AN ABSTRACT OF THE THESIS OF

Paul G. Forsyth for the degree of Doctor of Philosophy in Forest Products presented on August 27, 1993. Title: Decomposition of Basamid in Douglas-fir Heartwood

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Abstract approved: Jeffrey J. Morrell

Basamid® (3,5-dimethyl-1,3,5,2H-tetrahydrothiadiazine-2-thione) is a crystalline powder used as a soil sterilant. This fumigant acts in soil by decomposing to methylisothiocyanate (MITC), the primary active ingredient, as well as hydrogen sulfide, methylamine, and formaldehyde. In wood, Basamid decomposes too slowly to be efficacious against decay fungi unless amended with various catalysts. Environmental conditions also play a role in Basamid decomposition rates. This study explored the use of selected additives to enhance Basamid decomposition.

No Basamid decomposition was observed in Douglas-fir heartwood incubated at 12% MC or 5°C. The rate of Basamid decomposition increased with wood MC from 12 to 60 % and temperature from 5°C to 23°C. A pH 12 buffer powder increased decomposition; however, the primary breakdown product was carbon disulfide, a chemical which is fungitoxic but has no interaction with wood and, thus, no residual effect. Copper sulfate had a tremendous catalytic

effect on Basamid and favored the production of MITC over other compounds. The effect of copper sulfate was more pronounced soon after treatment, providing an initial burst of MITC release and then a steady, moderate rate of release. Manganese and magnesium, as well as wood alone, provided no catalysis in laboratory studies. No volatile decomposition products besides MITC and carbon disulfide were detected.

Field tests indicated that copper sulfate plus the pH 12 buffer were effective in catalyzing MITC production and providing a more evenly distributed protective chemical loading than was metham sodium (also known as Vapam), the most widely used wood fumigant. While MITC levels produced from metham sodium decreased substantially within 1 year, MITC release was constant at moderate rates for at least 3 years from Basamid amended with copper sulfate and the pH 12 buffer.

These tests indicate that Basamid, when amended with an appropriate additive, will release MITC at controllable levels that should provide protection against internal decay in utility poles. This solid chemical provides a safer and possibly longer lasting remedial treatment than the currently used conventional wood fumigants.

Decomposition of Basamid in Douglas-fir Heartwood

by

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DECOMPOSITION OF BASAMID IN DOUGLAS-FIR HEARTWOOD

CHAPTER 1.

GENERAL INTRODUCTION

Problem and Justification

Although wood is a versatile building material, it will degrade under certain conditions. To prevent insect and fungal deterioration, wood is treated with preservatives by a variety of processes. It is estimated that 941.3 million cubic feet of poles and piling alone were treated in the United States from 1970 through 1981, accounting for 27.5% of the total treated wood volume during that period [Barnes 1985]. Treated poles have an expected service life of 30 to 40 years, depending on exposure conditions. Approximately one million poles must be replaced annually due to biological deterioration, at a cost exceeding 500 million dollars. The Bonneville Power Administration reported an annual investment savings for their company alone of 2.25 million dollars by simply using chemicals for remedial treatments to control internal decay [Graham 1983]. Tremendous savings could be expected if average pole service life could be extended by several years.

Southern yellow pine (Pinus spp.) and Douglas-fir (Pseudotsuga menziesii (Mirb.)Franco) comprise nearly 90% of the poles used in the United States. While southern pine is

usually used for distribution poles, Douglas-fir poles account for a large percentage of distribution poles used in the West and nearly all transmission poles over 50 feet long used throughout the country [USDA 1987]. Southern pine has a thick, easily treated sapwood band. Failures in southern pine poles, except in those receiving poor treatment or having pretreatment decay, are generally caused by soft rot fungi which gradually erode the outer pole surfaces, reducing the diameter until the structure can no longer bear its intended load. Douglas-fir, conversely, has a narrow sapwood band surrounding an impermeable heartwood core that is only moderately decay resistant [Englerth and Scheffer 1955; Scheffer and Englerth 1952]. Failure to properly sterilize the heartwood before or during treatment, or exposure of the untreated interior render this species susceptible to internal decay by basidiomycetous fungi [Graham 1983]. Internal exposure may be caused by deep seasoning checks that penetrate beyond the protective shell, mechanical damage, or post-treatment machining such as field-drilled bolt holes. However internal decay occurs, the ultimate result is a thin, sound shell surrounding a virtually hollow core.

Although the heartwood of Douglas-fir is impervious to liquids, gases readily diffuse through it [Graham 1973a, 1973b; Hand et al. 1970]. Several volatile agricultural chemicals, known as fumigants, can be added as liquids to the interior of poles via downward sloping holes, where they

vaporize and move through the wood as gases. Poles treated in this manner have been found to be free of decay fungi up to 14 years after treatment [Helsing et al. 1984]. Sodium N-methyldithiocarbamate (NaMDC), Vorlex (20% methylisothiocyanate, 80% chlorinated C-3 hydrocarbons), chloropicrin (96% trichloronitromethane), and MITC-Fume (97% solid methylisothiocyanate (MITC)) are the only fumigants registered with the U.S. Environmental Protection Agency for wood application. However, three of these chemicals are applied as liquids, creating potential hazards in safety and handling. MITC-Fume has proven to be very effective as a wood fumigant and has the advantage of being a solid at room temperature; however, it is still highly volatile, expensive, and not yet widely used.

Another chemical that shows potential for use as a wood fumigant is Basamid (3,5-dimethyl-1,3,5,2H-tetrahydrothiadiazine-2-thione), a crystalline powder also used as a soil fumigant [Eslyn and Highley 1985; Graham and Corden 1980; Morrell et al. 1988]. Because Basamid is a solid, it is more attractive as a safe chemical for remedial treatments. Solids are not as readily absorbed through the skin as are liquids, and they are much more easily recovered in the event of a spill. Basamid must also decompose to be effective; however, in its pure form, this process occurs too slowly to adequately protect wood from decay [Highley and Eslyn 1986; Morrell et al. 1988]. The requirement for decomposition from

the solid form makes the chemical less volatile than the other fumigants, a favorable property for storage and safe application, but one that requires modification for it to be an effective fungicide. This modification forms the basis of this thesis.

Background

Development of Wood Fumigants

The use of fumigants to control soil pests has been studied since the late 1800's, with most intensive research coming since the turn of the century [Goring 1962]. Studies are continuing on fumigant movement, persistence, and toxicity in soil [Munnecke and Van Gundy 1979]. In 1959, Stabnikov reported the first use of fumigants for eliminating fungi from wood. He found that exposing Coniophora cerebella-infested oak flooring to 30 grams of chloropicrin per cubic meter of wood effectively killed the fungus. Two years later, Partridge [1961] found that methyl bromide and chloropicrin effectively eliminated the oak wilt fungus, Ceratocystis fagacearum, from small oak blocks. Jones [1963] later reported an effective method for eliminating the oak wilt fungus from sawlogs up to 0.6 meters in diameter.

In 1962, workers at Bonneville Power Administration discovered that chemicals in the gas phase could penetrate Douglas-fir sapwood and heartwood [Hand et al. 1970]. This led to the pioneering studies using fumigants to control

internal decay in wood transmission poles. Graham [1973a, 1973b, 1974] found that some agricultural soil sterilants could effectively stop and prevent internal decay in Douglas-fir poles. NaMDC, Vorlex, and chloropicrin [Graham 1973a, 1973b; Graham et al. 1976] were found to eliminate decay fungi in internally decaying Douglas-fir transmission poles and keep them relatively free from decay for up to 14 years [Helsing et al. 1984]. Recent evaluation of these same poles indicates that they are virtually free of decay fungi 19 years after treatment [Morrell 1988]. Fumigant treatment has also been tested in Douglas-fir piles [Graham 1977; Helsing et al. 1984, 1986], laminated timbers [Goodell et al. 1980; Graham 1978], waterfront timbers [Highley and Eslyn 1982], and southern pine poles [Zabel et al. 1982]. These chemicals have also been used to eliminate fungal pathogens from living trees or the roots of cut stumps [Goodell et al. 1984; Thies and Nelson 1987a, 1987b]. Morrell and Corden [1986a] and Morrell [1989] have written the only comprehensive reviews, aside from several theses [Cooper 1973; Goodell 1983; Zahora 1983; Zahora 1987], available on wood fumigation.

Evolution of Wood Fumigation Chemicals

Methyl bromide was the first fumigant that effectively controlled fungi in wood [Partridge 1961; Jones 1963; Ricard et al. 1968], and still has some uses [Schmidt et al. 1982]. More recently, methyl bromide has been studied for disin-

fecting imported Siberian timbers [USDA 1991] and for preventing oxidative discolorations in southern red oak logs [Schmidt and Amburgey 1993]. This chemical penetrates wood rapidly with little significant chemical interaction [Harris 1963; Michelsen 1960] and therefore, has little, if any, residual effect. Methyl bromide also has low odor, high volatility, and high mammalian toxicity, making it difficult to use safely in the field. For these reasons, other chemicals were investigated.

Hand et al. [1970] found that 500 ml of sodium-N-methyldithiocarbamate (NaMDC) added to poles via downward-sloping holes could effectively control decay for at least 4 years. NaMDC works by decomposing into MITC and other compounds [Gray 1962; Turner and Corden 1963]. The decomposition of NaMDC, usually applied as a 32.7% aqueous solution, has been studied not only in soil [Turner and Corden 1963; Smelt and Leistra 1974] but also in wood [Morrell and Corden 1986b; Morrell 1987; Turner and Corden 1963; Helsing et al. 1984; Miller and Morrell 1990]. These studies indicate that many of the NaMDC breakdown products found in soil, including MITC, are also produced in wood [Turner and Corden 1963]. MITC is also a component of Vorlex [Graham and Corden 1980], a fumigant that has received less attention because of its high toxicity and difficult handling characteristics. MITC alone, however, has been the subject of much recent research [Zahora 1983,1987; Zahora and Corden

1985a,1985b; Zahora et al. 1985; Highley 1987; Morrell et al. 1992]. In pure form, MITC is a solid with a melting point of 36°C [Zahora 1983], below which it sublimes to a gas. Solid MITC is much safer to handle than liquid fumigants, but must be encapsulated for use due to its caustic nature [Zahora and Corden 1985a].

Aside from NaMDC, Vorlex, and MITC, chloropicrin is the only other fumigant registered for use in wood. Though chemically dissimilar, chloropicrin is retained by wood for periods similar to MITC. However, strong lachrymatory properties have largely limited the use of chloropicrin to overland transmission poles where the risk of human contact is minimized [Morrell and Corden 1986a].

All but one of the registered wood fumigants are liquids, presenting potential safety problems during application and making cleanup of accidental spills difficult, if not impossible. MITC must be encapsulated in gelatin or glass for increased safety, but this is an expensive process that may limit its acceptance.

Basamid as a Wood Fumigant

An alternative to the currently registered chemicals is the use of crystalline solids that decompose to produce volatile fungitoxic by-products. One such chemical is Basamid, a soil sterilant. Chemically, Basamid is a heterocyclic ring containing carbon, nitrogen, sulfur, and

hydrogen (Figure 1.1). This chemical was first prepared by Delepine [in Herschler 1953] by reacting carbon disulfide with trimethyl-trimethylenetriimine. He called the chemical dimethylformo-carbothiadine. Ainley et al. [1944] later elucidated the actual structure of the compound as 3,5-dimethyltetrahydro-1,3,5,2H-thiadiazine-2-thione (CAS Registry No. 533-74-4). More recently [Merck 1989], the chemical has been prepared commercially by reacting carbon disulfide with methylamine and caustic soda. This chemical has been used under various commercial names including Mylone (Union Carbide Corp.), Crag Fungicide 974 (Union Carbide Corp.), Salvo (Stauffer Chemical Co.), N-521 (Stauffer Chemical Co.), Basamid (BASF AG), tiazon (USSR), Dazomet, and Fongosan. In agriculture, Basamid has been used as a fungicide, herbicide, nematocide, and insecticide [Keays and Zedler 1957; RSC 1987]. Other uses have been as a slimicide in pulp and paper manufacturing [Herschler 1953] and as a preservative in adhesives and glues [RSC 1987].

Basamid controls many plant pathogens [Anderson and Okimoto 1953; Baines et al. 1958; Burgis and Overman 1956; Campbell 1954; Davison and Vaughn 1957; Enebak et al. 1990; Hamilton 1956; Hansen et al. 1990; Harris 1990; Kendrick and Middleton 1954; Morgan et al. 1987; Overman 1958; Overman and Burgis 1956; Wilhelm and Ferguson 1953] and long exposures have controlled decay fungi in wood [Eslyn and Highley 1985; Graham and Corden 1980]. Slow decomposition could be useful

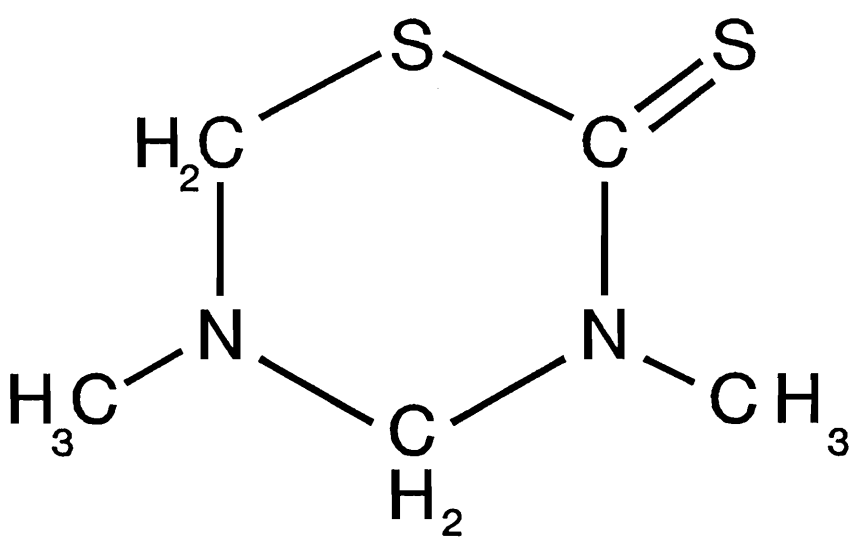


Figure 1.1. The chemical structure of Basamid.

if the chemical is applied to non-decayed wood at the time of installation where immediate decay eradication is not of concern. However, Basamid does not decompose rapidly enough to diffuse and kill actively growing decay fungi in wood. To be effective in this setting, a chemical must be able to eliminate an actively growing fungal colony within 6 months to 1 year after application.

