin.

Dosage (g)	Void b	Distance from	Average ch	doropicrin co	ntent (µg/g ove	n/dry wood) *
	(+/-)	void (m)	Οι	iter	Im	ner
			4 years	8 years	4 years	8 years
80	(+)	-0.9	8.1	0.3	114.4	0.3
		-0.3	205.0	15.7	442.1	30.3
		+0.3	93.3	26.8	339.0	3.5
		+0.9	4.3	0.2	26.3	0.1
80	(-)	-0.9	14.1	57.9	55.0	3.8
	•	-0.3	150.7	69.3	507.3	158.7
		+0.3	253.1	121.0	607.6	121.6
		+0.9	14.3	3.9	107.3	29.1
160	(+)	-0.9	27.0	5.9	223.8	4.8
		-0.3	357.8	18.1	821.8	31.1
		+0.3	236.3	19.8	620.9	48.2
		+0.9	21.7	6.8	335.5	17.4
160	(-)	-0.9	11.6	7.0	215.4	13.0
		-0.3	166.9	204.5	585.2	146.3
		+0.3	145.6	191.2	488.0	166.2
		+0.9	28.1	3.8	232.8	4.6

<sup>&</sup>lt;sup>a</sup> Values represent means of 9 replicates. Outer zone refers to the 25 mm section inside the treated shell while the inner zone represents the inner 25 mm of each sample.

b Poles were tested with (+) or without (-) voids.

Table I-28. Residual MITC at various sites above or below voids in Douglas-fir poles 3 to 8 years after treatment with selected dosages of metham sodium.

Dosage	Void b	Distance from	A	verage	MITC	content	(µg/g (	oven/dr	y wood	)•
(g)	(+/-)	void (m)		Oı	iter			In	ner	
			3 уг	5 уг	6 yr	8 yr	3 yr	5 yr	6 уг	8 yr
80	(+)	-0.9	3.7	0.0	0.0	13.0	3.0	0.0	0.0	17.3
	İ	-0.3	9.7	3.5	4.7	13.8	15.9	1.7	0.8	16.4
		+0.3	12.4	3.8	1.8	14.1	11.0	1.9	2.5	15.8
		+0.9	4.2	0.0	1.4	16.6	3.4	0.0	0.8	15.9
80	(-)	-0.9		0.8	4.4	21.8	2.5	0.0	2.0	24.8
	ł	-0.3	8.1	2.7	7.2	26.1	57.7	2.6	8.1	20.8
		+0.3	9.4	1.5	5.2	11.7	15.1	1.8	5.8	13.4
		+0.9		0.0	2.8	9.9	3.9	0.0	0.0	12.0
160	(+)	-0.9	4.2	0.0	3.7	16.4	10.5	0.0	4.0	15.5
		-0.3	13.1	1.2	10.1	14.2	32.4	0.0	7.1	14.2
		+0.3	8.9	5.1	4.4	11.4	20.0	5.9	4.4	11.3
		+0.9		1.5	1.2	9.3	5.3	2.9	1.4	12.1
160	(-)	-0.9	2.1	0.0	11.0	17.1	4.5	1.2	6.1	20.1
		-0.3	15.4	6.1	11.2	20.5	30.3	13.1	8.2	20.7
		+0.3	20.4	9.2	10.9	16.4	28.1	6.7	6.3	19.7
		+0.9	3.4	0.0	4.9	19.1	3.9	0.0	5.1	20.5

<sup>&</sup>lt;sup>a</sup> Values represent means of 9 replicates (--) denotes missing data.. Outer zone refers to the 25 mm section inside the treated shell while the inner zone represents the inner 25 mm of each sample.

b Poles were tested with (+) or without (-) voids.

Table I-29. Desorption/sorption ratios of Douglas-fir heartwood blocks 5 days after exposure of fumigated and non-fumigated blocks of varying dimension.

Wood moisture content (%)			tio of Chloropicrin in a			
	14*	25*	50 *	50*	66°	86 3
0	38.66	11.75	11.39	20.50	4.13	1.98
7	21.63	15.56	6.20	3.82	7.33	2.96
10	3.41	7.01	3.18	7.05	2.51	2.75
30	1.71	1.51	1.05	0.95	0.90	0.72
40	1.07	1.76	1.22	1.16	1.38	0.73

<sup>\*</sup> Chambers contained 0.5 cm³ of wood.

Table I-30. Desorption/sorption ratios of Douglas-fir heartwood blocks 10 days after exposure of furnigated and non-furnigated blocks of varying dimension.

Wood moisture content (%)			tio of Chloropicria in			
	14*	25*	Amount of furnigated 50 *	wood in chamber (%)	66 <sup>6</sup>	86*
0	0.04	0.08	6.52	4.92	2.48	2.18
7	6.24	6.04	4.75	3.37	1.85	1.55
10	2.94	2.77	3.67	1.97	2.02	0.75
30.	1.66	1.66	1.36	0.97	1.06	0.69
40	1.78	1.30	0.92	1.26	1.28	0.58

<sup>&</sup>lt;sup>a</sup> Chambers contained 0.5 cm<sup>3</sup> of wood.

b Chambers contained 3.0 cm3 of wood.

b Chambers contained 3.0 cm3 of wood.

# OBJECTIVE II IDENTIFY SAFER CHEMICALS FOR PROTECTING EXPOSED WOOD SURFACES IN POLES

A preservative treated shell provides an excellent barrier against fungal attack, but here are many instances where wood users either use naturally durable woods which still contain the non-durable sapwood or where preservative treated wood is fabricated after treatment, thereby exposing untreated wood to microbial attack. Formerly, the risk of damage in these products was minimized by applying pentachlorophenol in oil either during installation or at regular intervals thereafter. Concerns about the safety of penta have largely eliminated this application and there remains a need for safe, easily applied treatments which can protect wood in these exposures. In this objective, we have evaluated a wide array of chemicals under field and laboratory conditions.

A. LABORATORY AND FIELD TRIALS OF POTENTIAL PENTACHLOROPHENOL REPLACEMENTS FOR PROTECTING WESTERN REDCEDAR SAPWOOD FROM DECAY

Western redcedar poles have a large core of naturally durable heartwood that provides excellent protection against fungal and insect attack. As a result, untreated or butt-treated western redcedar poles have been extensively used in the United States. While these poles performed well, the outer sapwood, having little natural durability, tended to decay in service and eventually to separate from the pole, creating unsafe climbing conditions. Many utilities addressed this problem by spraying 10 percent pentachlorophenol in diesel oil along the pole length at 10- to 15-year intervals;

however, they have largely ceased this practice because of chemical drift during spraying and the restrictions placed on pentachlorophenol. Nevertheless, redcedar poles remain in service, even though climbing is restricted or the poles are replaced when their sapwood becomes decayed. The identification of safer biocides for remedial protection of sapwood would assist utilities as they seek to extend the service life of western redcedar in their pole systems. In previous reports, we described the performance of a variety of biocides. In this report, we describe how these same biocides are performing after 2 to 11 years of exposure.

Full-scale treatments of pole stubs: Twenty-three untreated western redcedar pole stubs (2.4 m long) were kerfed along their entire length to a depth of 7 cm at three equidistant points around the circumference and were set in the ground to a depth of 0.6 m at a site near Corvallis, Oregon. Metal sheets were placed on the kerfs on either side of the face to minimize drift onto adjacent faces. Exactly 1.25 l of one of seven chemicals were sprayed on each of two faces of each pole, beginning at the top and extending 1.8 m downward; the third face served as an untreated control (Table II-1). Each treatment was replicated on six faces. For the first 5 years, the poles were sprinkled with water from above for 3 hours/day during the summer to stimulate leaching and encourage microbial attack. This practice was then discontinued because of loss of a water source.

After 2, 8, and 11 years of treatment, chemical efficacy was assessed by removing

increment cores and plugs from the upper middle of each face. The increment cores were used in an Aspergillus niger bioassay. First, they were placed on potato dextrose agar that had been seeded with a suspension of A. niger spores; then the agar plates were incubated at room temperature until the fungus had produced a uniform mat of its typically dark spores. The zone of effect (ZOE), as delineated by absence of growth or lack of pigmented spores, was measured along the length of the core-0-6 mm from the pole surface was considered the outer core and 7-12 mm the inner core. This bioassay is responsive to a variety of fungus-inhibiting chemicals with limited water solubility.

The plugs were divided into wafers, each taken at a different distance from the pole's surface: 0-3.2, 3.2-6.4, 6.4-9.6, and 9.6-12.8 mm. Each wafer was ovendried at 54°C for 24 hours and weighed (nearest 0.01 g). Each was then exposed to 2.5 MRads of ionizing radiation from a Cobalt 60 source prior to being exposed in a modified soil block test. For this test, 60-ml glass bottles were filled with 25 ml of forest soil and enough water to raise the moisture content to 60 percent. A western hemlock feeder strip (0.5 mm long by 19 mm x 19 mm) was placed on the soil surface. The bottles were then capped and autoclaved for 40 minutes at 121°C. After the bottles cooled the feeder strips were inoculated with a 2-mm-diameter plug cut from the actively growing edge of a culture of Postia placenta on malt extract agar, and the bottles were incubated at room temperature until the fungus thoroughly colonized the feeder strips. A single wafer was then added to each bottle, and the bottles were incubated for 10 to 12 weeks. The test was terminated when selected untreated wafers had

undergone a 30 to 40 percent weight loss. The remaining wafers were removed, ovendried (54°C) to a constant weight, and weighed (to the nearest 0.01 g) to determine loss in wood weight over the exposure period.

Small-scale field trials: As the field trials progressed, it became increasingly difficult to obtain weathered but untreated redcedar poles for testing. As a result, smaller samples were substituted. Redcedar pole sections were cut into 150-mm-thick disks, and these disks were cut into smaller blocks, each containing a 150- x 150-mm sapwood face. The radial and inner tangential faces of each block were coated with epoxy resin to retard chemical uptake along these surfaces. Thirty formulations were tested, each on 6 blocks that were dipped, sapwood face down, for 30 seconds in the appropriate formulation (Table II-2).

The blocks were air-dried for 24 hours; then the untreated surfaces were coated with an elastomeric paint to protect the epoxy, and the blocks were cured for 14 days. They were then placed above ground on a south-facing fence at a 30° angle. During dry summer months, the blocks were watered for 3 hours each day to stimulate fungal attack and encourage leaching.