Under dry conditions and ambient temperatures, Basamid is stable and not considered biologically active. Instead, it requires decomposition into volatile, toxic compounds which diffuse through the treated substrate [Goksoyr 1964; Stauffer 1976, 1979]. The effectiveness of Basamid against target organisms depends on the decomposition products formed and the rate at which they are released.

Several studies have examined Basamid decomposition, usually in a soil or aqueous medium [Goksoyr 1964; Keller 1980; Munnecke et al. 1962; Munnecke and Martin 1964; Ruch and Johnson 1957]. Among the decomposition products reported are MITC, methylamine, hydrogen sulfide, and formaldehyde [Ruch and Johnson 1957; Torgeson et al. 1957]. Acid hydrolysis also yields carbon disulfide [Ruch and Johnson 1957; BCPC 1987; RSC 1987]. MITC is considered to be the most important volatile toxicant produced [Goksoyr 1964; Munnecke et al. 1962; BCPC 1987; Spencer 1981; RSC 1987] and has received the greatest amount of attention in Basamid evaluations. MITC production is dependent on several

environmental conditions including moisture, temperature, pH, and the presence of trace metals.

Water is required for Basamid decomposition [Stauffer 1976, 1979; Merck 1989]. Soil moisture should be at least 40% of saturation to attain desired decomposition rates [Keller 1980]. The amount of MITC released from Basamid-treated soil in lab tests increases with soil moisture up to approximately 80% of saturation [Munnecke and Martin 1964]. It is likely that moisture levels higher than this limit MITC detection by reducing the diffusion of this relatively water-insoluble chemical through the soil [Lambe 1960]. In the same study, little MITC was released from dry soil; however, soil which was treated dry and subsequently wetted showed a dramatic increase in MITC production following the addition of water. Total MITC production from the dry soils that were subsequently wetted never reached those levels produced from soils which were treated wet, even though an equivalent total amount of water was ultimately added to each. This indicated that some MITC, tightly bound under dry conditions, was not easily dislodged by water, or that these conditions favored the production of other compounds.

Increasing temperature also enhances Basamid decomposition [Keller 1980; Munnecke and Martin 1964]; However, Basamid is stable up to 35°C when moisture is excluded [RSC 1987]. Keller [1980] found no detectable Basamid residues 24 hours after treatment of soils at 22°C

while 96 hours was required for similar results at 3°C. Lambe [1960] demonstrated that Basamid fungitoxicity against Verticillium and Phytophthora increased with temperature and attributed this effect to enhanced decomposition of the chemical at higher temperatures. In another study, MITC release from soils treated at 23°C proceeded at a faster rate than from soils treated at 10°C or 1°C; however, an equivalent total MITC production was eventually achieved at all three temperatures [Munnecke and Martin 1964]. One recommendation for Basamid use is that soil temperature should be at least 7°C at a depth of 15 cm [BCPC 1987]. Label recommendations for Basamid Granular [Hopkins 1988] require at least 6°C soil temperature throughout the fumigation period with 12-18°C being optimum. It is also recommended that Basamid not be used above 39°C due to rapid loss of vapors from the soil.

The relative ratios of decomposition products formed from Basamid are also pH-dependent. Acidic media hydrolyze Basamid to carbon disulfide, formaldehyde, and methylamine [Ruch and Johnson 1957; RSC 1987]. Production of carbon disulfide or amines by acid hydrolysis is the basis of some analytical methods for Basamid as well as various dithiocarbamates [Bontoyan 1965; Callan and Strafford 1924; Goksoyr 1964; Pressley and Longbottom 1982; Ruch and Johnson 1957; Stevenson 1964; Thorn and Ludwig 1962]. Under neutral or basic conditions, the reaction shifts towards the

production of MITC and hydrogen sulfide along with formaldehyde and methylamine [Ruch and Johnson 1957]. Miller and Morrell [1989] demonstrated that MITC was produced at a greater rate at pH 10 than at pH 4 or 7. In soils, MITC production increased with pH up to 6.5, but then decreased up to pH 7.7 [Munnecke and Martin 1964]. Higher pH's, where more significant MITC production has been observed, were not tested in this study. Clay in soils increased the rate of MITC production from Basamid, possibly due to the buffering capacity of clay which stabilized the pH near the optimum for breakdown as observed in aqueous media [Munnecke et al. 1967]. In one of the first tests of Basamid in wood, high alkaline buffers (pH 10 and 12) greatly enhanced MITC production and fungal control in wood blocks [Morrell et al. 1988].

Decomposition of some dithiocarbamates can be enhanced by the addition of certain metals. For instance, NaMDC decomposition increases in the presence of copper, manganese, iron, and zinc [Ashley and Leigh 1963]. The oxidation of Nabam (disodium ethylene-bis-dithiocarbamate) is catalyzed by manganous salts [Thorn and Ludwig 1962]. Certain heavy metals also aid in the conversion of alkylene-bis-dithiocarbamates to isothiocyanates; e.g., the formation of isothiocyanates from ethylenethiuram monosulfide in the presence of iron and zinc salts [Ludwig et al. 1955] and the conversion of Nabam to an isothiocyanate in the presence of

ferric sulfate [Thorn and Ludwig 1962]. Goksoyr [1964] showed that very low levels of cupric sulfate synergistically decreased acetate respiration of yeast while simultaneously increasing the production of MITC from Basamid. Chandra and Bollen [1961] have suggested that soil minerals may actually catalyze the primary step in Basamid decomposition.

CHAPTER 2.

THE EFFECT OF SELECTED ADDITIVES AND CONDITIONS ON THE DECOMPOSITION OF BASAMID IN DOUGLAS-FIR HEARTWOOD

Introduction

Basamid is an effective soil fumigant which decomposes to form several fungitoxic compounds [Ruch and Johnson 1957; Torgeson et al. 1957]. The types of these compounds and the rate at which they are formed is dependent upon several factors including moisture [Keller 1980; Lambe 1960; Munnecke and Martin 1964], temperature [Keller 1980; Munnecke and Martin 1964], pH [Munnecke and Martin 1964; Ruch and Johnson 1957], and the presence of metals [Chandra and Bollen 1961]. However, most Basamid decomposition studies have been performed in soil or water [Goksoyr 1964; Keller 1980; Munnecke and Martin 1964; Ruch and Johnson 1957] and it is unknown if this chemical will react similarly in wood.

The following tests were performed to determine the effect of moisture and temperature as well as selected additives on the decomposition of Basamid in Douglas-fir heartwood. An initial screening of additives was performed to determine which compounds warranted further study. Two additives were selected to determine their effects on both the rate of decomposition and on the balance of decomposition products. Most of the results of these tests have been reported by Forsyth and Morrell [1992].

Materials and Methods

Initial Additive Screening

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

5% pH 12 buffer

1% copper sulfate

1% copper chloride

1% manganese sulfate

1% magnesium sulfate

Amounts are given as the percentage of metal added based on the weight of Basamid. The pH 12 buffer was composed of di- and tri-basic sodium phosphate. Copper sulfate was also tested at 0.5, 5, and 10% to determine optimum additive levels. Douglas-fir (*Pseudotsuga menziesii* Mirb.(Franco)) heartwood ground to pass a 3 mm screen and adjusted to 30 % moisture content (MC) was used in all tests. Vials that received only pH 12 buffer as an additive were tested at 12, 30, and 60% MC. Tests were performed by placing 3 oven-dry (OD) g sawdust that had been adjusted to the proper MC into a 40 ml glass vial. One hundred twenty mg of Basamid amended with the test additive was placed on top of the sawdust in an evenly distributed layer and covered with an additional 3 g of sawdust. The vials (3 per combination) were then tightly

capped with a Teflon-lined silicone septum and stored at 23°C.

Severals factors were considered in determining the physical parameters for these tests. Firstly, MITC evolution from Basamid in contact with wood was unknown. Because there was a possibility of wood/Basamid interaction, a large ratio of wood to Basamid was used to prevent wood from being the limiting factor. For similar reasons, good Basamid to wood contact was desired. Smaller wood particles may have achieved superior contact, but the size chosen was adequate to meet the requirements of the stated objective. The amount of Basamid added formed a thin layer which completely covered the surface of the first layer of wood, again maximizing the chemical to wood contact. Vial volume was large enough to allow for MITC production and accumulation, yet small enough to provide for detectable concentrations. The wood MC was chosen because it is typical of that in the heartwood of a Douglas-fir pole during the rainy season in the Pacific Northwest.

Basamid decomposition was determined 1, 3, 5, 7, 10, and 14 days after treatment by removing an air sample through the septum with an gastight syringe. Air sample volumes removed provided for detectable levels without removing enough volume to create a significant negative pressure. The sample was injected into a Varian 3700 gas chromatograph equipped with a flame photometric detector operating at the following

conditions: injector temperature, 150°C; oven temperature, 100°C; detector temperature, 240°C; nitrogen carrier flow rate 30 ml/minute; column, 10% Carbowax 20M on 80/100 Supelcoport (Supelco, Inc., Bellefonte, PA). MITC concentration was quantified by comparison with injections of known amounts of MITC dissolved in ethyl acetate.

Decomposition Study

Trials were established to determine the decomposition products of Basamid alone or amended with 5% pH 12 buffer and/or 1% copper sulfate. The powdered additives were measured as a percentage of Basamid by weight and were mixed thoroughly before treatment. Basamid (120 mg) amended with the appropriate additive was placed in an evenly distributed layer in the bottom of a 40 ml vial and covered with 1 OD g of sawdust that had been adjusted to 6 or 30% MC. A fine-meshed plastic screen was placed on top of the sawdust and an additional MC-adjusted 2 OD g of sawdust were placed on top. Each vial was sealed with a cap containing a Teflon-lined silicone septum and stored at 5, 23, and 32°C for up to 30 days. Controls were assembled using either no chemical or no wood to detect volatile components from untreated wood and stability of Basamid with additives in the absence of moisture. Three replicates were used for each treatment.

Two air samples were removed from the vials (3 per combination) at selected times and one was injected into a

Varian 3700 gas chromatograph and analyzed for sulfur-containing compounds as described above. The other sample was analyzed for non-sulfur compounds using a flame ionization detector on a second Varian 3700 gas chromatograph at the same operating conditions except: column temperature, 110°C; column, 4% Carbowax 20M on 0.8% KOH 60/80 Carbopack B (Supelco, Inc., Bellefonte, PA).

All tests were analyzed using a repeated measures analysis of variance (ANOVA) with an alpha level of 0.05 (SAS Institute, Inc., Cary, North Carolina). This analysis was chosen because each specimen was sampled multiple times over the test period. The statistical procedure includes time as an independent variable, thus eliminating the error associated with it from the error sum of squares (Cody and Smith 1987).

Results and Discussion

Initial Screening

Moisture greatly enhanced the decomposition of Basamid to MITC (Figure 2.1, Appendix A.1). No MITC was detected in any vial containing wood at 12% MC. MITC production from Basamid was consistently significantly greater in wood at 60% MC than at 30% MC. Using a pH 12 buffer also significantly enhanced MITC production, confirming previous results [Morrell et al. 1988], although the MITC levels associated

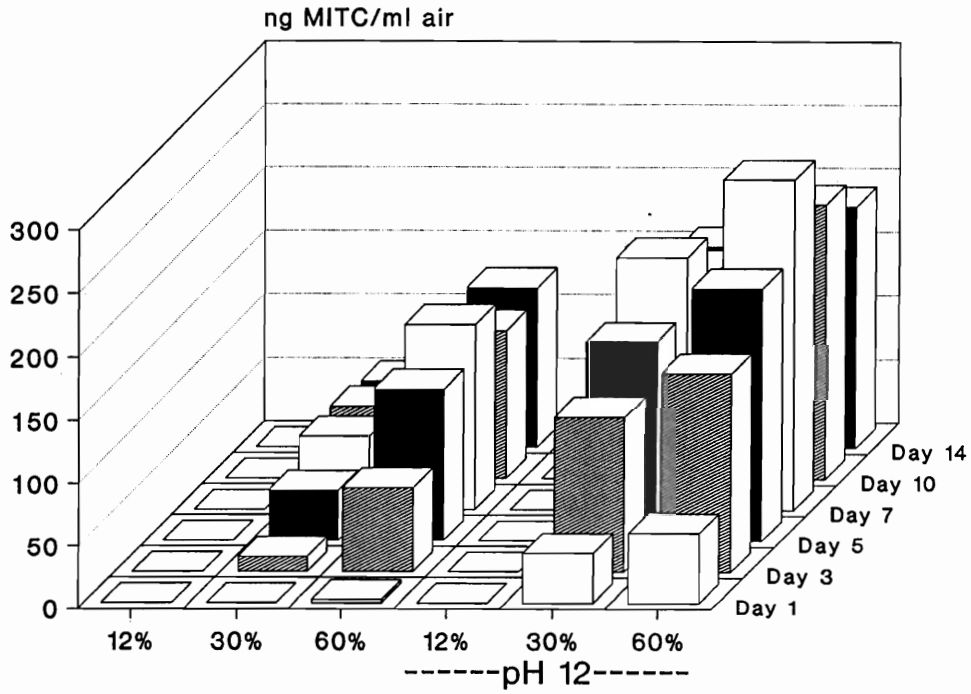


Figure 2.1. MITC levels at selected times in the headspace of sealed vials containing Douglas-fir heartwood at 12, 30, and 60% MC that was treated with Basamid alone or amended with a powdered pH 12 buffer.

with pH 12 buffer were still quite low. It is possible that much of the MITC released was bound to the wood [Zahora and Morrell 1988], although no effort was made to confirm this.

Both copper sulfate (Cu^{+2}) and copper chloride (Cu^{+1}) had a significantly greater enhancing effect on MITC production from Basamid than manganese or magnesium (Figure 2.2, Appendix A.2). Different copper compounds were evaluated to determine if valence state affected decomposition. Copper chloride produced significantly higher MITC levels than did copper sulfate. There was also a statistical increase in MITC production with the amount of copper added (Figure 2.3, Appendix A.3). These results confirm field test data obtained using Basamid amended with various additives [Forsyth and Morrell 1993]. In those tests, copper sulfate with a pH 12 buffer out-performed several other additives in elevating MITC production in Basamid-treated Douglas-fir pole sections over a 2 year period. The results of the screening tests indicated that one of the copper-containing additives warranted further study; copper sulfate was chosen because it could be more appropriately compared with previously established field tests using this additive.

Decomposition Study

Analyses for both methylamine and dimethylamine in the headspace of the test vials were inconclusive. If present, these compounds were below the limits of detection. There

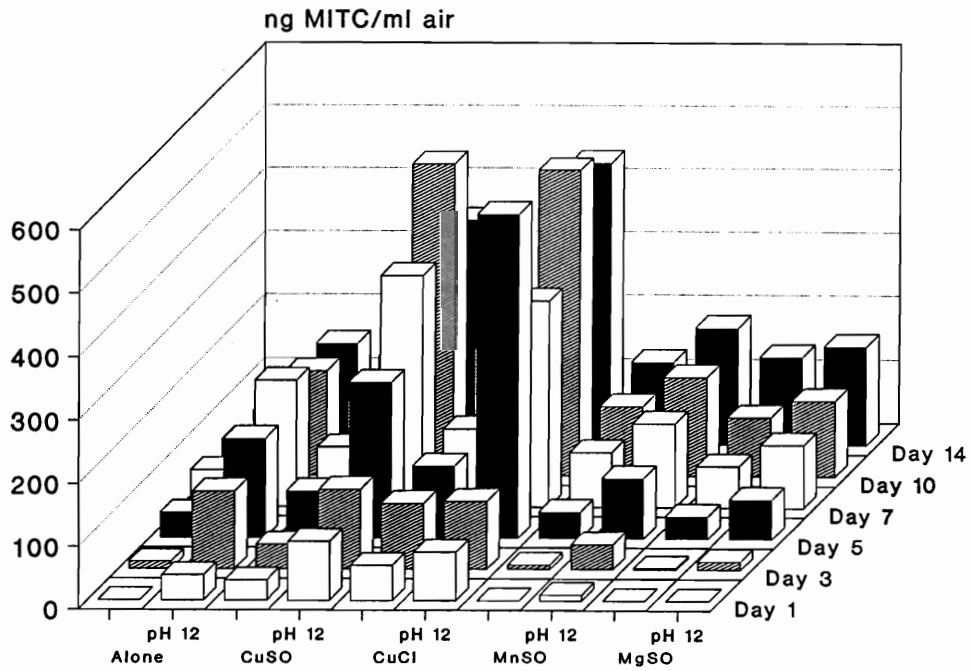


Figure 2.2. MITC levels at selected times in the headspace of sealed vials containing Douglas-fir heartwood at 30% MC that was treated with Basamid alone or amended with pH 12 buffer, copper sulfate, copper chloride, manganese sulfate, or mangesium sulfate.

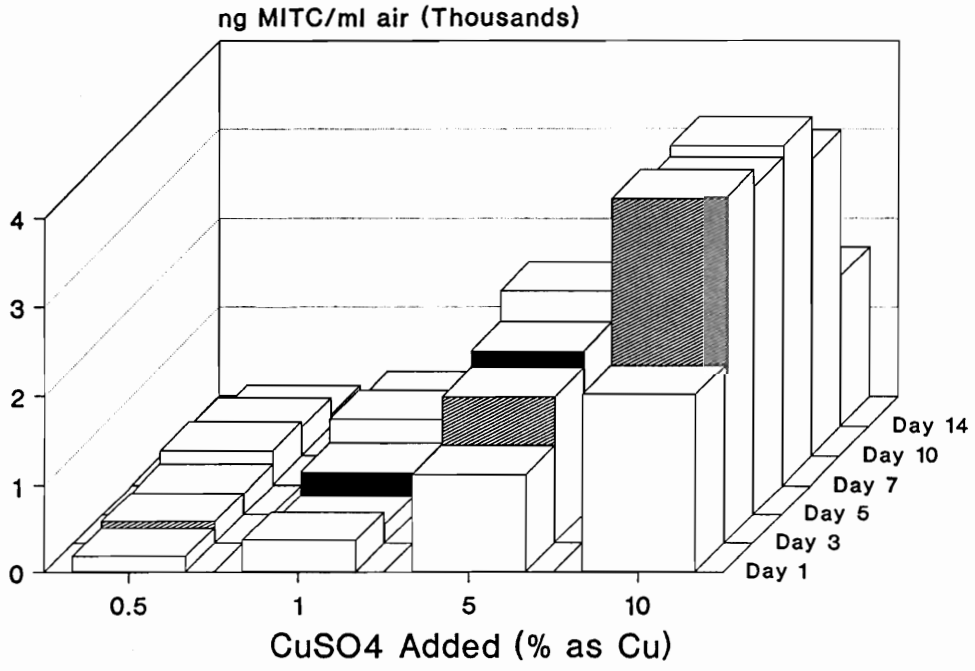


Figure 2.3. MITC levels at selected times in the headspace of sealed vials containing Douglas-fir heartwood at 30% MC that was treated with Basamid amended with various amounts of copper sulfate.

were, however, several unidentified compounds produced in small quantities in the higher MC and temperature exposures.

The presence of copper sulfate resulted in MITC production from Basamid even in the absence of wood or added moisture. This may make it necessary to mix this additive with Basamid immediately prior to treatment to prevent premature fumigant decomposition.

Both MITC and carbon disulfide (CS_2) were identified in the headspace of the test vials. As in the screening experiments, higher MC's resulted in increased MITC production regardless of the additive or temperature used (Figure 2.4, Appendix A.4). Higher temperatures also enhanced MITC production. These results were similar to trials with metham sodium [Turner 1962; Turner and Corden 1963; Morrell 1992]. Similar trends were noted for CS_2 production (Figure 2.5, Appendix A.5); however, these levels were much higher than those found for MITC on a weight to weight basis. It is evident that levels for both compounds were decreasing after 30 days in most treatments. This decline may be due to recombination of various decomposition products to form non-volatile compounds or loss from the vials.

The effects of pH and copper sulfate on decomposition were noted as in the initial screening tests. Trends in MITC production when pH 12 buffer was added to Basamid were nearly identical to those without the buffer, but the levels were

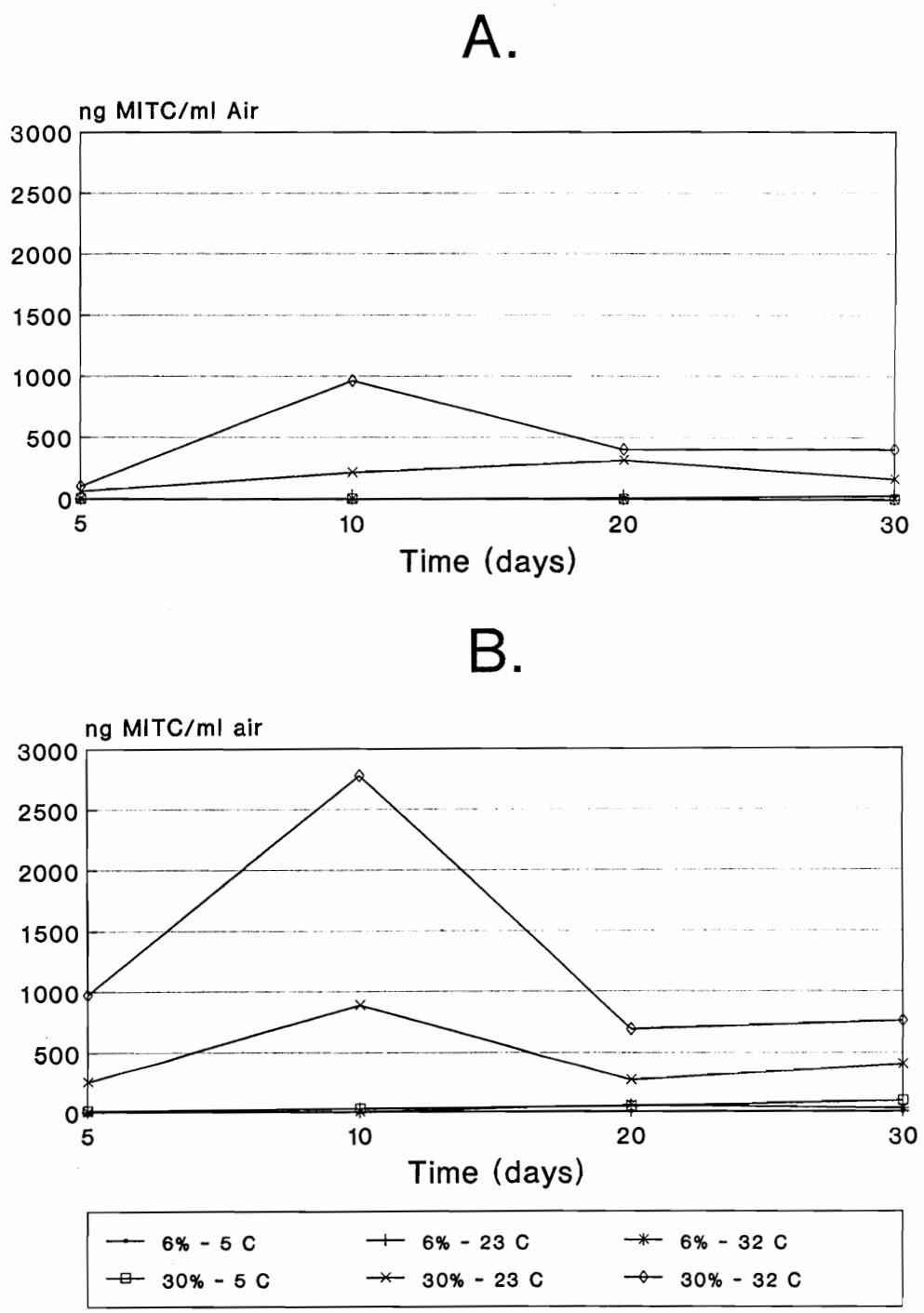
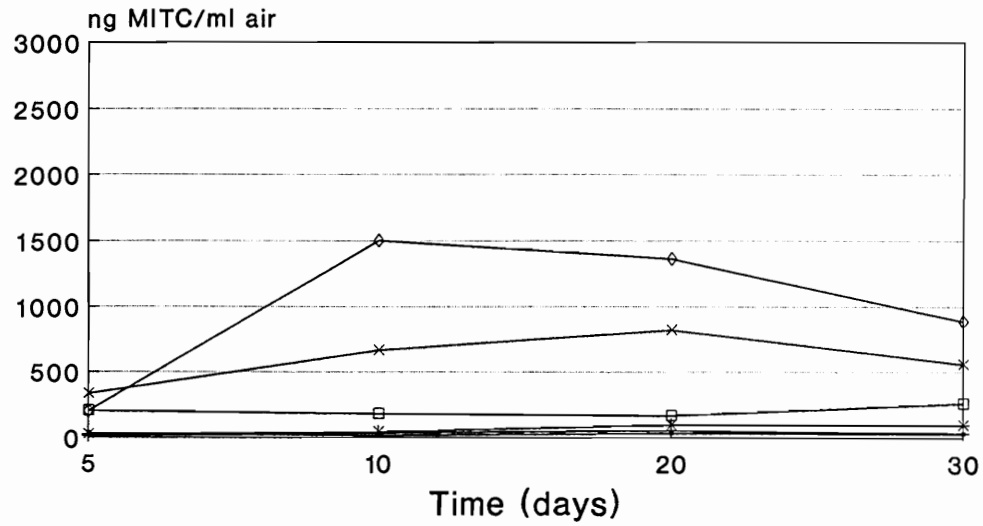


Figure 2.4. MITC levels over a 30 day period in the headspace of sealed vials containing Douglas-fir heartwood at 6 and 30% MC that was treated with (a) Basamid alone or amended with (b) pH 12 buffer, (c) copper sulfate, or (d) both buffer and copper sulfate and stored at 5, 23, or 32°C.

C.