Two and 5 years after exposure, the blocks were evaluated. A 5-mm-diameter by 12-mm-long increment core was removed from each block and used in an Aspergillus niger bioassay as described above. A single 9-mm-diameter by 12-mm-long plug was also removed from each block and cut into wafers as described for the full-sized poles. These wafers were evaluated for resistance to residual decay by using the modified soil block described above. For purposes of evaluation, biocides were classified as providing good (<10% wt. loss), moderate

(10 to 25% wt. loss), minimal (26 to 35% wt. loss), and no (>35% wt. loss) protection to the wood.

Full-scale treatments of pole stubs: Aspergillus niger bioassays 2 years after treatment indicated that inhibitory levels of penta remained in many stubs, while other chemicals produced little or no ZOE (Table II-3). In bioassays conducted 8 and 11 years after treatment, ZOE's around cores from stubs treated with penta declined slightly, particularly those around outer core segments, but measurable levels of penta remained in cores treated with either the oilor the water-based chemical applied at a 10 percent concentration. Penta is an extremely active and persistent biocide that affords excellent long-term protection; our results confirm the difficulty of finding an equally effective replacement.

Soil block tests indicated that the two 10 percent penta formulations provided excellent protection to the wood surface 2 years after treatment (Table II-4). oil-based formulation provided protection at deeper levels than did the water-based one. This difference may indicate that oil solvents increase the ability of some formulations to penetrate weathered wood. Similar tests of samples removed 8 years after treatment indicated that only the oil-based penta continued to provide high levels of protection against fungal attack. None of the chemicals provided a high degree of protection to the outer wood surface 11 years after application, although penta in oil continued to provide some protection deeper within the wood. Such protection would be useful to a utility company because a primary cause of accidents to lineworkers is the separation of the sapwood-heartwood interface. Thus, chemicals that protect this

inner zone might be as useful as those that provide only surface protection.

For some reason, oil-based Oxine copper apparently provided better protection 8 years after treatment than it did after 2 years (Table II-4). Whatever the reason for these unexpected results, the 11-year data on this formulation suggest that the 8-year results were anomalous and should be interpreted with caution.

A continuing problem with the interpretation of soil block tests is that laboratory tests in which wood is exposed to large quantities of actively growing mycelium are used to assess decay resistance under field conditions, where fungal spores or mycelial fragments landing in small checks are the primary source of inoculum. It may be possible to provide equivalent protection with less active biocides having better leach resistance than afforded by the chemicals tested here; however, such biocides would tend to perform poorly in soil block tests.

Small-scale field trials: When tested in the Aspergillus niger bioassay, the cores removed 2 years after being treated with 20 of the 30 formulations produced measurable ZOE's (>1 mm) (Table II-5). Arquad C-50 and several of the other chemicals tested are so strongly fixed to wood that they would not be expected to produce ZOE's. Bioassays 5 years after treatment showed that only Amical 48, Kathon 930, MGARD 553, penta, and TBTO produced measurable ZOE's in the outer core segments. All of these chemicals except MGARD 553 were oil-borne and apparently exhibited greater resistance to leaching than did the other formulations, an example of the extreme sensitivity of the Aspergillus niger bioassay to a variety of biocides.

Soil block tests 2 years after treatment showed that wafers treated with

Amical 48, 4 percent Busan 1009 plus Busperse 47, Kathon 930 with or without Busperse, TBTO, and penta had average weight losses below 10 percent in the area closest to the pole surface (Table II-5). Wafers treated with 13 other chemicals had weight losses between 11 and 25 percent in the outermost area, an indication that these chemicals provided moderate protection. Wafers treated with still another 11 chemicals had weight losses between 25 and 35 percent in the outermost area, an indication that these chemicals provided only minimal protection 2 years after treatment.

Soil block tests 5 years after treatment showed that none of the treated wafers had weight losses less than 10 percent. These results reflect the leaching severity to which the wood samples were exposed. Four chemicals provided moderate protection (weight losses 10 to 25%) 5 years after treatment. Among them were penta and Kathon 930 with or without Arquad C-50, all three of which also performed well 2 years after treatment.

Oxine copper performed far better after 5 years than it did after 2 years, just as it did in the full-scale tests. These results may reflect the usual performance of this chemical, or perhaps the wood samples removed after 5 years had retained more of the chemical than did those removed after 2 Another 10 chemicals provided minimal protection (25 to 35% weight loss) against fungal attack 5 years after application, while the remaining 16 chemicals provided no protection. Although many of the latter were moderately effective 2 years after treatment, their subsequent decline in protection suggests that they are not appropriate for the 10- to 15-year retreatment cycles currently used for this application. The results indicate that a number of chemicals are capable of providing protection to western redcedar sapwood at levels approaching those provided by penta. Many of these chemicals are susceptible to leaching and may need reapplication at shorter intervals than those formerly employed with penta.

Table II-1. Chemicals evaluated in field tests near Corvallis, Oregon, for protection of western redcedar sapwood.

Chemical	Solvent	Trade name	Source	Concentration (%)
Ammonium bifluoride	Water	Ammonium bifluoride	Van Waters and Rogers	20
3-iodo-2-propynylbutyl carbamate	Water	Polyphase	Troy Chemical Co.	2
Pentachlorophenol	Oil	<u>-</u>	Vulcan Chemical Co.	10
Pentachlorophenol	Water	Duratreat	Idacon, Inc.	10
Ammoniacal pentachlorophenol	Water	PAS	Reichhold Chemical Co.	25
Oxine Copper	Oil	Pole Spray 675	ISK Biotech	0.121 (Cu)
Oxine copper	Water	Nylate 10-BFG	Seymour Chemical Co.	0.90 (Cu)

Table II-2. Preservative formulations tested on western redcedar sapwood in small blocks.

	,			
Amical 48	Diiodomethyl p-tolyl sulfone	Akzo Chemie, N. Chicao, IL	0.5 oil ans 0.5	1.0
Arquad C-50	Trimethyl cocammonium chloride ITCAC)	"	Water	5.0
Busan 1009	Methylene bisthiocyanate and thiocyanomethyl thiobenzothiazole	Buckman Laboratories, Int., Memphis, TN	r	4.0
Busan 1009	Methylene bisthiocyanate and thiocyanomethyl thiobenzothiazole	Buckman Laboratories, Int., Memphis, TN	Water	2.0
Busan 1009 and Busperse 47 <sup>b</sup>	Methylene bisthiocyanate and thiocyanomethyl thiobenzothiazole plus Busperse	Buckman Laboratories (both)	Water	4.0 (Busan) and 5.0 (Busperse)
Busan 1009 and Busperse 47 <sup>b</sup>	Methylene bisthiocyanate and thiocyanomethyl thiobenzothiazole plus Busperse	Buckman Laboratories (both)	Water	2.0 (Busan) and 2.5 (Busperse)
Busan 1030	Thiocyanomethyl thiobenzothiazole	Buckman Laboratories (both)	Water	4.0
Busan 1030	Thiocyanomethyl thiobenzothiazole	Buckman Laboratories (both)	Water	2.0
Busan 1030 and Busperse 47 <sup>b</sup>	Thiocyanomethyl thiobenzothiazole plus Busperse	Buckman Laboratories (both)	Water	4.0 (Busan) and 5.0 (Busperse)
Busan 1030 and Busperse 47 <sup>b</sup>	Thiocyanomethyl thiobenzothiazole plus Busperse	Buckman Laboratories (both)	Water	2.0 (Busan) and 2.5 (Busperse)
Oxine copper	Copper-8-quinolinolate	Nuodex, Inc. Piscataway, NJ	Water	0.3 (Cu)
Cunap	Copper naphthenate	Tenino Wood Preservatives, Seattle, WA	Oil	2.0 (Cu)
Trade name *	Chemical name	Source	Solvent	Concentration (% a.i.)
CWP-44	Copper hydroxide/methanolamine/dimethyl dialkyl ammonium chloride	ISK Biotech., Memphis, TN	Water	10.0
Kathon 930	Dichloro-n-octyl-isothiazolone	Rohm and Haas, Inc., Inc., Spring House, PA	Oil	1.0
Kathon 930 and Arquad C-50	Dichloro-n-octyl-isothiazolone plus TCAC	Akzo Chemie and Rohm and Haas	Oil	0.5 (kathon) and 3.0 (Arquad)
Kathon 930 and Busperse 47 <sup>b</sup>	Dichloro-n-octyl-isothiazolone plus Busperse	Pohm and Hass and Buckman Laboratories	Water	1.0 (kathon) and 5.0 (Busperse)

Trade name *	Chemiogliname	Source	Solvent	Concentration (% a.t.)
MGARD 550	Zinc naphthenate	OMG Chemical Co., Cleveland, OH	Water	4.0
MGARD 553	Zinc naphthenate	OMG Chemical Co., Cleveland, OH	Water	4.0
MGARD 553	Zinc naphthenate	OMG Chemical Co., Cleveland, OH	Water	2.0
NW 100 SS	Dodecyl dimethyl benzyl ammonium salt of naphthenic acid	Nuodex, Inc. Piscataway, NJ	Oil	8.0
NW 100 WD	Dodecyl dimethyl benzyl ammonium salt of naphthenic acid	Nuodex, Inc. Piscataway, NJ	Water	8.0
Penta	Pentachlorophenol	ISK Biotech., Memphis, TN	Oil	10.0
Pole Spray 675	Cooper-8-quinolinolate	ISK Biotech., Memphis, TN	Oil	0.12 (Cu)
Trade name *	Chemical name	Source	Solvent	Concentration (% a.i.)
Polyphase	3-iodo-2-propynyl butylcarbamate	Troy Chemical Co., Rahway, NJ	Water	2.0
Polyphase and Arquad C-50	3-iodo-2-propynyl butylcarbamate plus TCAC	Troy Chemical Co. and AKZO Chemie	Oil	1.0 (Polyphase) and 3.0 (Arquad)
Polyphase and Burperse 47 <sup>b</sup>	3-iodo-2-propynyl butylcarbamate plus Bursperse	Troy Chemical Co. and Buckman Laboratories	Oil	1.0 (Polyphase) and 5.0 (Burpserse)
Rodewood SC-5033	1-{[2-(2,4-diichlorophenyl}-1,3-dioxolan-2yl]- methyl}-1H-1,2,4 triazole	Janssen Pharmaceutica, Beerse, Belgium	Water	0.3
Rodewood SC-5033	1-{[2-(2,4-diichlorophenyl)-1,3-dioxolan-2yl]-methyl}-1H-1,2,4 triazole	Janssen Pharmaceutica, Beerse, Belgium	Water	0.15
ТВТО	Tributyltinoxide	M&T Chemical, Inc. Rahway, NJ	Oil	5.0
Woodlife	3-iodo-2-propynl butylcarbamate	DAP Inc., Dayton, OH	Oil	0.5

All trade names are register except Oxine copper, CWP-44, Penta, Pole Spray 675, and TBTO.
 Chemical name unavailable from manufacturer.