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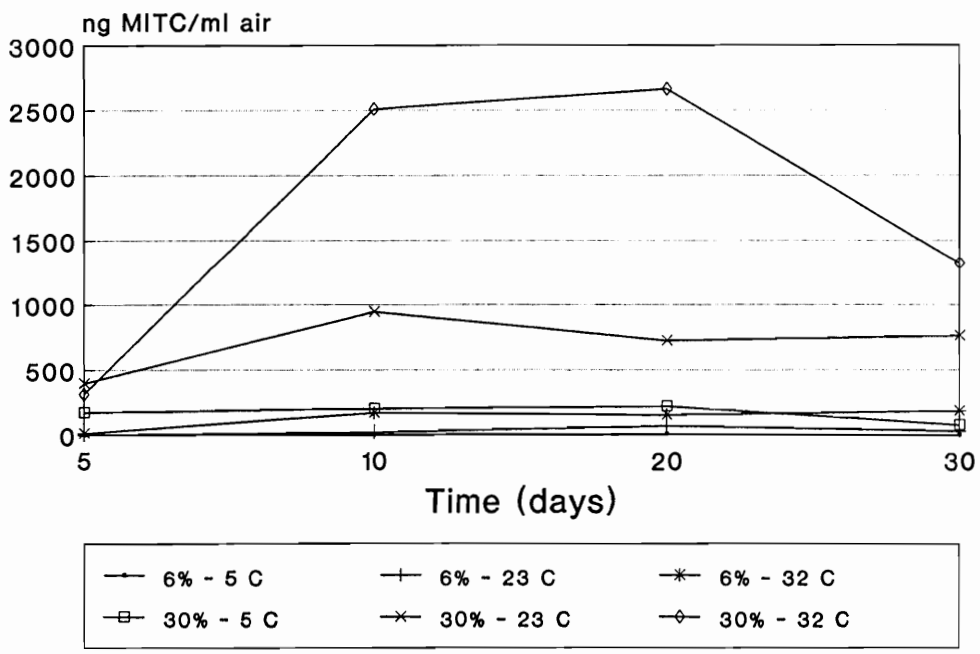


Figure 2.4, continued.

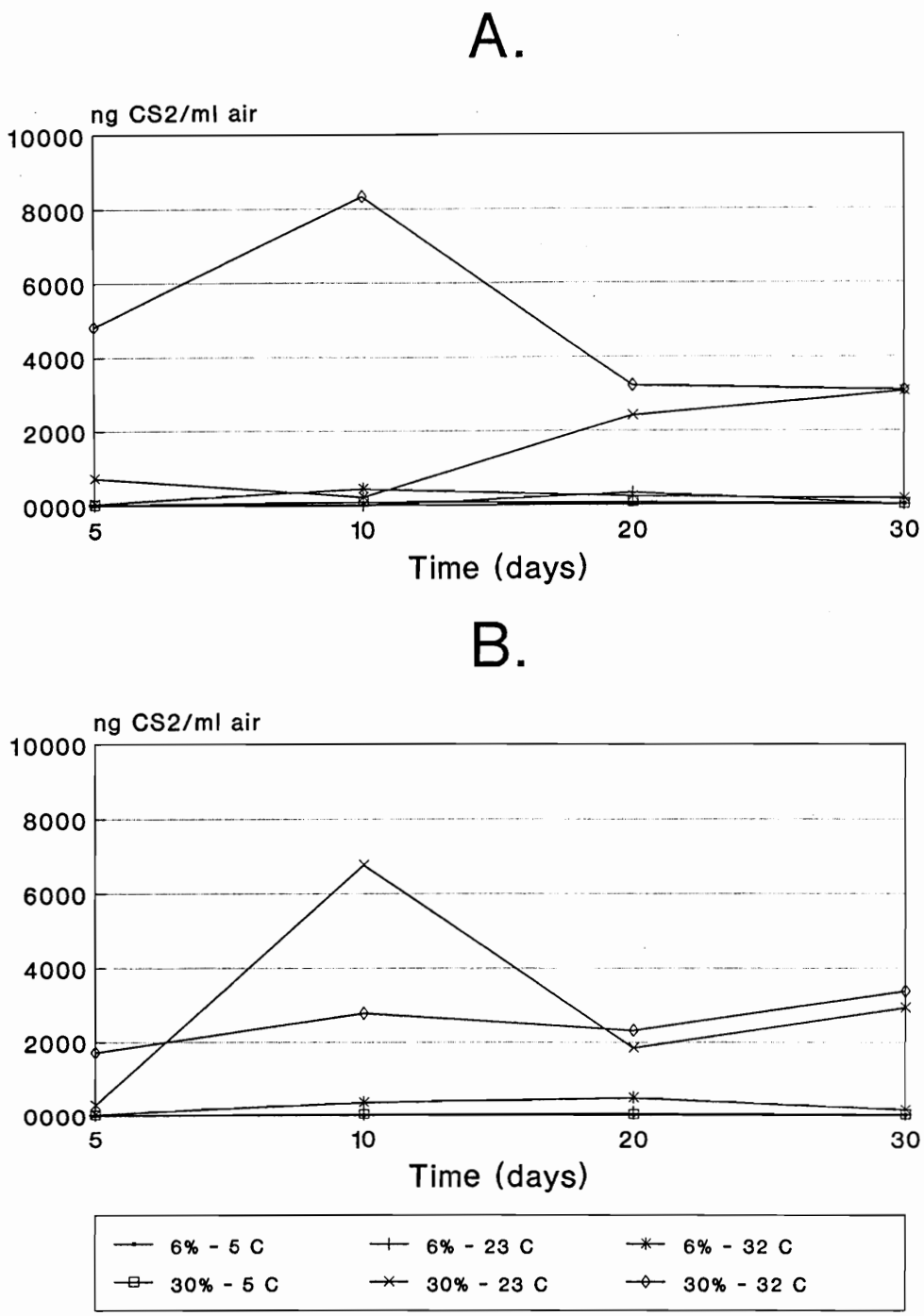
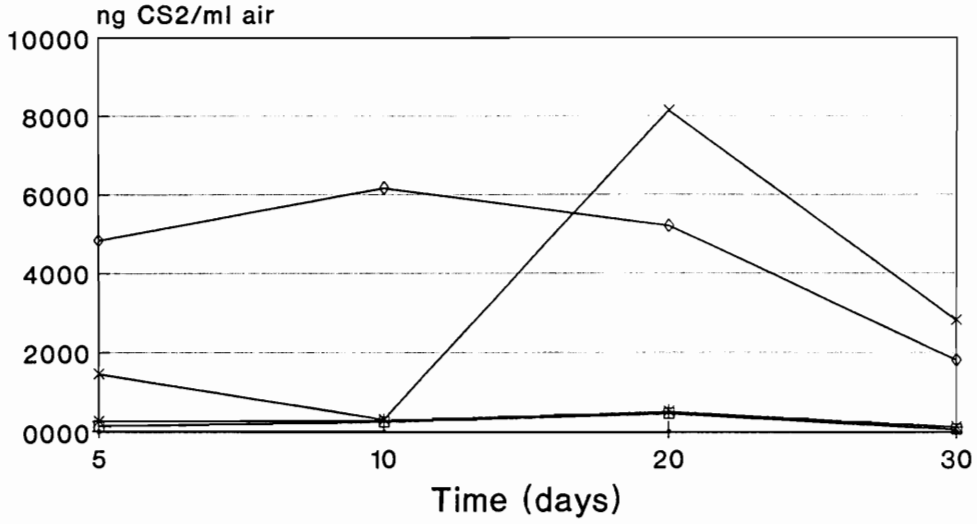


Figure 2.5. CS_2 levels over a 30 day period in the headspace of sealed vials containing Douglas-fir heartwood at 6 and 30% MC that was treated with (a) Basamid alone or amended with (b) pH 12 buffer, (c) copper sulfate, or (d) both buffer and copper sulfate and stored at 5, 23, and 32°C.

C.



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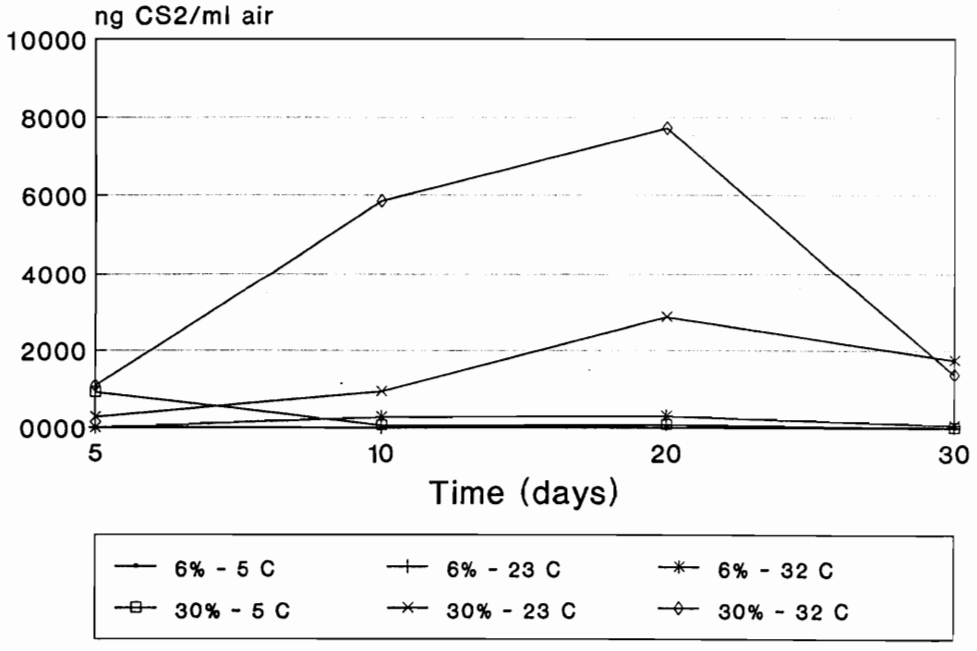


Figure 2.5, continued.

much higher. Addition of copper had the same enhancing effect, but the effects were delayed and the levels of MITC did not decline as rapidly as in those treatments receiving no copper. Once again, these results follow those found in Basamid field tests [Forsyth and Morrell 1993]. Combining both buffer and copper sulfate had an added effect on initial and prolonged MITC production, especially at 30% MC and 32°C.

CS_2 production was increased by the addition of pH 12 buffer and copper in some treatments; however, CS_2 release in relation to MITC was not as dramatic when copper was added. One goal of this research was to identify additives to enhance Basamid decomposition to effective fungicides. These compounds must also interact sufficiently with wood and not immediately volatilize, leaving the wood unprotected. While copper increased CS_2 production slightly, it increased MITC levels markedly, causing the ratio of CS_2 to MITC detected to decrease an order of magnitude in many instances (Figure 2.6). These decreases were statistically significant, especially when both additives were used in tandem (Appendix A.6). There are two possible pathways for MITC production through cleavage of the Basamid ring. One of these pathways involves the same carbon atom involved in CS_2 evolution, explaining their diametric production rates. Although CS_2 is fungitoxic, it is less effective than MITC and volatilizes rapidly, providing no residual wood protection. MITC, conversely, has been shown to remain in