Table II-3. Zone of effect (ZOE) of outer (06 mm from surface) and inner (7-12 mm from surface) segments of increment cores removed from western redcedar pole stubs 2, 8, or 11 years after application of selected external preservatives and subjected to an <u>Aspergillus niger</u> bioassay.

				Zone	Zone of effect (mm) at	mm) at indicated year and core	l core "	
			Year 2	r2	Ye	Year 8	Year 11	-
Chemical	Concentration	Solvent	Outer core segment	Inner core segment	Outer core	Inner core segment	Outer core segment	Inner core
Ammonium bifluoride	20.0	Water	0(0)	0(0)	0(0)	0/0)	0(0)	1(1)
Oxine copper	0.12 (cu)	Oil	2(3)	1(2)	2(2)	1(1)	1(1)	10)
Oxine copper	0.90 (cu)	Water	0(0)	0(0)	0(0)	0(0)	3(2)	30)
3-iodo-2-propynyl	2.0	Water	2(3)	OVO	O(O)			1
				3(3)	0(0)	v(o)	0(0)	4(2)
Pentachlorophenol	10.0	Oil	11(12)	8(8)	10(11)	7(8)	7(3)	3(2)
Pentachlorophenol	10.0	Water	6(8)	3(3)	6(6)	0(0)	5(3)	2(3)
Pentachlorophenol	2.5	Water	2(2)	0(0)	1(2)	0(0)	1(2)	0(0)
Values represent average of 12 replicates per treatment. Values in parentheses represent one dendered decision.	ates ner treatment Values	in noranthanao rannarant						2(3)

Table II-4. Percentage of weight loss in wafers removed at yarious distances from the surfaces of western redcedar pole stubs and exposed to Postia placenta in a modified soil block test conducted 2, 8, and 11 years after chemical treatment.

Chemical	Concentration	Solvent		Y	Year 2			Y.	Year 8			Year 11	=	
			0-32 mm	3.2-6.4	6.4-9.6 mm	9.6-12.8 mm	0-3.2	32-6.4	6,4-9,6	9.6-12.8	0.3.2	32-6.4	6.4-9.6	9.6-
						*****		III	IIIII	mm	mm	mm	tum	12.8 mm
Ammonium billuoride	20.0	Water	32(20)	47(10)	41(16)	46(13)	24(18)	27(20)	22(22)	20(19)	14(11)	20(11)	20(11)	23(21)
Oxine copper	0.12 (cu)	Oil	28(19)	31(21)	42(18)	27(24)	9(1)	(1)	21(15)	22(18)	33(12)	26(18)	25(12)	16/10)
Oxine copper	0.90 (cu)	Water	38(12)	45(13)	41(15)	42(12)	23(19)	27(24)	31(28)	31(29)	36(22)	31(22)		
3-iodo-2-propynyl	2.0	Water	36(15)	37(15)	40(12)	37(11)	21(19)	15(8)	31(24)	30(28)	34 <sup>b</sup>	19(7)	45(3)	25(18)
Pentachlorophenol	10.0	<u>Oi</u>	2(2)	2(1)	2(1)	13(12)	9(1)	9(2)	12(4)	10(1)	22(16)	11(10)	\$(a)	17/13)
Pentachlorophenol	10.0	Water	4(6)	21(22)	35(18)	36(19)	22(11)	24(16)	40(18)	49(12)	1977)	22(11)	37(5)	
Pentachlorophenol	2.5	Water	25(16)	35(16)	35(17)	32(19)	22(23)	34(27)	30(28)	-	25(14)			30(13)
Control c	0	ı	36(21)	<b>'</b>	<u> </u>		77/70			<b>-</b>  -		+-	┿	20(13)

There was only one sample.
 Weight loss for control wafers differ little by position and were combined for presentation.

Table 5. Zones of effect from Aspergillus niger bioassays and weight losses in a soil block test of wood samples removed from treated western redcedar blocks after 2 or 5 years of exposure.\*

MGARD 553	MGARD 550	Kathon 930/Busperse 47	Kathon 930/Arquad C- 50	Kathon 930	CWP	Cunap	Oxine copper	Busan 1030/Busperse 47	Busan 1030/Busperse 47	Busan 1030	Busan 1030	Busan 1009/Busperse 47	Busan 1009/Busperse 47	Busan	Busan 1009	Arquad C-50	Amical 48		I rade name	<b>1</b>
2.0	4.0	1.0/5.0	0.5/3.0	1.0	10.0	2.0 (Cu)	0.3 (Cu)	4.0/5.0	2.0/2.5	4.0	2.0	4.0/5.0	2.0/2.5	4	2	5	1		Concentration (%)	
Water	Water	Oil	Oil	Oil	Water	Oil	Water	Water	Water	Water	Water	Water	Water	Water	Water	Water	Oil		Solveni	2
11	0	11	9	12	0	0	4	10	11	8	10	9	10	5	7	0	18	Inner	Year 2	Zone o
7	0	10	7	11	0	0	0	2	3	1	5	4	5	1	1	0	12	Outer	ıг 2	Zone of effect (mm) at indicated year
0	0	5	2	4	0	0	0	1	1	1	1	1	. 0	1	0	0	5	Inner	Year 5	t (mm) at in year
0	0	2	2	4	0	0	0	1	_	2	1	-	0	0	0	0	1	Outer	ı; S	dicated
33	32	11	9	8	25	13	31	15	, 16	16	33	8	12	15	33	22	9	0-3.2 mm		
34	33	8	9	5	29	18	27	23	27	21	40	17	17	17	30	23	.8	32-64 mm   64-96 mm	Y	W
25	36	9	15	8	39	29	45	24	40	31	33	27	31	18	32	22	11	6.4-9.6 mm	Year 2	Wood weight lo
34	38	9	19	8	37	27	36	.25	35	26	47	26	28	16	35	20	8	9.6-12.8 mm		weight loss (%) in wafer at indicated year and distance
46	45	31	16	25	42	38	16	36	34	24	33	29	41	30	43	27	40	0-3.2 mm		at indicated
46	46	25	-31	20	27	44	17	44	47	40	28	38	36	36	37	27	33	3.2-6 4 mm	Ye	year and dista
38	34	34	25	18	28	23	19	41	36	40	39	35	41	36	24	20	33	6,4-9,6 mm	Year 5	nce
38	37	43	28	24	30	21	18	29	31	35	42	31	43	34	13	34	31	9.6-12.8 mm		

			Zoneć	Zone'of effect (mm) at indicated year	(mm) at ii year	ndicated		M	Wood weight to	weight loss (%) in wafer at indicated year and distance	at indicated	year and distar	ice	
Trade name	Concentration (%)	Solvent	Year 2	ır 2	Ye	Year 5		J.	Year 2			Yeu	Year 5	
			liner	Outer	Inner	Outer	0-3.2 mm	0-32 mm   32-64 mm   6	6.4-9.6 mm	9.6-12.8 mm	0-3.2 mm	0-3.2 mm 3.2-6.4 mm	64-9.6 mm	9.6-12.8 mm
MGARD 553	4.0	Water	7	3	2	2	24	29	31	28	44	41	40	45
NW 100 SS	8.0	Oil	1	2	0	0	11	10	21	18	32	35	24	18
NW 100 WD	8.0	Water	0	0	0	0	27	36	42	42	27	23	27	35
Penta	10.0	Oil	17	12	9	5	10	9	8	10	11	36	32	46
Pole Spray 675	0.12 (Cu)	Oil	5	0	0	0	20	17	34	34	31	27	36	<b>5</b> 0
Polyphase	2.0	Water	0	0	0	0	26	30	35	23	45	47	36	32
Polyphase/Arquad C-50	1.0/3.0	Oil	2	0	0	0	34	29	29	31	42	44	32	34
Polyphase/Busperse 47	2.0/5.0	Oil	1	4	0	1	37	35	37	32	43	40	33	36
Rodewood SC-5033	0.30	Water	0	0	0	0	32	36	28	36	38	36	24	29
Rodewood SC-5033	0.15	Water	0	0	0	1	33	35	37	47	38	41	25	29
TBTO	5.0	Oil	19	15	12	8	7	7	9	8	40	44	16	21
Woodlife	0.5	Oil	14	4	1	1	28	27	30	31	45	41	41	47
Control b	-		0	0	0	1	35	1	-	ŧ	34	1	1	1

Values represent averages of 6 replicates per treatment.
 Weight losses for control wafers differed little by position and were combined for presentation.

cultures from increment cores. Table II-6. Basidomyceles and other fungi found in preservative-treated Douglas-fir poles 6 to 13 years after bolt holes were drilled and treated in the field as shown by

Field Treatment							Perc	Percentage of cores of	ores conta	containing						
				Basidio	Basidiomycetes							Other Fungi	ungi			
	6 уг	7 уг	8 уг	9 37	10 уг	11 уг	12 уг	13 уг	6 уг	7 yr	8 yr	9 уг	10 уг	11 уг	12 yr	13 yr
Ammonium bifluoride (n=32)	0	2	0	2	2	2	2	2	5	2	16	42	9	47	39	38
Boracol <sup>®</sup> (n=32)	0	2	0	0	3	0	3	8	18	27	33	66	16	70	42	59
Patox® washer	5	5	8	14	13	11	8	14	12	22	31	66	27	55	45	48
Pentachloropheniol (n=32)	2	2	8	5	6	5	6	10	25	17	25	51	25	80	61	67
Boron (n=32)	0	0	0	2	2	2	0	3	11	25	25	37	14	75	39	59
Control (n=64)	3	9	17	9	8	11	3	5	30	26	46	70	33	86	55	81

# B. EVALUATE TREATMENTS FOR PROTECTING FIELD DRILLED BOLT HOLES

The process of drilling holes into freshly treated poles for installation of various fixtures compromises the original treatment exposing untreated wood inside to potential attack by decay fungi. Most specifications require that these holes be protected by supplemental application of a preservative, but most line personnel dislike the oil-based chemicals used for this purpose. Furthermore, it is virtually impossible to tell whether the line personnel actually treated the hole, making it a procedure which is easily overlooked during line construction. This problem will become increasingly important as holes made by cable companies age and begin to decay. There is a continuing need to identify easily applied treatments for protecting field drilled bolt holes with products which will be accepted by line personnel for all of the pole users. To this end, we continue to sample a previously established field trial of treatments for field drilled bolt holes.