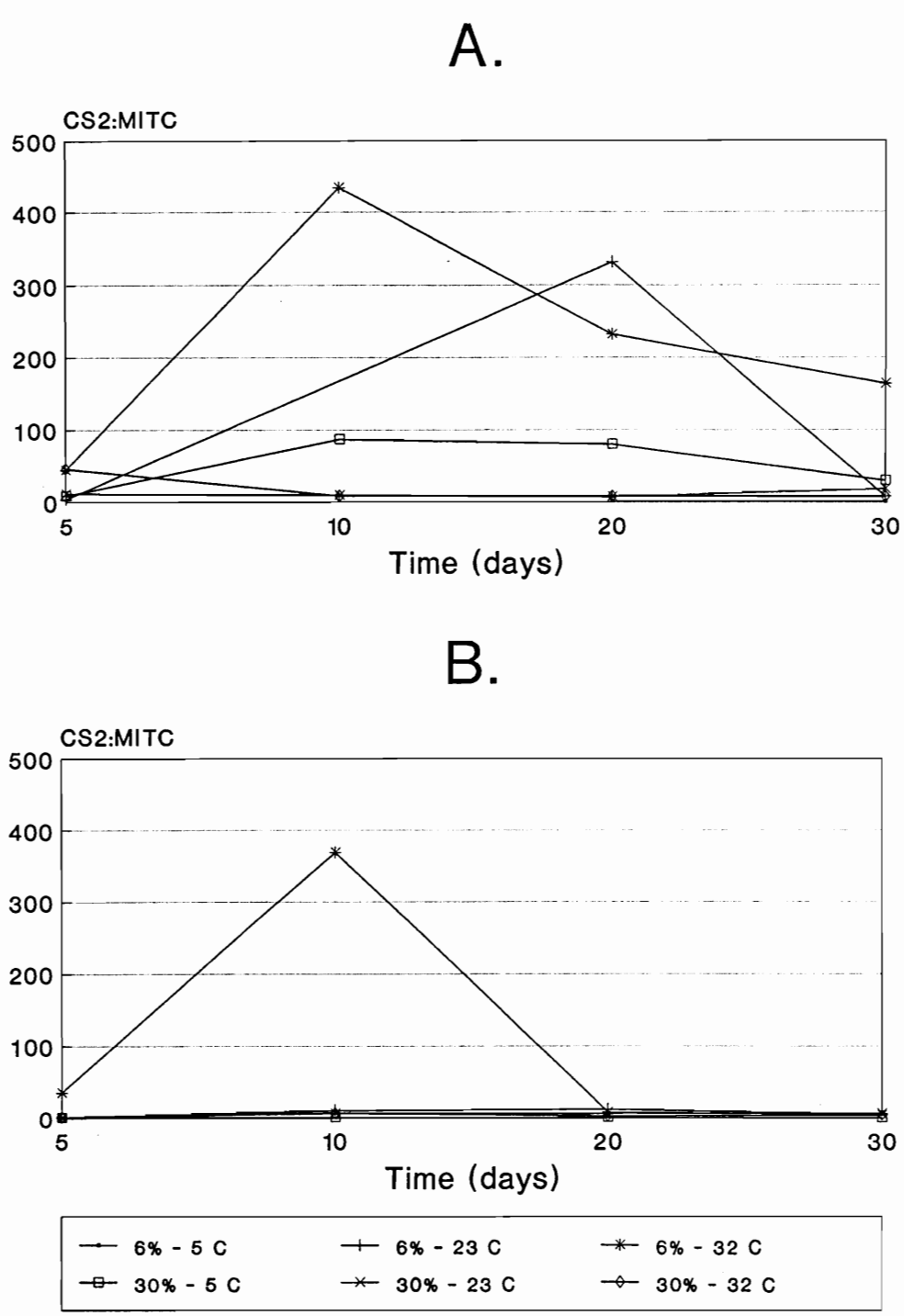
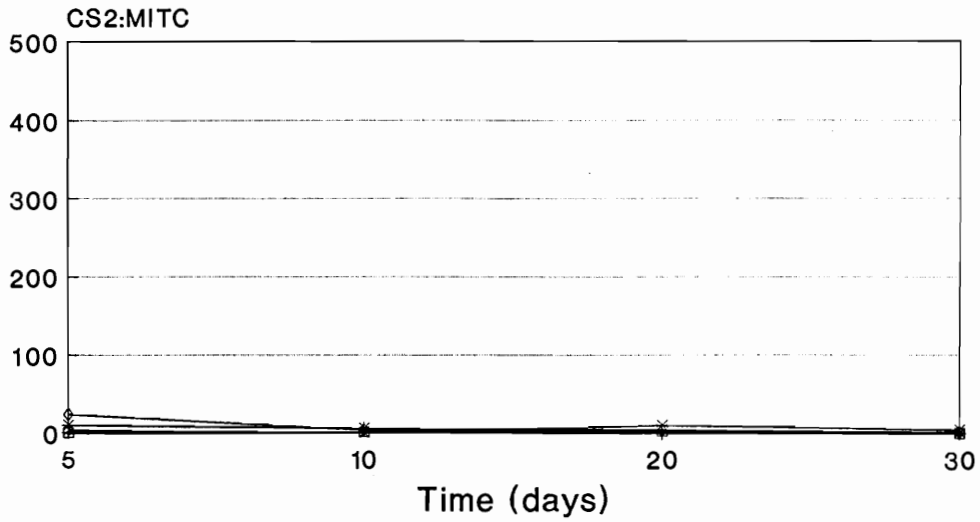


Figure 2.6. Ratio of CS_2 to MITC levels over a 30 day period in the headspace of sealed vials containing Douglas-fir heartwood at 6 and 30% MC that was treated with (a) Basamid alone or amended with (b) pH 12 buffer, (c) copper sulfate, or (d) both buffer and copper sulfate and stored at 5, 23, and 32°C.

C.



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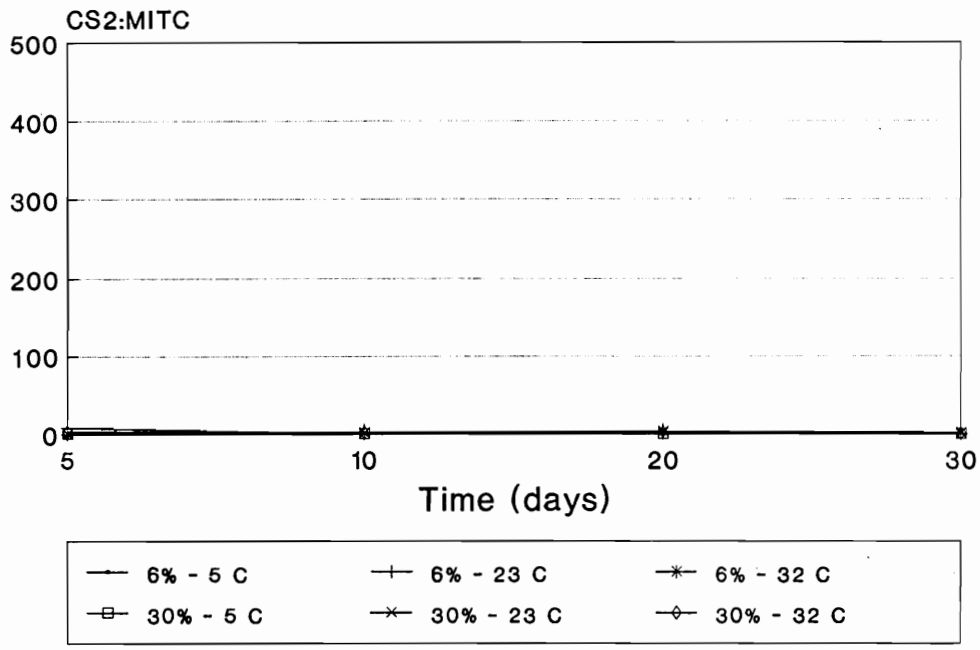


Figure 2.6, continued.

wood for long periods of time providing long-lasting protection [Zahora and Morrell 1988]. These differences emphasize the importance of producing the optimum decomposition products in addition to enhancing the rate of that breakdown.

Conclusions

Increasing temperature and moisture content enhanced Basamid decomposition. Decomposition of Basamid was enhanced by addition of powdered pH 12 buffer; however, this additive greatly favored the production of CS_2 over that of MITC. Copper sulfate enhanced the production of MITC from Basamid while reducing CS_2 evolution. This was especially true when copper sulfate was used in combination with the pH 12 buffer. Basamid was unstable in the presence of copper sulfate, even without added moisture, making it necessary to keep this additive separate from the fumigant until immediately prior to treatment. Although amines are potential Basamid decomposition products, none were detected in this study and their possible role in Basamid effectiveness remains unknown.

CHAPTER 3.

THE EFFECT OF WOOD AND SELECTED ADDITIVES ON BASAMID DECOMPOSITION RATES

Introduction

Previous laboratory [Forsyth and Morrell 1992] and field tests [Forsyth and Morrell 1993] have indicated that certain additives greatly affect the decomposition rate of Basamid in Douglas-fir heartwood. Temperature and moisture content of the wood are also key factors affecting these rates. However, it is unknown if these additives act alone or if wood or wood components play any role in catalysis.

The following tests were designed to determine the effect of wood and promising additives on the rate of Basamid decomposition and the efficiency of MITC production over other decomposition products including primary amines and carbon disulfide.

Materials and Methods

Glass vials (40 ml) equipped with Teflon-lined silicone septa as used in previous laboratory experiments were employed in these tests. Each vial received 100 mg Basamid either alone or amended with 50 mg Douglas-fir heartwood sawdust at 9% MC (ground to pass a 20-mesh screen), 5 mg pH 12 buffer powder, 2 drops pH 12 buffer solution, 2 drops pH 12 NaOH in water, 2.5 mg copper sulfate, or 2 drops 1N acetic

acid. Each dry additive was tested alone or in tandem with 2 drops of water to determine if the additive required moisture to be effective. The vials were stored at room temperature (20-24°C) for the duration of the experiment.

Two headgas samples were removed from each vial through the septum with a gastight syringe. Each sample was injected into one of two Varian Model 3700 gas chromatographs operating at the following conditions: (1) amine analysis -- injector temperature 200°C, oven temperature 75°C, flame ionization detector temperature 240°C, 6 feet long by 2 mm inner diameter glass column packed with 4% Carbowax 20M on 0.8% KOH 60/80 Carbopack B, nitrogen carrier flow rate 30 cc/minute, or (2) sulfur analysis -- injector temperature 150°C, oven temperature 100°C, flame photometric detector temperature 240°C, 6 feet by 2 mm inner diameter glass column packed with 10% Carbowax 20M on 80/100 Supelcoport, nitrogen carrier flow rate 30 cc/minute. Standard amine solutions were made using distilled water as the solvent and MITC and carbon disulfide solutions were made in ethyl acetate. Concentrations of all detected compounds were determined by comparison with appropriate standards. A repeated measures ANOVA and least squares means separation were run on the data to determine statistical differences in treatments.

Results and Discussion

Unamended Basamid produced no detectable decomposition

products throughout the test period (Table 3.1) indicating the chemical was very stable when kept dry at room temperature. Wood at 9% MC also had no effect on decomposition. However, adding water had a substantial effect on MITC production in both instances. MITC production in the wood plus water treatment did not increase substantially in comparison with Basamid receiving only water, indicating that wood was not a major catalyst in Basamid decomposition to MITC. However, carbon disulfide levels in the wood with water treatment increased dramatically over those receiving water only. It should be noted that this analytical method resulted in two overlapping sulfur peaks, one being carbon disulfide (retention time approximately 0.41 minutes) and the other being unidentified (retention time approximately 0.36 minutes). The unidentified peak, believed to be either carbonyl sulfide or hydrogen sulfide, often overshadowed carbon disulfide, preventing integration of the carbon disulfide peak. Further experiments are needed to fully separate, identify, and quantify the more volatile sulfur-containing compounds.

The effect of pH on MITC production was evident, but moisture appeared to be necessary for this enhancement. Liquid NaOH was more effective than the powdered buffer solution indicating the phosphate compounds in the powder may have reduced its effect as a catalyst. Acetic acid also increased MITC production, but to a lesser degree than the

Table 3.1. MITC and CS_2 concentrations over a 48 hour period in headspace of vials containing 100 mg Basamid amended with selected additives.

	MITC Concentration			CS_2 Concentration		
	ng/ml air					
Additive	4 Hrs	24 Hrs	48 Hrs	4 Hrs	24 Hrs	48 Hrs
None	0	0	0	0	0	0
Water	0	410	236	0	T	0
Wood	0	0	0	0	0	0
Wood plus water	79	324	292	63	345	523
pH 12 powder	5	6	0	0	0	0
pH 12 powder plus water	108	421	334	2	14	0
pH 12 solution (from powder)	64	340	242	2	5	4
pH 12 solution (NaOH)	324	546	299	3	1	0
Copper sulfate	539	306	108	0	0	0
Copper sulfate plus water	2895	705	270	323	1091	850
Acetic acid	223	193	90	288	537	373

higher pH treatments. Acetic acid, however, had an enhancing effect on carbon disulfide production, similar to the wood with water treatment. This was not surprising since Douglas-fir heartwood has a low pH similar to acetic acid; however, the obviously different decomposition pathways at lower versus higher pH's are poorly understood.

Copper sulfate clearly affected decomposition more than any other additive tested (Appendix A.7 and A.8). This result was not unexpected as previous experiments have yielded similar results [Forsyth and Morrell 1992,1993]. It was interesting to note that no added moisture was necessary for this phenomenon; however, the addition of water greatly enhanced the effect. Moisture also greatly increased carbon disulfide production in this treatment. Chromatograms indicated that water shifted the production of early-eluting sulfur compounds exclusively to carbon disulfide while an unidentified sulfur compound was noted in the absence of water.

Interestingly, neither mono- nor di-methylamine were detected in these experiments. This was perhaps the most baffling result of these tests, especially in those treatments which produced high levels of carbon disulfide. When carbon disulfide is removed from the Basamid molecule, presumably as sulfur from position 1 and carbon from the #2 position along with its double-bonded sulfur, the only remaining atoms are carbon, nitrogen, and hydrogen. It would

seem very likely that at least some amine component would be produced in detectable quantities from this residue. Since this was not the case, further tests are needed to determine the fate of nitrogen-containing residues.

CHAPTER 4.

ANALYSIS OF AIR PASSED THROUGH DOUGLAS-FIR HEARTWOOD AND RESIDUAL CHEMICAL LEVELS FOLLOWING BASAMID TREATMENT

Introduction

Previous tests (Chapter 2) to determine the volatile fungitoxic decomposition products of Basamid produced when in contact with Douglas-fir heartwood were incomplete in that not all of the expected products were detected. In addition, the levels of compounds that were detected in closed chambers decreased over time, suggesting that volatile products were escaping from the vials or were reacting within the wood. This made it necessary to design tests that would purge and trap all volatile decomposition products before they could escape the test apparatus. It was also of interest to determine the amount of residual chemical within the wood. The following tests were performed to determine the total cumulative amounts of volatile decomposition products produced from Basamid in Douglas-fir heartwood and to determine residual chemical levels.

Materials and Methods

The chemical collection method employed was modelled after tests previously used with various fungicides in soil [Munnecke et al. 1962; Munnecke and Martin 1964]. It was based on solvent scrubbing of air which had been slowly

passed through glass cylinders packed with Basamid-treated sawdust. Chemical analyses of the solvent allowed for identification and quantification of trapped volatile decomposition products.

Chemical Collection Assembly

Douglas-fir heartwood was ground to pass a 3 mm screen and adjusted to 30% MC by adding an appropriate amount of distilled water. A 1.75 g (oven-dry basis) aliquot of this wood was packed into a glass column (11 cm long X 1.6 cm diameter) and lightly tamped with a wooden dowel. A plastic screen was placed on top of the wood to separate it from the chemical treatment. Approximately 0.125 g (oven-dry basis) of wood was placed on top of the screen and tamped before adding an evenly distributed layer of Basamid. The chemical layer was then covered with an additional 0.125 g of wood. The entire assembly was finally tamped with the wooden dowel, resulting in 5 linear cm of wood in the glass column (Figure 4.1).