The trials evaluating the effectiveness of various treatments for protecting untreated wood exposed in field drilled bolt holes were established in 1981 in a series of Douglas-fir poles which were lightly treated with pentachlorophenol in P9 Type A oil. A series of eight 2.5 cm diameter holes were drilled at 90 degree angles into the poles beginning 60 cm above the groundline and extending upward at 45 cm intervals to within 45 cm of the top. The holes were treated with 10 % pentachlorophenol in diesel oil (an accepted standard bolt hole treatment at the time of test establishment), powdered ammonium bifluoride (ABF), powdered disodium octaborate tetrahydrate (Boron), or 40 % boron in ethylene glycol (Boracol). Each treatment was replicated on 8 holes in each of 4 poles. Eight other poles were left untreated to serve as control. An additional set of 4 poles did not receive chemical treatment, but chemically impregnated washers containing 37.1 % sodium fluoride, 12.5 % potassium dichromate, 8.5 sodium % pentachlorophenate, 1 % sodium tetrachlorophenate, and 11 % creosote were used to attach bolts to these poles. The remainder of bolt holes were filled with galvanized hardware along with either metal or plastic gain plates.

For the first 5 years, increment cores were only removed from the control poles from sites directly below the gain plate on one side of the pole and from sites directly above the washer on the opposite side. The cores were cultured on malt extract agar and observed for evidence of basidiomycetes over a one month period. After 5 years, all poles were sampled annually in the same fashion.

Cultural results 13 years after treatment continue to show trends similar to those found over the last 3 years (Table II-6). The pentachlorophenol treatment continues to contain low levels of decay fungi as do the Patox treatment and the controls. As discussed in earlier reports, the penta appeared to be unable to migrate for substantial distances and was therefore unable to protect wood which was exposed beyond the original treatment hole. Despite its potent array of fungicides, the chemical in the Patox washer appeared poorly positioned to migrate into the bolt hole and was therefore ineffective. In previous sampling, the Boracol treatment provided excellent protection; however, this protection appears to be declining. Fungal levels in both the ABF and boron treatment continue to remain low, suggesting that these treatments are still providing strong protection against This degree of protection is fungal invasion. extremely important given the inability to routinely revisit bolt holes and reapply chemical to supplement the original treatment.

Levels of non-decay fungi in the various treatments continue to be high, but we have not identified this flora and, therefore do not know whether any of these fungi are altering the ability of decay fungi to colonize the substrate. Further evaluations of these poles are planned.

### **OBJECTIVE III**

#### DETECT EARLY DECAY AND ESTIMATE RESIDUAL STRENGTH OF WOOD POLES

Although the majority of effort on the Cooperative involves the development of improved remedial treatments, it is also important to ensure that poles are initially specified properly and that there are methods for detecting decay and other defects before substantial damage occurs. We are continually seeking new devices which can be used to evaluate the internal condition of wood poles, particularly those which can do so in a non-destructive manner. This past year, no new devices were evaluated, however, we are seeking two new acoustic devices for evaluation and hope to have results for the next report. In addition, we continue to evaluate methods for improving the treatment of Douglas-fir poles while maintaining maximum wood strength. This year we continued our efforts to identify improved patterns for through-boring.

# A. THROUGH BORING OF DOUGLAS-FIR POLES USING REDUCED HOLE PATTERNS

Through boring is widely used for improving the treatment of Douglas-fir poles at the groundline and this practice has markedly reduced the levels of internal decay in poles of this species. Many utilities continue to resist the use of through boring because of concerns about the potential strength impacts of this practice. In 1994, reported we on the retentions pentachlorophenol in Douglas-fir poles receiving conventional through boring patterns employed by Bonneville Power Administration and Portland General Electric

as well as patterns with slightly wider hole spacings ('94 Annual Report, pages 50-51). The results indicated that penta levels were well above the threshold for fungal attack well into the wood. As a result of these trials and the results of a survey which indicated the absence of decay in the through bored zone of Douglas-fir poles, even when untreated skips were present, we explored further expansion of the through boring patterns.

A series of 20 freshly peeled Douglas-fir pole sections (25 to 30 cm in diameter by 3 m long) were obtained from a local treater. The sections were end-coated with GacoFlex to retard end checking. The pole sections were then divided into 600 mm long zones beginning 300 mm from each end. The 300 mm zone on each end along with the end coating was intended to retard endpenetration which might interfere with the through boring pattern. These zones were then randomly assigned to one of 10 treatment groups (Table III-1, Figure III-1)). The poles were through bored using a 10.9 mm diameter drill bit. Each pattern was replicated on 6 sections.

The poles were then treated with pentachlorophenol to a nominal retention of 7.2 kg/m³ in a commercial treating cylinder using a cycle typical of that used to treated utility poles. Following treatment, the effect of the various through boring patterns on treatment was assessed by removing increment cores from the middle of each of the diamond shaped through boring patterns. Preservative penetration was then visually

assessed on each core. The depth and locations of any untreated wood was recorded. The cores were then divided into zones corresponding to 0 to 25 mm, 25 to 62.5 mm, and 62.5 to 125 mm from the wood surface. Segments from a given zone from cores from the same pole section were combined and ground to pass a 20 mesh The resulting material was then screen. analyzed using an ASOMA 8620 x-ray analyzer. fluorescence Preservative penetration was generally good in all of the through bored sections, with average percent penetration ranging from 92 to 100 % (Table Ш-2).

Penetration did vary more widely as pattern distance increased, with the highest variably in pattern 9. This pattern had the greatest longitudinal distance between holes. Even within this pattern, however, the average degree of penetration in the sections ranged from 86 to 100 percent of the cross section. The effects of treatment skips performance of through-bored poles remains unknown. In principle, a skip which was otherwise surrounded by treatment would have only a minimal risk of decay. If decay occurred, it is likely to have little effect on overall pole strength owing to the small size of the skips. This, a requirement

Table III-1. Through boring patterns tested for improving the treatment of Douglas-fir pole sections.

	Distance (mm) along side *										
Pattern	A	В	С	D							
1	114	250	38	83							
2	135	250	45	83							
3	114	270	38	90							
4	135	270	45	90							
5	114	300	38	100							
6	135	300	45	100							
7 .	135	360	45	120							
8	135	390	45	130							
9	135	400	45	140							
10	-	<u>-</u>	<u>-</u>	-							

<sup>&</sup>lt;sup>a</sup> For explanation of sides, see Figure III-1.

for 100 % treatment of the through-bored zone may be excessive in terms of improving pole service life. A more reasoned approach may involve the specification of a minimum zone where complete treatment without skips is required (for example, 0 to 50 mm), followed by a percentage of minimum penetration for the remaining inner core (80 to 90 %). In this way, the specification ensures that the most important segment of the pole for mechanical properties is thoroughly protected.

Small skips deeper in the pole should not adversely affect performance. One advantage to this approach is the ability to spread the through boring pattern across the pole, thereby reducing any potential strength impacts.

Penta retentions tended to be fairly even with depth in the pole, although the retentions varied somewhat among the various patterns (Table III-3). The current American Wood Preserver's Association Standards specify a retention of either 3.7 or 4.8 kg/m<sup>3</sup> depending on whether the outer zone retention is 7.2 or 9.6 kg/m<sup>3</sup>. The threshold for fungal attack with

Table III-2. Average penetration of pentachlorophenol in Douglas-fir pole sections with various densities of through boring.

Boring pattern *	Pre	servativ	e penetr (%	ation by	pole se	Average preservative	Range	
	1	2	3	4	5	6	penetration (%)	
1	100	100	100	100	100	100	100	100
2	100	77	77	100	100	97	92	79-100
3	100	100	100	96	100	100	99	85-100
4	100	100	100	100	97	100	99	79-100
5	100	95	95	89	98	100	95	70-100
6	100	100	99	100	100	98	99	96-100
· 7	94	100	100	100	100	95	98	79-100
8	100	100	97	98	94	75	94	31-100
9	100	90	93	86	96	100	94	14-100
10	47							

a See Table III-3 for code to patterns.

Table III-3. Pentachlorophenol retentions in Douglas-fir poles receiving various through boring patterns.

Boring pattern *	Preservative (pcf) retention by assay zone (mm)										
	0-25	25-62.5	62.5-125.0								
1	8.2(1.8)	5.2(2.4)	6.7(1.9)								
2	15.2(2.5)	6.8(1.5)	5.1(2.3)								
3	7.5(1.2)	5.6(0.9)	7.0(1.9)								
4	8.9(2.2)	6.2(2.0)	6.1(1.8)								
5	9.7(1.8)	6.7(1.1)	6.3(2.2)								
6	9.9(1.7)	8.1(2.8)	6.5(1.8)								
7	9.1(2.7)	5.9(2.4)	5.6(2.6)								
8	7.7(1.7)	6.8(1.4)	7.1(2.2)								
9	5.2(1.3)	4.1(1.5)	4.4(1.5)								
10	5.7(1.0)	3.6(20)	2.8(1.3)								

See Table III-3 for code to patterns.

pentachlorophenol in soil block tests ranges from 3.2 to 4.0, depending upon the test conditions, so a internal retention of 3.2 to 3.7 would seem to be a reasonable target for preventing internal attack in the through bored zone. Using this range as a target value, it all of the test patterns produced retentions in the inner assay zone which exceeded the minimum protective level. These results suggest that adequate loadings of penta can be delivered into the wood with virtually all of the through boring patterns tested, although pattern # 9 would appear to produce results which were close to the threshold value.

Along with relatively high retentions in the inner zone, the through bored poles tended to have relatively shallow preservative gradients from the outer to inner zones (Figure III-2), reflecting the longitudinal penetration associated with the through borings.

As a result, it is likely that any skips in treatment would be surrounded by preservative treatment at levels far above those generally thought to represent a threshold for this chemical.

b Values represent means of 6 replicates/zones. Figures in parenthese represent one standard deviation.

Figure III-1. Sample of through boring pattern employed to improve treatment of Douglas-fir pole sections.