The columns received 100 mg Basamid alone or amended with $CuSO_4$ (1% as copper per weight of Basamid). Control columns with no chemical treatment were also tested to determine if the wood alone would produce volatile products that might be trapped in the solvent and interfere with analyses. Three replicates per treatment were used.

Air was passed through the glass columns at a rate of

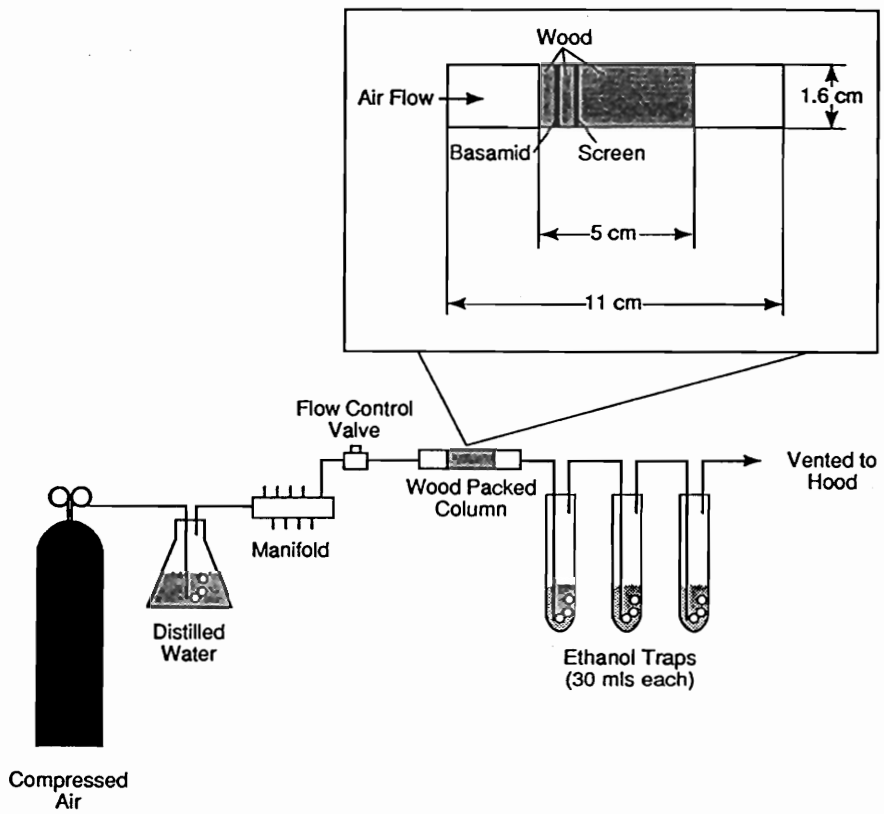


Figure 4.1. Schematic of purge and trap method used to collect volatile decomposition products from Basamid alone and amended with copper sulfate over a 28 day period.

10-20 ml per minute. Before passing through the columns, the air was bubbled through distilled water in order to maintain a high humidity and prevent dessication of the wood. The effluent air stream of each column was bubbled through 3 consecutive solvent traps, each containing 30 ml of 95% ethanol. Ethanol was chosen as a solvent based on solubility properties for the majority of the compounds expected to be produced [Merck 1989; Anonymous 1984]. The ethanol in each trap was completely exchanged after 1,2,3,5, and 7 days, then every 3 days through day 28.

Volatile Chemical Analyses

The trapping solvents were analyzed by injecting 5 ul of each into one of two Varian Model 3700 gas chromatographs equipped for sulfur or amine analysis as described in Chapter 2, except that an oven temperature program was required to completely separate all compounds. These programs were as follows: (1) sulfur compounds - 40°C for 2 minutes, then increasing at 80°C per minute to 120°C for 2 minutes, and (2) amines - 50°C for 2 minutes, then increasing at 80°C per minute to 150°C for 4 minutes. Compounds detected were quantified by comparisons to chromatograms of injected standards.

Residue Analyses

After 28 days, the packed glass columns were disassembled and analyzed for Basamid and decomposition

product residues. The 1.75 g portion of wood on the down stream side of the plastic screen was extracted in 95% ethanol for 48 hours at room temperature. The extract was then analyzed for volatile decomposition products as described above. The extracted wood was oven-dried at 100°C overnight and ground to pass a 30-mesh screen before being analyzed for total carbon, nitrogen, and sulfur.

The remaining 0.25 g of wood containing the Basamid layer was analyzed for Basamid residue using a modification of the method described by Elzner [1980]. The wood and chemical were placed in a test tube and extracted with 20 ml of dichloromethane for 10 minutes on a rotary shaker. The extract was then filtered through a 0.45 um syringe filter and analyzed using a Shimadzu LC6A high performance liquid chromatograph. Analysis conditions were as follows: liquid phase, 95% dichloromethane : 5% hexane; flow rate, 3.5 ml per minute; column, Nucleosil 100 silica 5 micron (250 mm long X 4.6 mm inner diameter)(Alltech Associates, Inc., Deerfield, IL); UV detector, 280 nm; injection volumn, 10 ul. Basamid residues were quantified by comparison to chromatograms of injected Basamid standards in dichloromethane. Percent recoveries were performed by spiking 0.25 g of the same Douglas-fir wood with measured amounts of Basamid and comparing chromatograms to those of Basamid with no wood.

Results and Discussion

Volatile Chemicals

MITC was always produced in higher amounts from Basamid that was amended with $CuSO_4$ (Figure 4.2a), confirming previous tests [Forsyth and Morrell 1992; Forsyth and Morrell 1993]. Production rates for MITC from copper-amended treatments, however, were higher only during the first 7 days. After this time, rates were very comparable for each treatment. For instance, total MITC production from Basamid alone between 7 and 28 days was 216 ug while MITC production from the copper-amended treatment was 238 ug for that same period, a difference of only 22 ug. This indicated that copper effectively catalyzed an initial burst of MITC production from Basamid, but then played no significant role in prolonged production. Similar trends were observed by Munnecke et al. [1962] in Basamid-treated soil, only the levels were higher. This was probably due to the complete mixing of the chemical with the soil using a water suspension. The initially higher rates of MITC production may have been caused by early catalytic effects of soil minerals as suggested by Chandra and Bollen [Chandra and Bollen 1961]. After 28 days, the total production of MITC in the air effluent of the copper-amended treatment was approximately twice that of Basamid alone.

Only one specimen treated with Basamid alone produced

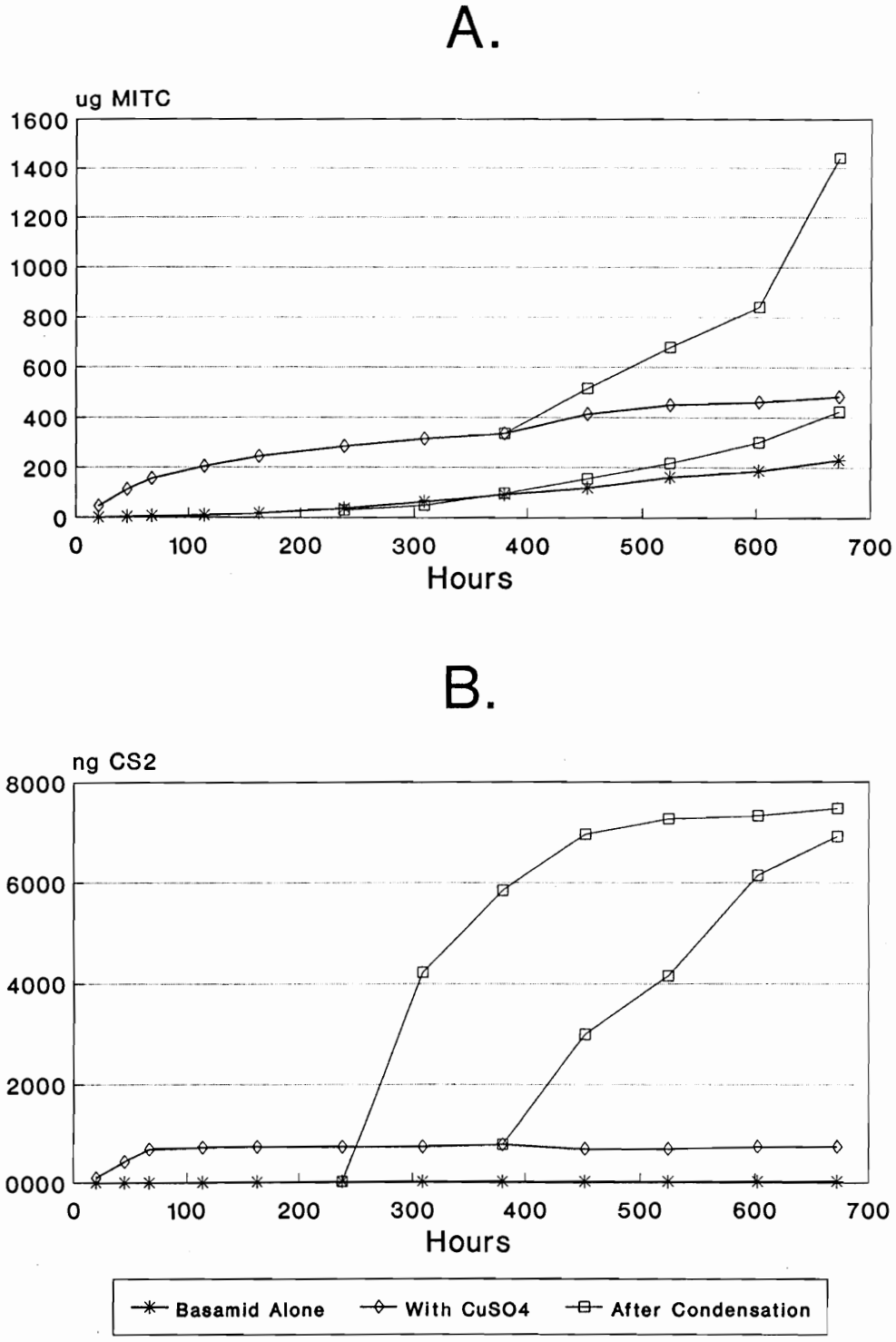


Figure 4.2. Average cumulative MITC (a) and CS_2 (b) production from 100 mg of Basamid either alone or amended with copper sulfate in Douglas-fir heartwood at 30 % MC as determined by purging and trapping in 95% ethanol over a 28 day period. Those values shown after condensation indicate averages of all three samples after water condensed within one sample for each treatment.

carbon disulfide, but only at one time point. Carbon disulfide levels produced from copper-amended Basamid were very low and were only detected during the first 3 days of the test, reflecting the early production of MITC (Figure 4.2b).

It should be noted that one glass column assembly from each treatment was not included in final calculations due to the condensation of water inside the air lines and glass columns. However, this event proved serendipitous in that it further illustrated the effect of moisture on Basamid decomposition. Figure 4.2 includes data from these water-contaminated columns and clearly shows the immediate catalytic effect that water has on Basamid.

Residues

MITC residues in the extracted wood averaged 141.5 ug and 26.8 ug for Basamid alone and with copper, respectively (Table 4.1). This was unexpected since those samples amended with copper produced far more total MITC as detected in volatile analyses. CS_2 residues for both treatments were very low.

Recoveries in Basamid-spiked wood samples ranged from 95.7% to 100.9%. These values were much higher than those reported by Elzner [1980] whose highest recovery was 82.2%. This was probably due to the added sample cleanup and

Table 4.1. Volatile and residual chemicals produced from 100 mg Basamid alone or amended with copper sulfate as determined by a purge and trap method with 95% ethanol.

Sample	Added $CuSO_4$	Volatile MITC(mg)	Volatile CS_2 (mg)	Volatiles (% Total)	Residual MITC(mg)	Residual CS_2(ng)	Residual Basamid(mg)	Total % Recovered
4[a]	-[b]	0.8087	0.0224	0.91	0.3705	509	81.0	82.3
5	-	0.2002	0.0000	0.20	0.1347	0	97.5	97.5
6	-	0.2629	0.0000	0.26	0.1484	397	89.5	89.9
7	+	0.4299	0.0010	0.43	0.0421	0	93.0	93.0
8	+	0.5369	0.0004	0.53	0.0115	0	97.1	97.6
9[a]	+	3.3594	0.0193	3.38	1.4312	5999	69.3	69.3

[a] Samples were contaminated by water condensation.
[b] "+" indicates 1% copper sulfate (% copper per weight of Basamid) was added.

concentration that was required in soil samples, resulting in loss of chemical.

Residual Basamid levels were quite high for both treatments, 93.5 mg and 95.5 mg, respectively, for Basamid alone and copper-amended (Table 4.1). These levels indicate there is a large resevoir of Basamid remaining to provide long-term MITC release.

Conclusions

As shown in previous chapters, copper sulfate catalyzed increased MITC production from Basamid. This increase in production rate seemed to be confined to the first few days following treatment in these tests, however, as rates for both amended and non-amended Basamid were similar during the later time points. This suggests that copper sulfate may boost MITC production to levels necessary for fungal control soon after treatment. Accidental contamination by water indicated the immediate catalytic effect this had on Basamid. High Basamid residues remaining in the wood at the end of the test suggest that this chemical decomposes slow enough to provide a long-lasting resevoir of chemical for future MITC release.