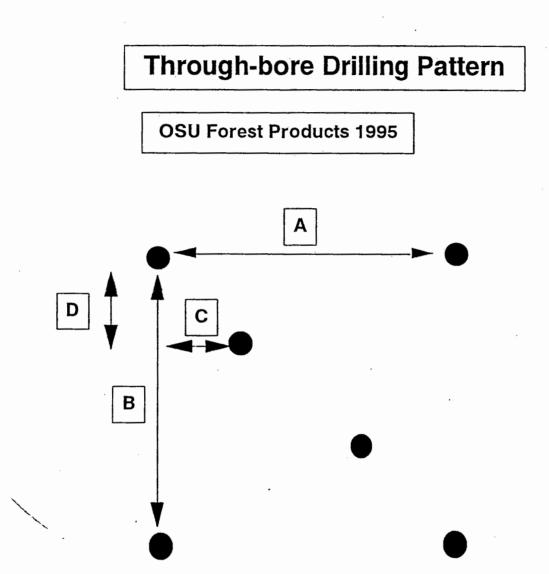
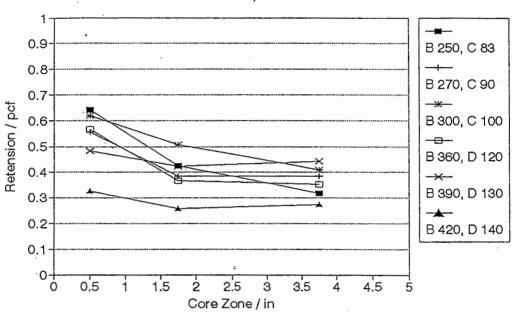


Figure III-2. Pentachlorophenol retentions at selected depths in Douglas-fir poles receiving different through boring patterns.

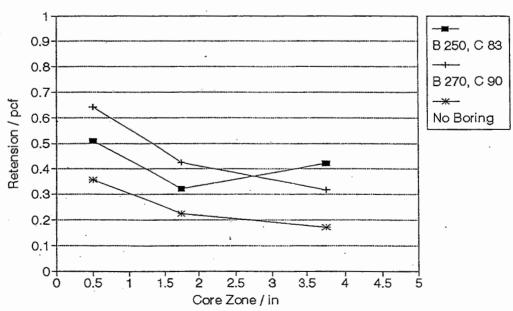
## Through Boring Penta Treatment

A: 135 mm, C: 45 mm



## **Through Boring Penta Treatment**

A: 114 mm, C: 38 mm



# OBJECTIVE IV EVALUATE THE POTENTIAL FOR DECAY DEVELOPMENT DURING AIR SEASONING AND IDENTIFY CONTROL STRATEGIES

The cooperative has been involved with the fungi which colonize air-seasoning Douglas-fir poles since 1981. We have identified the fungi which invade poles at various sites, characterized their effects on wood, and explored the temperatures required for eliminating these fungi once they become established. In addition, we have studied techniques for preventing fungal colonization during the air seasoning process including short dips and sprays in either boron or fluoride. These diffusible fungicides have the potential to move with moisture into the wood as checks and other seasoning defects open. **Preliminary** studies with ammonium bifluoride showed that a short dip in a 20 % dip of this chemical limited fungal colonization for up to 2 years. Similar trials with boron were less effective, but they illustrated the potential for boron as an air-seasoning To further these efforts, the treatment. following trials were performed.

### A. IDENTIFY METHDOS FOR PREVENTING OR ELIMINATING FUNGAL COLONIZATION IN AIR-SEASONING DOUGLAS-FIR POLES

1. Use of borate thermal treatments to eliminate fungi from freshly peeled Douglas-fir logs: The inability to effectively limit fungal colonization during air seasoning has encouraged a search for alternative treatment technologies. One potential mitigation alternative is dip diffusion in a water soluble fungicide such as boron or flouride shortly after bark

removal. The fungicide can then diffuse with any free water present in the wood, presumably completely penetrating the log. Previous studies suggest that conventional dip treatments may not deliver adequate loadings of boron on the wood surface for subsequent diffusion, however, thermal treatments may enhance initial uptake, providing a larger reservior for diffusion. Previous studies with southern pine suggest that steaming enhances uptake in this manner, but there are no reports on other less permeable species. In the report we describe the results of a series of thermal boron treatments on Douglas-fir log sections.

Ideally, logs of species destined for importation into the United States should be used for such trials, however, these species can not currently be imported without treatments to limit pests and such treatments might alter the subsequent receptivity of the logs to boron. Furthermore, the long delays in shipping could permit drying which might adversely affect boron diffusion. Freshly peeled Douglas-fir (250-300mm in diameter) were cut into 600mm long sections. The sections were end-sealed with a two-part epoxy to retard longitudinal penetration of solution and cured for a minimum of 24 hours at room temperature. Care was taken to cover the sections during curing to retard surface drying. Selected log sections were also equipped with copper constantin thermocouples embedded to depths of 50, 100 and 150mm from the wood surface. These thermocouples were connected to a CR-21X datalogger and were used to

measure heat changes during and after treatment as previously described. sealed log sections were used to evaluate a variety of potential thermal treatment combinations (Table IV-1). For each treatment, three logs were immersed in a large vat containing a 20 or 40% solution (boric acid equivalent) of disodium octaborate tetrahydrate (DOT). Following heating, the logs were immersed in a cooler bath containing 25% BAE of DOT. Each treatment was replicated twice on a total of 6 log sections. The log sections were then stored outdoors under plastic to retard drying. Boron movement was assessed 30, 60 and 90 days after treatment by removing 150mm long increment cores from locations randomly selected around each log.

The cores were then divided into zones corresponding 0 to 12.5, 12.5 to 25, 25 to 50, 50 to 100, 100 to 150, 150 to 200, 200 to 250 and 250 to 300mm from the wood surface.

Segments from cores from a given log section were combined and ground to pass a 20 mesh screen prior to analysis for boron according to the Azomethine-H method. Retentions were then calculated on a %BAE/wood weight basis. For practical purposes, the threshold for boron against most wood degrading fungi ranges from 0.25 to 0.60% BAE depending on the wood/fungal species combination.

Table IV-1. Borate treatment regimes applied to Douglas-fir logs.4

	First Treatmer	Ą	Second Treatment							
Boron concentration (%BAE)	Bath temperature	Immersion Time (minutes)	Boron concentration (%BAE)	Bath temperature	Immersion Time (minutes)					
20	40	10	20	20	60					
20	60	60	20	20	60					
20	60	120	20	20	60					
20	80	60	20	20	60					
20	80	120	20	20	60					
. 40	80	60	40	20	60					
40	80	120	40	20	60					
40	80	180	40	20	60					

<sup>\*</sup> Each treatment was replicated on 6 log sections treated in two batches of 3 sections each.

2. Internal temperature monitoring: The initial log temperatures ranged from 10 to 20C, a range somewhat above that which might be found on logs in many countries during a typical winter. Thus, our data

should be considered optimistic with regard to the degree of heating possible through thermal boron treatment. Thermal treatment at 40C had minimal effect on internal temperature, reflecting the relatively small

difference between the bath and the starting temperature of the wood. (Figure IV-1.) Heating for two hours at 60C resulted in a temperature of 47C fifty mm from the wood surface but temperature at the pith failed to reach 30C in the same logs (Figure IV-2). Exposure to 80C produced the most marked effect on internal temperature. Temperatures 50mm from the surface approached 60C after 2 hours of immersion and 60 to 65C after 3 hours (Figure IV-3). Internal temperatures 100 or 150mm from the surface, however, never exceeded 45C, suggesting that thermal treatment with boron under the conditions employed would have little effect on survival of pests deep in the wood. The treatment regimes were selected to provide a broad range of possible treatment scenarios. Given the large volumes of wood which would need to be treated at a typical facility and the energy costs associated with such treatments, it is doubtful that such facilities would choose longer thermal periods, although such treatments would eventually produce effective heat sterilization to the desired depths.

Figure IV-1. Internal temperatures at selected depths in Douglas-fir log sections during thermal treatment at 40C for 10 minutes with 20% boron.

Hot Tank; 40C; 10 Min.; 20%

Cold Tank: R.T.; 1 Hour; 20%; 1-13

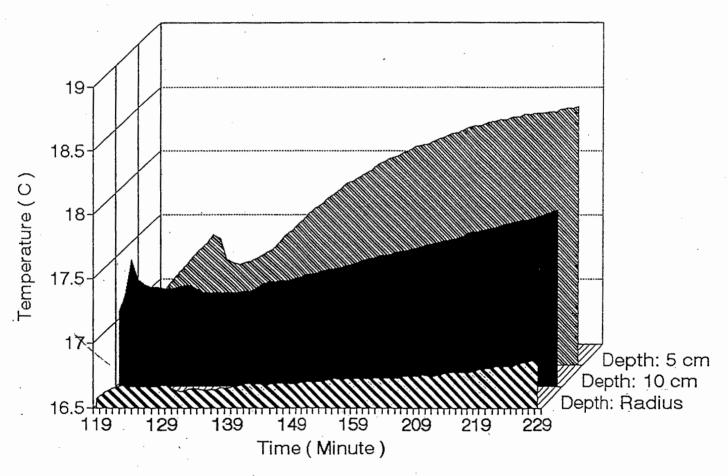
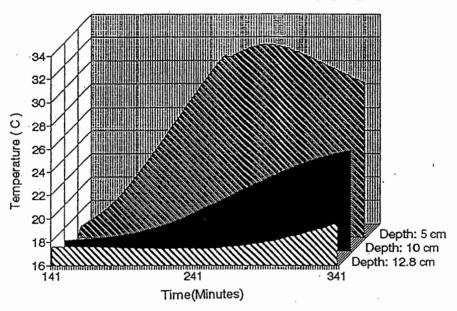


Figure IV-2. Internal temperatures at selected depths in Douglas-fir log sections in a thermal treatment at 60C for a) 60 or b)120 minutes with a 20% BAE solution.

Hot Tank: 60C; 1 hour; (20%); Cold Tank: R.T.; 1 hour; (20%); [2-4]



Hot Tank: 60C; 2 hours; (20%); Cold Tank: R.T.; 1 hour; (20%); [4-1]

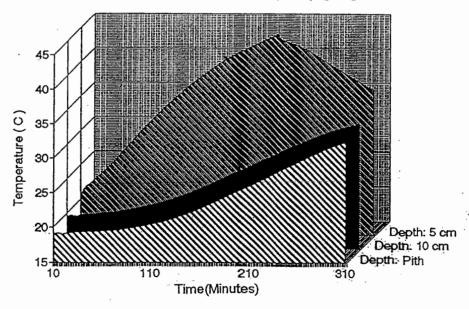


Figure IV-3. Internal temperatures at selected depths in Douglas-fir log sections during thermal treatment at 80C for a)60, b)120, or c)180 minutes with 40% BAE solution.