CHAPTER 5.

PRELIMINARY FIELD TRIALS USING THE SOLID FUMIGANT BASAMID AMENDED WITH SELECTED ADDITIVES

Introduction

A variety of compounds are reported to enhance Basamid decomposition in soil [Chandra and Bollen 1961; Merck 1989], but there are few reports on the effects of these additives in wood. Additives may be less effective in wood under field conditions owing to a sharply reduced reactive medium, in comparison to soil, and a wide range in moisture levels. Laboratory tests (Chapters 2, 3, and 4) have confirmed these effects; however, the field performance of Basamid amended with additives has not been tested. Field tests are necessary to determine whether a fumigant will perform adequately under natural, uncontrolled conditions.

The following field tests were established to determine if additives could enhance MITC production within Basamid-treated pole sections at levels necessary to protect against or control fungal attack. The results of the first 2 years of these tests have been reported by Forsyth and Morrell [1993].

Materials and Methods

Eighty untreated air-seasoned Douglas-fir (Pseudotsuga menziesii Mirb.(Franco)) pole stubs (20-25 cm diameter by 1.6

m long) were capped on top with roofing felt to prevent excessive end-grain water absorption. Three 2.2 cm diameter by 30.5 cm deep holes were drilled at approximately 60 degree angles 10 cm apart vertically and equally spaced around the center section of each pole. Each hole received 50 g of Basamid alone or amended with 1% copper sulfate, 10% glucose, 10% ammonium lignin sulfonate, 5% sodium octaborate tetrahydrate, or 50 ml of ethanol, methanol, acetone, or water. All powdered additives were tested with and without a pH 12 buffer powder. The latter liquids were applied based upon previous reports of increased decomposition of Basamid (reported as Dazomet) in the presence of these substances [Merck 1989]. Control poles received either Basamid alone (50 g per hole), no chemical, or metham sodium (150 ml per hole) as a commercial standard. Five poles per treatment were exposed above ground in a vertical position at the Oregon State University Peavy Arboretum test site near Corvallis, Oregon for 2 years.

All poles were sampled 6 months after installation by removing 3 equally spaced increment cores (0.5 cm diameter to the pith) 15 cm above and below the treatment zone. The poles were sampled 1, 2, and 3 years following treatment by removing increment cores 15 and 45 cm above and below the treatment zone. The cores were broken in half, each half being placed into a test tube containing 5 ml of ethyl acetate and extracted for at least 48 hours at room

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

Results and Discussion

MITC was detected in all poles at all sampling periods indicating that Basamid decomposition was occurring (Table 5.1); however, most MITC levels were quite low. A one-way analysis of variance indicated significant differences in the different treatments at all sampling periods; however, least square differences (alpha = 0.05) indicated that the relative effects of the additives on MITC levels changed over time. After 6 months, metham sodium treated poles had significantly higher MITC levels than any Basamid treatment including Basamid amended with copper sulfate with buffer. MITC levels

Table 5.1. MITC distribution in Douglas-fir pole sections 0.5, 1, 2, and 3 years after internal treatment with metham sodium or Basamid amended with selected additives.

			ug MITC/OD g wood								
			+ 45 cm[a]		+ 15 cm		- 15 cm		- 45 cm		
Treatment	pH 12[b]	Year	Outer[c]	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Mean[d]
Metham sodium	-	0.5	-[e]	-	113.3	195.6	173.4	104.2	-	-	147
	-	1	9.6	79.1	29.9	80.4	19.8	54.5	12.2	34.5	40
	-	2	8.4	15.7	5.0	21.3	5.3	14.3	2.3	5.0	10
	-	3	1.7	3.7	5.3	10.6	4.3	3.5	2.5	3.1	4
Basamid Alone	-	0.5	-	-	9.5	16.6	12.9	19.9	-	-	14
	-	1	5.2	13.7	9.7	10.8	5.9	26.5	1.1	5.6	10
	-	2	2.6	3.7	4.1	8.1	6.1	7.7	3.8	3.1	5
	-	3	11.6	14.8	6.0	20.0	15.3	60.7	9.7	12.4	18
	+	0.5	-	-	9.3	14.6	16.4	100.5	-	-	44
	+	1	0.0	5.7	0.2	13.5	11.0	44.8	0.1	10.8	11
	+	2	0.0	0.6	0.0	7.2	3.6	32.5	1.7	8.3	7
	+	3	3.1	5.8	10.9	21.9	24.9	49.0	9.3	16.6	18
Basamid plus $CuSO_4$	-	0.5	-	-	15.9	45.9	10.2	39.1	-	-	27
	-	1	20.8	17.8	11.2	45.7	13.5	48.6	0.0	3.9	20
	-	2	5.9	9.1	10.3	47.1	11.7	66.7	0.4	6.8	20
	-	3	3.4	12.7	34.1	104.9	43.1	95.2	14.5	5.4	39
	+	0.5	-	-	55.3	58.1	90.5	95.4	-	-	75
	+	1	8.2	76.3	22.0	120.8	21.4	203.1	6.7	64.3	65
	+	2	49.2	47.6	69.9	63.9	99.7	96.5	95.8	124.5	81
	+	3	50.1	48.5	60.7	59.4	72.1	69.6	79.9	78.9	65
Basamid plus Glucose	-	0.5	-	-	7.6	13.2	1.3	20.5	-	-	11
	-	1	0.5	0.2	1.7	17.1	4.8	32.8	2.6	3.7	8
	-	2	0.0	0.0	2.7	13.8	7.8	30.9	0.0	3.5	7
	-	3	2.2	7.8	33.2	62.1	35.2	112.4	16.0	30.0	38
	+	0.5	-	-	16.6	37.1	17.6	62.8	-	-	33
	+	1	1.8	20.0	6.8	76.9	81.7	14.2	33.1	21.6	32
	+	2	0.6	1.9	9.0	33.5	21.2	54.5	2.3	5.0	16
	+	3	1.2	3.9	9.3	29.4	48.7	91.8	9.0	23.9	27

(Continued next page)

Table 5.1 (Continued)

Basamid plus	-	0.5	-	-	0.2	5.5	1.3	23.2	-	-	8
Lignin	-	1	1.4	2.8	2.9	24.9	4.8	93.1	2.1	14.0	18
	-	2	1.5	2.5	4.0	17.8	15.5	52.1	3.1	18.7	14
	-	3	2.3	6.6	8.7	20.8	16.0	33.0	13.7	5.8	12
	+	0.5	-	-	3.3	27.0	4.2	41.3	-	-	19
	+	1	3.2	17.4	7.0	63.6	16.1	79.6	5.5	3.0	24
	+	2	0.0	1.6	1.2	26.4	7.7	50.7	0.0	9.8	12
	+	3	2.1	1.6	19.3	13.5	35.3	28.9	3.1	9.2	14
Basamid plus	-	0.5	-	-	9.5	17.9	18.9	33.1	-	-	20
Boron	-	1	0.4	11.3	6.6	30.8	15.0	49.6	0.1	5.2	15
	-	2	0.6	1.6	4.5	12.7	5.8	25.5	1.2	2.9	7
	-	3	0.3	0.3	7.6	17.9	21.6	27.1	2.6	2.6	10
	+	0.5	-	-	7.0	11.6	8.0	30.4	-	-	14
	+	1	0.0	11.8	7.7	24.2	17.2	33.5	1.0	5.6	13
	+	2	0.2	1.1	3.5	13.0	9.2	29.3	2.0	5.8	8
	+	3	29.2	54.5	8.8	17.7	66.5	33.8	11.3	49.1	34
Basamid plus	-	0.5	-	-	3.0	6.0	0.1	12.0	-	-	5
Ethanol	-	1	0.0	2.1	0.4	15.3	0.2	7.3	0.0	0.0	3
	-	2	0.0	0.5	1.8	4.7	1.8	6.3	0.4	0.2	2
	-	3	0.1	0.8	1.0	8.4	3.0	12.5	0.7	1.4	4
Basamid plus	-	0.5	-	-	2.8	7.2	0.8	16.0	-	-	8
Methanol	-	1	0.0	0.1	0.0	3.7	0.2	9.5	0.3	0.6	2
	-	2	0.0	0.5	0.8	3.3	2.6	8.6	0.0	0.1	2
	-	3	0.2	0.9	9.6	11.6	19.0	28.7	7.2	5.0	10
Basamid plus	-	0.5	-	-	1.2	4.4	1.0	8.2	-	-	4
Acetone	-	1	4.3	18.3	9.3	17.0	15.2	26.1	15.6	12.9	15
	-	2	0.0	0.0	2.8	8.3	7.2	16.0	0.9	1.3	5
	-	3	2.0	4.2	9.3	27.3	14.0	38.2	7.0	15.3	14
Basamid plus	-	0.5	-	-	1.0	3.0	1.6	14.8	-	-	5
Water	-	1	0.0	1.2	0.0	2.3	0.4	8.3	0.0	0.0	2
	-	2	0.3	2.0	1.5	7.3	5.1	22.1	2.6	7.7	6
	-	3	0.0	0.2	1.6	6.0	9.6	79.8	6.2	5.5	14

[a] Values are distance above (+) and below (-) treatment zone.
[b] "+" indicates the addition of powdered pH 12 buffer (5% by weight) to Basamid.
[c] Cores were broken in half and analyzed separately as "outer" and "inner" segments. Values represent mean of 15 core segments.
[d] Mean values for all 120 core segments within each treatment group.
[e] "-" indicates no core was taken at this location.

in all remaining treatments were significantly lower than the copper sulfate with buffer treatment. Addition of pH 12 buffer increased MITC levels in all treatments except when used with boron. Boron was tested not only because it was a metal, but also because of the alkaline buffering capacity of the formulation used. It is unclear why boron with buffer reduced MITC production.

After 1 year, copper sulfate with buffer produced significantly higher MITC levels than any other treatment, including metham sodium. This trend was repeated after 2 and 3 years of exposure. Interestingly, metham sodium treated poles had MITC levels that were not significantly different from the other amended Basamid treatments after 2 years, reflecting high initial levels of decomposition to MITC which rapidly declined over time. This trend has been found in laboratory trials with metham sodium in different wood species [Morrell 1992] and helps to explain the need for relatively short retreatment cycles with this fumigant [Morrell and Corden 1986a]. While MITC levels declined between 6 months and 1 year with copper sulfate-buffer amended Basamid, the decline was less dramatic than that observed with metham sodium. These levels rebounded during the second year and 3 year results were similar to 1 year data, indicating a slow, continuous decomposition of Basamid with this treatment. Munnecke et al. [1962] also noted that the rate of evolution and dissipation of MITC from soil was

more rapid for NaMDC than for Basamid. Other tests have indicated that solutions of Basamid were more effective as they aged, reflecting the slow decomposition to toxic compounds [Goksoyr 1964; Herschler 1953]. It was also noteworthy that MITC levels in the copper sulfate-buffer treatment were more equally distributed throughout the pole stubs (Table 5.1), providing an evenly distributed protective barrier rather than high levels only in the zone immediately adjacent to the treatment holes. There are no definitive studies showing the exact MITC levels required for fungal control, owing to the difficulty of accurately maintaining wood moisture, chemical levels, and fungal viability over a test period; however, Zahora [1983] found that low residual levels of MITC provided a long-term protection against invasion from decay fungi. Other studies [Eslyn and Highley 1985; Highley 1991] have shown that long exposures to Basamid can effectively control fungal growth. Application of Basamid before internal decay has caused substantial wood loss may greatly increase the service life of Douglas-fir utility pole.

Conclusions

The results of these field tests indicate that copper sulfate plus a pH 12 buffer can significantly enhance decomposition of Basamid to MITC, thereby increasing the prospects for successful elimination of established decay

fungi. MITC levels remained relatively constant and were more evenly distributed throughout Basamid-treated pole stubs than in treatments with metham sodium. These data indicate that Basamid may represent a longer term, more complete internal protection for wood poles. Simultaneous application of Basamid and additives can increase MITC production from this solid, less volatile compound, providing a substantial increase in applicator and environmental safety.

CHAPTER 6.

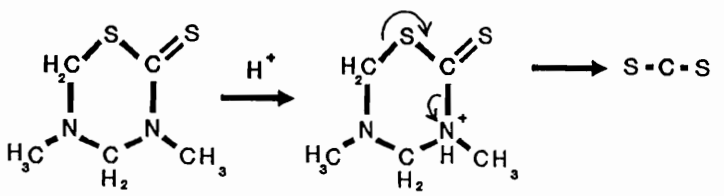
GENERAL CONCLUSIONS

For a preservative to be acceptable, it must be effective against target organisms at levels that are both economical and not dangerous to the environment or the applicator. Furthermore, these systems must have long-term effectiveness. Remedial treatments must also be able to diffuse throughout the treated substrate at fungitoxic levels.

Chemical Aspects of Basamid Decomposition

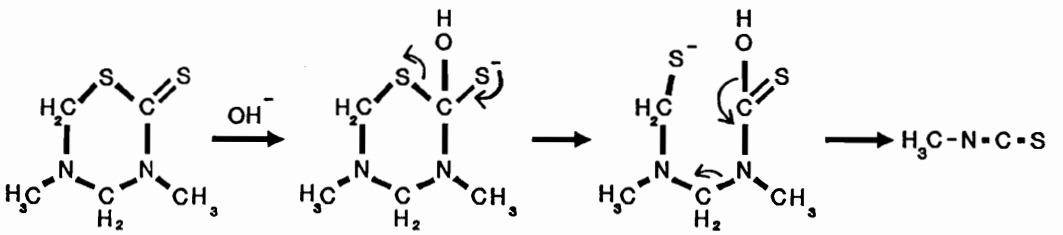
One of the goals of this thesis was to determine the effects of additives on the rate of Basamid decomposition and the chemicals being produced during that process. The chemistry of Basamid decomposition in soil has been elucidated; however, wood is a drastically different substrate which affected chemical interactions differently. It is clear that certain conditions and additives altered decomposition, but in different ways.