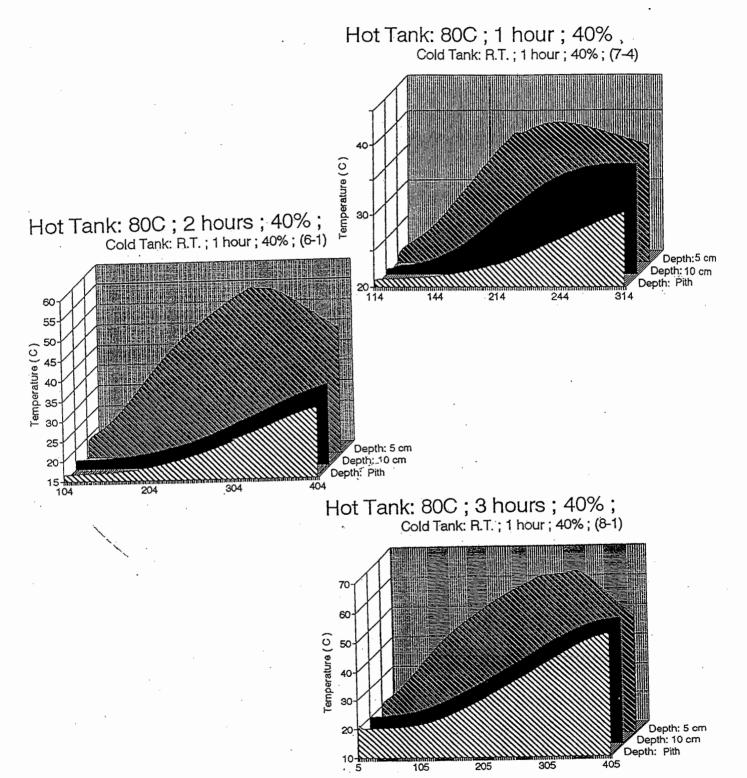
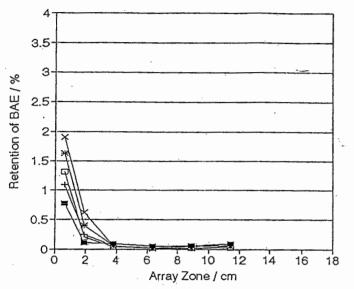


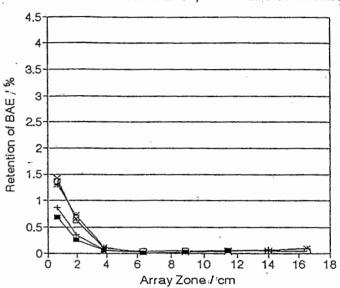
Figure IV-4. Residual boron levels (% boric acid equivalent) at selected depths in Douglas-fir log sections treated with various thermal boron schedules using 20% BAE DOT and storing for: a) 30 days, b) 60 days or c) 90 days after treatment.

# Boron Retention 30 days Conc. 20%, Cold 20 C X 60 min.



## Boron Retention 60 days

Conc. 20%, Cold 20C X 60 min.



## Boron Retention of Timber Log, 90 days Conc. 20%, Cold 20 C X 60 min.

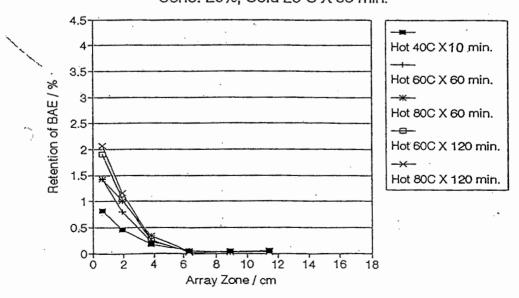
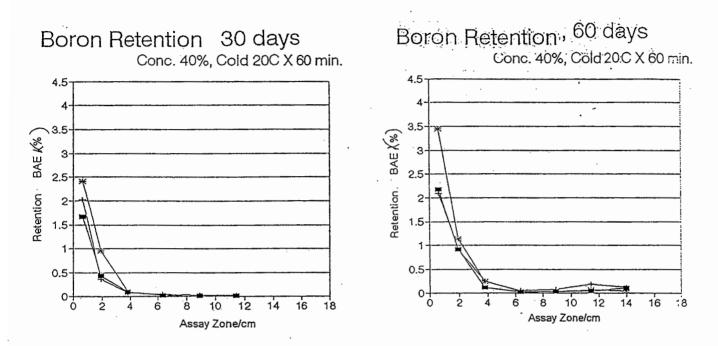
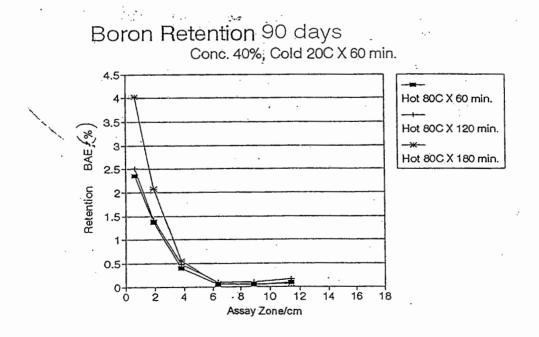


Figure IV-5. Residual boron levels (as % boric acid equivialent) at selected depths in Douglas-fir log sections treated with various thermal boron schedules using 40% BAE DOT and storing for: a) 30 days, b) 60 days or c) 90 days after treatment.





Incomplete heating Boron\_diffusion: during thermal processing may be acceptable if subsequent diffusion of boron results in complete penetration of the chemical at levels capable of eliminating established fungal or insect infestations. While boron concentrations nearest the surface were generally above those required for effective control of many pests, the boron levels declined precipitously with distance from the wood surface (Figures IV-4 and 5). Borate levels were generally higher in log sections treated at the higher DOT concentrations, but doubling the treatment solution concentration did not always result in twice as much chemical in the wood. This effect suggests that some screening of boron occurs as the solution enters the wood. This would be due to the different viscosities of the treating solutions, or differences in diffusivity due to the different concentrations.

As expected, boron levels tended to increase at selected depths into the wood with increasing diffusion time, but there was little evidence of boron penetration beyond the 50 to 100mm assay zone even at the highest solution concentration, highest temperature and longest immersion period. While prolonged diffusion storage might improve the internal boron levels, it is doubtful that exporters would be willing to hold 3 to 6 months of log production under cover to retard drying and facilitate diffusion to a degree necessary to achieve enhanced boron movement.

As expected, the upper thermal temperature tested (80°C) produced the best results in terms of residual boron levels, although the differences were sometimes slight and were often only evident upon prolonged diffusion (Figure IV-5). While slightly higher temperatures might further enhance uptake, the evaporation rate from the treatment tanks might pose difficulties with regard to main-

taining a stable solution.

The inability of boron to diffuse through Douglas-fir heartwood at biocidal levels may reflect either the inherent impermeability of the species or variations in wood moisture content. Douglas-fir heartwood ranges from moderately permeable to virtually impermeable to penetration of liquids. In a number of tests, this species appears to be less amenable to diffusion treatments than many pines including Pinus sylvestus, a species also known for its resistance to heartwood It is possible that heartwood penetration. extractives deposited on pit membranes interfere with boron diffusion. Another factor potentially affecting boron movement is wood moisture content. The logs in the current test had initial moisture contents ranging from 80 to 100% in the sapwood and 40-50% in the heartwood. While some drying likely occurred as the end coating cured, the logs were covered with plastic to minimize this risk and were otherwise sprinkled to maintain wood moisture levels. Thus, the moisture profiles were likely typical of those which would be present in a freshly peeled log. In addition, the trials occurred between January and March, when the test site received nearly 750mm of rain. The initial moisture levels were well above those considered necessary for boron diffusion.

The inability of thermal treatments to markedly affect temperature beyond 50mm from the surface and the generally poor diffusion of boron inward following treatment suggest that thermal boron treatments cannot serve as a stand alone treatment for mitigating the risk of pest introduction in imported logs. Further studies related to the efficacy of such treatments in more permeable wood species with higher initial moisture levels more suited to boron movement may, however, be worthwhile.

#### OBJECTIVE V

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

The presence of a well-treated preservative shell is normally an excellent barrier against fungal attack. As poles age or when they are placed in environments such as concrete sidewalks where they cannot be inspected below the groundline, it is sometimes advisable to provide supplemental protection to the wood surface. For many years, this supplemental protection consisted of combinations of pentachlorophenol, creosote, sodium fluoride and an array of other compounds. In principle, these multicomponent systems were designed to have water soluble components which could diffuse for short distances into the wood to eliminate fungi and an oil soluble component which remained near the surface and prevented renewed invasion from the surrounding soil. The U.S. Environmental Protection Agency decision to restrict the use of creosote, penta and the inorganic arsenicals encouraged the development of alternative systems without these compounds. In general, new formulations employed combinations of copper naphthenate, boron and sodium fluoride. While each of these compounds is a proven fungicide, there was little data on the performance of these compounds in groundline bandages.

### A. PERFORMANCE OF MODIFIED GROUNDLINE PRESERVATIVE SYSTEMS IN CORVALLIS, OR

Douglas-fir poles sections (25 to 30 cm in diameter by 1.8 m long) were seasoned for 6 months then treated with one of the following formulations:

CUNAP WRAP (CSI) containing 2.0 % copper naphthenate (as copper) on an absorbent pad.

CuRAP 20 (ISK Biotech) a paste containing 18.16 % amine based copper naphthenate and 40 % sodium tetraborate decahydrate.

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

COP-R-Plastic (Osmose Wood Preserving Inc.) a paste containing 19.25 % copper naphthenate and 45 % sodium fluoride.

Pole-Nu 15-15 (ISK Biotech) a grease containing 12.9 % pentachlorophenol, 15 % creosote, and 1.5 % chlorinated phenols.

Pole Nu (ISK Biotech) a grease containing 10.2 % pentachlorophenol.

The latter two formulations were included to provide comparisons between the new and old formulations. Each formulation was evaluated on 5 pole sections.

All formulations were applied according to the manufacturer's instructions. All but the self-contained CUNAP WRAP were covered with polyethylene film prior to being set to a depth of 45 cm in the ground. The pole tops were then capped with roofing felt to retard wetting from above. The test site receives an average of 105 cm of rainfall per year, mostly between November and May. Site conditions were described in previous reports ('94 Annual Report pages 71-72). Of some importance was a long period of below average rainfall for the first 3 years of the test. For the last 2 years, however, rainfall has been slightly above average.

Preservative performance has been examined 18, 30, 42, and 54 months after treatment by removing increment cores or 1 cm diameter plugs from 3 equidistant sites

around each pole section 15 cm below the groundline. These samples were then divided into zones corresponding to 0 to 4, 4 to 10, 10-16, and 16-25 mm from the wood surface. Zones from pole sections with the same treatment were combined and ground to pass a 20 mesh screen.

Copper and pentachlorophenol containing samples were analyzed using an ASOMA 8620 x-ray fluorescence analyzer (XRF). Boron containing samples were analyzed using the Azomethine H method as described previously ('92 Annual Report, page 73). Fluoride analyses were performed by Mr. Richard Ziobro (Osmose Wood Preserving Inc) on a blind sample basis using American Wood Preservers' Association Standard A2 Method 7.

Chemical levels in the pole sections continue to decline in most zones 5 years after treatment (Table V-1), although there are some exceptions. Pentachlorophenol levels in both Pole Nu formulations declined this paste year, with the Pole Nu 15-15 declining by over 50 % in the outer zone. Pole Nu declined by only 28 % in the same zone. The reasons for the more rapid decline with Pole Nu 15-15 are unclear since both formulations contain approximately the same level of penta. Both chemical levels near the surface are currently below those considered the threshold for penta for protecting wood against fungal attack. In practice, residual preservative from the original treatment would also be present, thereby prolonging the protective period; however, our results suggest that the benefits of the remedial treatment have declined substantially within 5 years of application. Chemical levels further into the wood are generally also low and indicate that the protective effect of both of these formulations is limited to a shallow surface zone in Douglas-fir.

Copper analyses of the various copper naphthenate treatments showed a similar variation in protection. For comparative purposes, we will use the ground contact retention of copper naphthenate for wood poles as specified in the AWPA Standards as our threshold for protection (0.96 kg/m³). Based upon this value, all four copper based biocides continue to provide protection with copper levels in the outer (0 to 4 mm) assay zone ranging from 1.14 to 3.63 kg/m³. Copper levels tended to decline with depth, with little detectable copper beyond 10 mm from the surface.

As with the copper compounds, boron in the CuRAP 20 formulation has declined to detectable limits across the assay zone. This compound is water diffusible and its rapid loss over the past 2 years is not surprising given the above average rainfall at the test The absence of boron near surface leaves this treatment as essentially a single biocide wrap system, although copper levels in the zone nearest the surface remain those required for fungal protection. Unlike boron, fluoride remains in the Cop-R-Plastic treated poles at levels well above those required for fungal protection. Although fluoride levels have declined in the inner zones, they remain relatively high nearest the wood surface. When combined with the copper naphthenate in this system, the total chemical loadings are well above those required for preventing fungal attack.

The results indicate that biocide levels in all of the formulations continue to remain at or above the threshold for fungal attack. The lowest protective levels were found with the two penta based systems, while the copper naphthenate/sodium fluoride based system had the highest chemical loadings 4.5 years after treatment. The poles in this test have begun to decay above the groundline and it is

likely that they will be sampled only one more time before they become too badly decayed for further use.

### B. PERFORMANCE OF MODIFIED EXTERNAL PRESERVATIVE BANDAGES ON DOUGLAS-FIR, PONDEROSA PINE, AND WESTERN REDCEDAR IN CALIFORNIA

The field trials established in Oregon have proven useful for evaluating the ability of the various modified groundline systems to move through otherwise untreated Douglas-fir sapwood, but a number of questions have arisen concerning the validity of this data with regard to poles with a preservative treated shell or to poles of other species. To help answer these questions, a series of Douglas-fir, ponderosa pine and western redcedar poles located in the Pacific Gas & Electric system near Merced, CA were pre-sampled by removing increment cores from sites around the groundline. These cores were ground to pass a 20 mesh screen and analyzed for pentachlorophenol by x-ray fluorescence. The results of the analyses were used to segregate the poles into 3 groups of nine poles per wood species so that each group had the same approximate preservative retentions.

The poles were then treated with CUNAP wrap (CSI), CuRAP 20 (ISK Biotech), or Patox II (Osmose Wood Preserving Inc.). The CUNAP and CuRAP formulations were described in Section A, while Patox II contained 70.3 % sodium fluoride. The systems were applied to the zone extending from 8 cm above to 45 cm below the groundline.

The poles were sampled 1, 2, and 3 years after treatment by removing increment cores or plugs from three sites 120 degrees apart 15 cm below the groundline on one

third of the poles in a given treatment. This frequency of sampling was established to minimize the potential strength effects on any single pole. The cores were then divided into zones corresponding to 0-4, 4-10, 10-16, and 16-25 mm from the pole surface and zones from a given pole were combined prior to being ground to pass a 20 mesh screen. The wood was then analyzed for copper, boron, or fluoride as described in Section A of this Objective.

Analyses indicated that copper levels were highest in the CuRAP 20 treatments, while those in the CUNAP Wrap were at the threshold for fungal attack in ponderosa pine and slightly below the threshold for Douglasfir and western redcedar (Figure V-i). The reasons for these variations are unclear particularly given the similar performance of these systems in the Corvallis test. Copper levels tended to follow a steeper gradient in the CuRAP 20 treated poles, while the gradient in the CUNAP Wrap poles was slight to flat. Interestingly, the copper levels were highest in ponderosa pine. This effect was most noticeable in the CUNAP Wrap treated poles.

Boron levels in the CuRAP 20 were lowest in the Douglas-fir poles and highest in the western redcedar (Figure V-2). general, boron levels declined markedly in all species over the last year. This effect was most noticeable in Douglas-fir. Boron levels in the ponderosa pine poles were lowest near the surface and increased slightly into the inner sampling zone. This gradient suggests that the boron originally present in the wrap has been depleted. Boron levels in the western redcedar were fairly uniform. This species has a very thin sapwood (<12 mm thick) and an impermeable heartwood. It is possible that this combination has helped maintain boron at a higher level than in the

more permeable wood species.

Fluoride levels in Patox II treated poles were well above the threshold near the wood surface, and declined steadily with increasing distance from the surface (Figure V-3). Fluoride levels were relatively similar among the three wood species, although levels in ponderosa pine were slightly higher than those in the other two species. Unlike the boron analyses, fluoride levels did not appear to experience the marked decline between years 2 and 3 in either Douglas-fir or ponderosa pine (western redcedar was not sampled in year 2 owing to a difficulty in obtaining solid cores). This formulation has high levels of fluoride which should provide a large reservoir to replenish chemical which is lost through diffusion deeper in the wood as well as that which is leached from the pole into the surrounding soil. At present, it would appear that the reservoir remains adequate for providing protection to the wood surface. One interesting finding with these trials is the lower levels of fluoride present in comparison with those at the Corvallis site at similar time points after treatment, despite the presence of higher fluoride levels in the Patox II treatments. The reasons for this variation are unclear, although they may reflect relative fluoride availability in each of the formulations.

The results of the California trial tend to follow those of the Oregon studies, although the rates of chemical loss differ slightly. This study will be sampled in 1996 to assess the 5 year release rates.

#### C. PERFORMANCE OF GROUNDLINE BANDAGES IN SOUTHERN PINE AND WESTERN REDCEDAR POLES

While the California and Oregon studies of groundline bandages have provided useful data, most bandages used in North America are applied to southern pine poles. In order

to develop better data on this species, a series of southern pine and western redcedar poles in service for periods ranging from 10 to 70 vears were identified near Binghamton, NY. The test line contains a total of 15 cedar and These poles will be 27 pine poles. remedially treated with CuRAP 20, CUNAP Wrap, or COP-R-RAP as described above. The poles will then be sampled to determine chemical movement 1, 2, and 3 years after treatment by removing cores or plugs 15 cm below the groundline or as close to that zone as possible. The cores will be divided into zones corresponding to 0-4, 4-10, 10-16, and 16 to 25 cm from the wood surface as described above prior to grinding and analysis for the various bandage components. In addition, an inner 25 to 50 mm assay core will be taken from the southern pine poles to assess movement deeper in the poles. These poles were scheduled to be treated in October of this year.

#### D. IDENTIFY THRESHOLD VALUES FOR MIXTURES OF SELECTED GROUNDLINE PRESERVATIVE SYSTEMS

In last year's report, we described trials to identify threshold values for the various groundline preservative systems using a soil burial trial ('94 Annual Report, pages 111-115). These trials were completed, but the results suggested that there might be some treatment anomalies. This trial is in the process of being repeated. Weight losses in untreated control blocks after 16 weeks ranged from 5 to 9 percent. This level was deemed too low for assessing differences in performance. As a result, the blocks will be incubated for an additional 6 weeks to ensure that the test is sufficiently rigorous. Results from these trials will be reported in the 1996 Annual Report.

Table V-1. Chemical content at selected depths from the wood surface of Douglas-fir post s 18, 30, 42, or 54 months after treatment with selected groundline bandage systems.

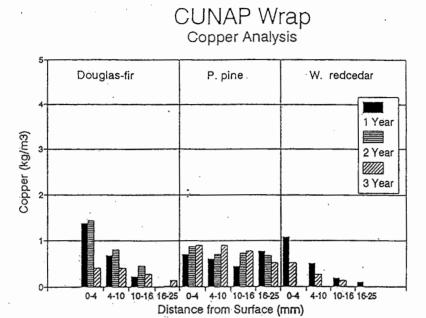
A CONTRACTOR OF THE PROPERTY O

			Pol-Nu 15-15			PLASTIC	COP-R-				CuRAP 20				Cop-R-Rap				CUNAP		Tramen	Chemical	
54	42	30	18	54	42	30	18	54	42	30	18	54	42	30	18	54	42	30	18		(months)	Exposure	
:	:	:	:	3.63	2.88	2.88	3.84	1.43	2.88	2.40	3.36	1.14	2.40	2.24	2.72	1.54	2.24	1.600	2.56		# 94		
:	:	1		1.13	0.96	0.64	1.12	0.32	0.48	0.48	0.80	0.67	0.64	0.64	0.64	1.23	1.76	1.28	1.60	G.	#10 dum	Coj	
1	:	1	1	0.47	0.48	0.32	0.48	0	0.16	0.16	0.16	0.52	0.32	0.32	0.32	1.71	0.96	0.64	0.80	(kg/m²)	10-16 mm	Copper	
:	:	:	ı	0.15	0.32	0.16	0.16	0	0	0	0	0.28	٥	0	۰	0.51	0.48	0.16	0.32		16-25 mm		
0.73	1.60	2.40	3.36	t	1	1	,	,	.1	ı	,	,	,		,	1	1	1	1		0-4 mm		
0.56	0.96	0.96	1.44	ı	,	,	,	,	1	1	, ,	,	,	,	1	i .	1	,	,	(kg/m²)	4-10 mm	PENTA	Average C
0	0.32	0.32	0.48	-	1	'	-	ı	1	ı	,	1	;	1	;	1	1	1	,	m,	10-16 mm	ΑF	Average Chemical Level
0	0.16	0.16	0.16	1	,	1	١	-			,		1	;	1	١	ı	,			16-25 mm		ć.
:	;	1 2	1	1	<u> </u>			0.07	0.15	0.27	1.75	1	,	1	1	1	'	'	<u> </u>		mm 0.4		
1		;	1	,	ı	1	1	0.05	0.22	0.27	1.41	,				,	1	,	,	(ЯВАЕ)	4-10 mm	Boron	
:	1	1		1	1	1	-	0.04	0.26	0.28	0.87	;	1	-	1	1		1	1	A.E.	10-16	8	
-	-	1	,	1	١	-	;	0.05	0.17	0.23	0.51	1	,	'	'		-				16-25 mm		
:	ı	1	<u>'</u>	1.45	1.32	2.38	2.38		1	ı	:	ı	'	1		<u> </u>	1	,	ļ,		m 04		
-	:	1	<u> </u>	0.55	0.71	1.23	1.21		'		1	1	'	-	ļ, 	Ŀ		<u> </u>		(%BAE)	4-10 mm	Sodium Fluoride	
-	;	,	۱,	0.39	0.57	0.81	0.55	-	<u>                                     </u>	'	<u>'</u>	١.	<u> </u>	<u> </u>	'	1	ŀ	. 1	,	(3)	10-16 mm	luoride	
1	,	1	1	0.19	0.52	0.55	0.35	1	,			ı	ı	-	<u> </u>	1	,	!	ı		16-25 mm		

			Pol-Nu	Chemical Treatment
54	42	30	18	Exposure Period (months)
-	i	:	1	12
		:		Copper 4-10 1 (kg/m²)
-		ı	١	mm 0-16
:		<u> </u>	<u> </u>	16-25 mm
1.98	2.72	4.32	6.24	0-4 mm
1.03	1.44	1.76	2.56	Average Chemical Level  PENTA  #10 10-16 mm mm mm
0.20	0.32	0.64	0.80	emical Lev
0	0.16	0.16	0.16	16-25 mm
i 	1	1	1.	0.4 mm
1	ı	1	1	Boron 4-10 1 mm 1
	,	1	1	mm 0-16
<u> </u>	1	<u> </u>	ı	16-25 mm
		'	1	0.4 mm
1	 	1	1	Sodium Fluoride 4-10 10-16 mm mm
-	I	1	ı	
ı	'	1	ı	16-25 mm

<sup>\*</sup> By distance (mm) from wood surface.

Figure V-1. Copper levels in Douglas-fir, western redcedar, and ponderosa pine poles 1 to 3 years after treatment with CuRAP 20 or CUNAP Wrap.



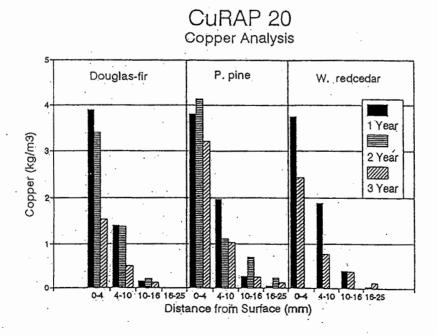


Figure V-2. Boron levels in Douglas-fir, western redcedar, and ponderosa pine poles 1 to 3 years after treatment with CuRAP 20.



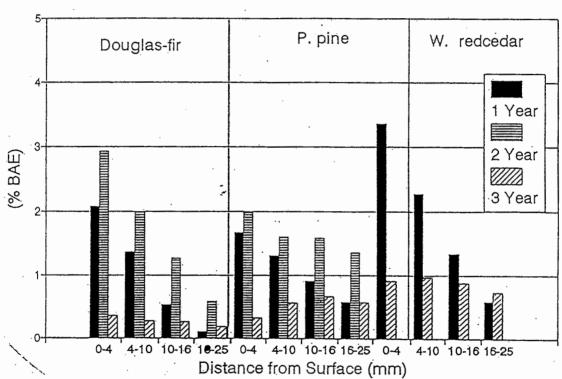
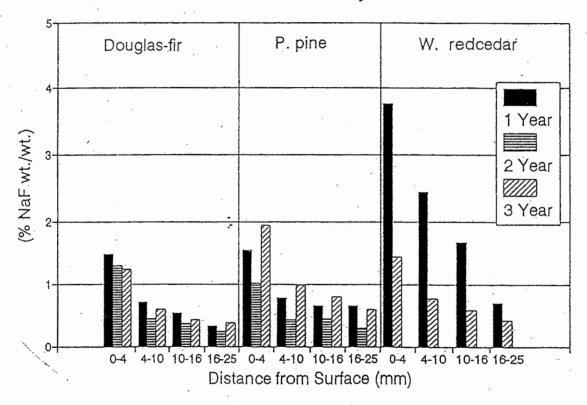


Figure V-3. Fluoride levels in Douglas-fir, western redcedar, and ponderosa pine poles 1 to 3 years after treatment with Patox II.

## Patox II Fluoride Analysis



#### OBJECTIVE VI

#### PERFORMANCE OF COPPER NAPHTHENATE TREATED WESTERN WOOD SPECIES

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

The naturally durable heartwood of western redcedar makes it a preferred species for supporting overhead utility lines. For many years, utilities used cedar without treatment or only treated the butt portion of the pole to protect the high hazard ground contact zone. The cost of cedar, however, encouraged many utilities to full-length treat their cedar poles. While most utilities use either pentachlorophenol or creosote for this purpose, there is increasing interest in less toxic alternatives. Among these chemicals is copper naphthenate, a complex of copper and naphthenic acids derived from the oil refining process. Copper naphthenate has been used for many years, but its performance as an initial wood treatment for poles remains untested on western redcedar.

Copper naphthenate performance on western redcedar was evaluated by cutting sapwood stakes (12.5 by 25 by 150 mm long) from either freshly sawn boards or from the above ground, untreated portion of poles which had been in service for about 15 years. Weathered stakes were included because of a desire by the cooperator to retreat cedar poles in their system for reuse. In prior trials, a large percentage of cedar poles removed from service due to line upgrades were found to be serviceable and the utility wanted to recycle these in their system. The stakes were conditioned to 13 % moisture content prior to pressure treatment with copper naphthenate in diesel oil to produce retentions of 0.8, 1.6, 2.4, 3.2 and  $4.0 \text{ kg/m}^3$ . Each retention was replicated on 10 stakes.

The stakes were exposed in a fungus cellar maintained at 28 C and approximately 80 % relative humidity. The soil was a garden loam with a high sand content. The original soil was amended with compost to increase the organic matter. The soil is watered regularly, but is allowed to dry between waterings to simulate a natural environment. The condition of the stakes has been assessed annually on a visual basis using a scale from 0 (failure) to 10 (sound). Results months after treatment continue to show a difference in performance levels between stakes cut from freshly sawn sapwood and weathered wood (Table VI-1). differences most probably reflect the fact that the increased permeability of the weathered material makes it more susceptible to leaching losses. This effect is most noticeable with both the diesel control and the lower retentions. The freshly sawn stakes have ratings of 8.0 for the diesel control while similarly treated weathered stakes had ratings which averaged 3.4. Treatment with copper naphthenate to the retention specified for western redcedar in the American Wood Preservers' Association for pressure processes (1.92 kg/m<sup>3</sup>) continues to provide excellent protection to both weathered and freshly sawn samples. These stakes will be evaluated in the coming year to continue assessing the performance of this chemical/wood species combination. present, copper naphthenate appears to be providing excellent protection to western redcedar sapwood.

#### B. EVALUATION OF COPPER NAPHTHENATE TREATED DOUGLAS-FIR POLES IN SERVICE

The trials to evaluate the performance of Douglas-fir poles treated with copper naphthenate were not evaluated this past year. Attempts will be made to arrange an inspection in 1996.

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 64 months.

Target		New Samples													
Retention (kg/m²)	Actual Retention		Ave	rage Dec	ay Ratii	ng <sup>2</sup>		Actual		A	rerage E	ge Decay Rating 2			
	(kg/m²)	6 mos	14 mos	26 mos	40 mos	52 mos	64 mos	Retention (kg/m²)	6 mos	14 mos	26 mos	40 mos	52 mos	64 mos	
Control	1	4.7	0.9	0.4	0.1	0	0	_	6.6	3.2	1.3	1.1	1,1	1.0	
diesel	-	8.5	6.8	5.3	3.8	3.4	3.4	-	9.9	8.4	8.0	8.6	8.4	8.0	
0.8	1.6	9.0	8.0	7.5	6.9	5.7	5.6	0.6	10.0	9.6	9.4	9.5	9.6	9.3	
1.6	1.4	9.5	8.9	8.8	9.0	8.0	7.8	1.3	10.0	9.4	9.3	9.2	9.4	9.1	
2.4	2.1	9.6	9.2	9.1	8.6	8.2	8.2	1.9	10.0	9.4	9.4	9.2	9.3	9.2	
3.2	2.7	9.6	9.1	9.0	8.8	8.1	8.1	2.6	10.0	9.2	9.2	9.0	8.9	8.9	
4.0	4.0	9.9	9.2	9.1	9.1	8.7	8.3	3.4	10.0	9.5	9.4	9.4	9.3	9.2	

<sup>&</sup>lt;sup>1</sup> Retention measured as (kg/m³) (as copper).

7/ines of time

<sup>&</sup>lt;sup>2</sup> Values represent averages of 10 replicates pretreatment, where 0 signifies completely destroyed and signifies no fungal attack.