Under acidic, or unbuffered, conditions, large quantities of carbon disulfide were produced. A possible pathway for this production is:

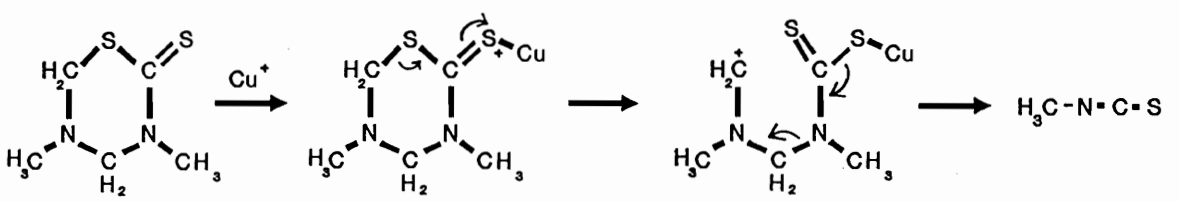


Although carbon disulfide is fungitoxic, it does not interact with the wood substrate, leaving it unprotected after a short time. Unfortunately, Douglas-fir heartwood is acidic and would likely support a similar reaction when moisture is present. It is necessary to alter this condition through the use of alkaline buffers.

Under basic conditions, higher amounts of MITC are produced. A possible scenario for this reaction is as follows:



Even though MITC production is increased when using a pH 12 buffer, there are still large quantities of carbon disulfide being produced. This is likely due to concomitant reactions with the acidic heartwood. If the system could be further altered to favor MITC production, an increased efficiency of chemical used would be achieved and longer term protection afforded. Copper sulfate greatly enhanced MITC production. Although this mechanism is not clearly understood, one possibility is:



This additive, coupled with the pH 12 buffer, provided for a greatly increased efficiency in MITC production. If the two pathways for these additives shown above are correct, then MITC is being produced through two separate pathways. This should provide for a delivery system that is efficient, controllable, and long-lasting.

Solid Versus Liquid Fumigants

Of the four fumigants registered for wood use, three are applied as liquids, creating a hazard to the applicator as well as the environment. Liquids are more easily splashed onto the skin or into the eyes or mouth than are solids. They are also much more difficult to recover in the event of a spill. The improved safety aspects of solid fumigants makes these chemicals worthy of further investigation for potential use.

Controlling Release

While remedial treatments cannot provide protection comparable to conventional treatments, they are expected to perform for the length of a typical 10 to 15 year maintenance cycle. With the exception of chloropicrin and Vorlex, which can be effective for nearly 2 decades in some applications, the most commonly used fumigant, NaMDC, provides 3 to 7 years of protection, depending on wood species. Controlling the release of the active ingredient may represent an ideal

method for increasing the service life of fumigants.

Controlled release of a chemical can be accomplished in 2 ways; encapsulation or controlled catalysis. Encapsulation is based on holding a biocide in a container which allows the chemical to slowly escape into the surrounding substrate. The container may be either permeable or impermeable to the chemical. The only fumigant that is currently applied as a solid, MITC-Fume, is encapsulated in a glass or aluminum vial that has a restricted opening in one end to allow for slow escape of MITC. It has proven effective against internal decay in utility poles, but this product also has drawbacks. The delivery system, though effective, is an added expense that some utility companies cannot afford. The safety of this treatment has also been questioned in the event that a pole containing glass-encapsulated MITC-Fume vials is struck by a vehicle, thus exposing people in the immediate area to the volatile chemical. These drawbacks have limited widespread use of this very effective product.

Using containers that are permeable to the fumigant is another form of encapsulation. No opening is required to release the fumigant; instead the chemical diffuses through the container wall usually made of a polymer that allows for chemical diffusion at a rate that is fast enough to be effective while slow enough to retain a reservoir of chemical to provide long-term protection. This promising method of

controlled release is currently under investigation.

A third form of encapsulation is the containment of a fumigant in a material that will solubilize within the treated substrate. This method has been tested extensively using gelatin-encapsulated MITC [Zahora 1983; Zahora et al. 1985]. Gelatin capsules are filled with liquid MITC and allowed to solidify before being placed into a utility pole. Moisture in the pole, either added during treatment or absorbed from the environment, solubilizes the gelatin coating and allows the MITC to sublime to a gas. Unfortunately, the entire capsule wall solubilizes at approximately the same time. This means that release of MITC is only delayed and not slowly accomplished over time. Microencapsulation is a variation on the same theme, whereby small amounts of active ingredient are coated with varying thicknesses of soluble material or with dissimilar materials that solubilize at different rates. Using this method, small amounts of chemical are released at different times rather than all at once. The use of coatings with differing solubility rates can provide an effective long-term treatment. However, this method is also very expensive and has not been tested for wood use. Furthermore, these systems do not change the safety aspects of treatment since they still employ volatile, toxic liquids which can be released if the encapsulating material ruptures.

An alternative method for slowing the release of

fumigants is through controlling the catalysis of the applied chemical into one or more active ingredients. Chemical decomposition into desirable compounds has been applied extensively in agriculture. For instance, benomyl, a post-harvest fungicide decomposes to carbendazim, a fungicidal compound that prolongs the shelf-life of many fruits and vegetables [Zwelg and Gao 1983]. Chemical catalysis may be affected by environmental conditions, such as moisture and temperature, which are often uncontrollable. The process may also be affected by substrate chemistry, including pH or the presence of metals.

NaMDC, the most widely used wood pole fumigant, is an excellent example of a compound which must catalyze to become effective. This chemical decomposes to MITC which acts as the primary fungicide. However, tests have shown that NaMDC decomposition occurs at a very rapid rate, explaining the need for shorter retreatment cycles when using this chemical as a wood fumigant. Wood is known to accelerate NaMDC decomposition [Graham and Corden 1980]. Morrell [1992] found that NaMDC decomposes at vastly different rates in different wood species. This may be attributed to differences in wood chemistry, especially pH, of the various species. NaMDC decomposition to MITC in soil is not always complete and may also be influenced by soil pH [Turner and Corden 1963; Smelt and Leistra 1974].

Basamid must also decompose to be effective. Like

NaMDC, Basamid decomposition is affected by the pH of the substrate (Chapters 2, 3, and 5). Wood and environmental factors affect not only the rate of decomposition, but also the types of compounds formed. The desired decomposition product, MITC, is not formed at pH's comparable to those of Douglas-fir heartwood (pH 2 to 3). Alkaline buffers enhance MITC production from Basamid, but do not seem to enhance the efficiency of MITC production over other compounds, as large amounts of CS_2 are also produced. The addition of $CuSO_4$, however, enhances not only the production of MITC, but also the efficiency of the process. Basamid performs very well in mineral-rich soils. Wood, however, is notoriously mineral-deficient and requires the presence of either metals or buffers to encourage sufficient MITC production from Basamid. This phenomenon is actually very favorable for the use of Basamid as a wood fumigant. As indicated in Chapter 2, MITC production increased linearly with the addition of $CuSO_4$. Catalysis to MITC can not only be encouraged, it can also be successfully regulated to optimum rates for fungal control by the addition of an appropriate amount of $CuSO_4$. Field tests with this additive (Chapter 5) indicate that MITC production remains relatively constant over 3 years, while MITC in NaMDC-treated poles decreased dramatically within 1 year. One concern, however, is that initial rates of MITC production from copper-amended Basamid may be too low to eliminate actively growing decay fungi.

A more appropriate use of Basamid as a utility pole fumigant may be as a pre-installation treatment, before decay has occurred so that long-term, low-level MITC production will provide protection against fungal invasion. Gray [1962] showed that less NaMDC was required to kill weed seeds in soils that provided for slow chemical decomposition than in those which rapidly catalyzed breakdown. Basidiospore germination is more sensitive to fumigants than is actively growing mycelium [Bjurman and Goodell 1991]. Also levels of MITC that are not fungitoxic, but are fungistatic, to actively growing mycelium will prevent fungal invasion of utility poles for some time [Zahora 1987].

The development of Basamid-based systems which optimize MITC production at rates which are sufficient to prevent germination of spores or growth of hyphal fragments may represent ideal systems for providing long-term protection to large wood members.

Future Research Needs

As with any wood preservative, this chemical requires in-service field tests to prove its efficacy as a wood fumigant. The field tests reported in Chapter 5 will continue to be sampled through at least 5 years. In-service field tests have also been initiated by researchers at Oregon State University.

This thesis concentrated on the volatile decomposition

products of Basamid; however, non-volatile decomposition products have also been reported in soil studies. Some of these compounds are fungitoxic and their potential for enhancing the performance of Basamid in wood is unknown. Future work is needed to determine the presence and identity of these non-volatile compounds.

The absence of volatile primary amines is difficult to explain. It is possible that these highly reactive compounds were tightly bound to the wood, but no amines were isolated even when ethanol extraction was employed. It is also possible that these compounds recombined with other decomposition products to form non-volatile compounds as mentioned above.

Improving our understanding of Basamid decomposition and the relative toxicities of these breakdown products would permit the development of safer, more effective remedial treatments which perform over longer periods than conventional fumigants. These systems will become increasingly important as utility companies examine the cost-benefits of pole maintenance programs.

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APPENDICES

APPENDIX A.1

ANOVA Table

Source	DF	Sum of Squares	Mean Square	F-value	Prob > F
Model	10	613427.5	61342.7	72.4	0.0001
Error	97	82183.8	847.3		
Total	107	695611.3			

LSD Groupings

MC (%)	Buffer	N	Mean	Grouping*
60	Yes	18	180.3	A
30	Yes	18	140.5	B
60	No	18	96.6	C
30	No	18	36.7	D
60	Yes	18	0.0	E
30	No	18	0.0	E

*Means with the same letter are not significantly different at alpha = 0.05.

APPENDIX A.2

ANOVA Table

Source	DF	Sum of Squares	Mean Square	F-value	Prob > F
Model	12	2123227.5	176935.6	42.3	0.0001
Error	131	547965.8	4182.9		
Total	143	2671193.3			

LSD Groupings

Additive	Buffer	N	Mean	Grouping*
CuCl	Yes	18	324.5	A
$CuSO_4$	Yes	18	279.4	B
CuCl	No	18	137.4	C
$MnSO_4$	Yes	18	103.1	C D
$CuSO_4$	No	18	82.9	D E
$MgSO_4$	Yes	18	75.2	D E
$MnSO_4$	No	18	62.8	D E
$MgSO_4$	No	18	55.9	E

*Means with the same letter are not significantly different at alpha = 0.05.

APPENDIX A.3

ANOVA Table

Source	DF	Sum of Squares	Mean Square	F-value	Prob > F
Model	8	100265668	12533208.5	65.6	0.0001
Error	63	12028757	190932.6		
Total	71	112294424			

LSD Groupings

Copper (%)	N	Mean	Grouping*
10	18	3064.7	A
1	18	1350.5	B
0.5	18	438.5	C
0	18	249.2	C

*Means with the same letter are not significantly different at alpha = 0.05.

APPENDIX A.4

ANOVA Table

Source	DF	Sum of Squares	Mean Square	F-value	Prob > F
Model	26	61994303	2384396.3	24.6	0.0001
Error	261	25331847	97056.9		
Total	287	87326149			

LSD Groupings

Additive	MC(%)	Temp.(°C)	N	Mean	Grouping*
Both	30	32	12	1701.5	A
Buffer	30	32	12	1300.8	B
Copper	30	32	12	990.3	C
Both	30	23	12	708.5	D
Copper	30	23	12	542.0	D E
None	30	32	12	468.8	D E
Buffer	30	23	12	451.4	E F
Copper	30	5	12	205.0	F G
None	30	23	12	190.6	G
Both	30	5	12	167.9	G
Both	6	32	12	130.4	G
Copper	6	32	12	68.1	G
Buffer	30	5	12	43.1	G
Copper	6	5	12	29.4	G
Both	6	23	12	28.9	G
Copper	6	23	12	26.8	G
Buffer	6	32	12	21.0	G
None	6	5	12	10.5	G
Buffer	6	23	12	1.3	G
Both	6	5	12	1.2	G
None	6	32	12	0.0	G
Buffer	6	5	12	0.0	G
None	30	5	12	0.0	G
None	6	23	12	0.0	G

*Means with the same letter are not significantly different at alpha = 0.05.

APPENDIX A.5

ANOVA Table

Source	DF	Sum of Squares	Mean Square	F-value	Prob > F
Model	26	835714175	32142852.9	13.1	0.0001
Error	261	641198377	2456698.8		
Total	287	1476912552			

LSD Groupings

Additive	MC(%)	Temp.(°C)	N	Mean	Grouping*
Copper	30	32	12	5001.9	A
Both	30	32	12	4481.9	AB
Buffer	30	32	12	4211.9	AB
None	30	32	12	3733.8	B
Copper	30	23	12	3305.0	B
Buffer	30	23	12	2037.3	C
None	30	23	12	1789.3	C
Both	30	23	12	1537.5	C D
Copper	6	32	12	322.3	D E
Both	6	32	12	321.4	D E
Copper	30	5	12	252.4	E
Buffer	6	32	12	213.1	E
None	6	32	12	161.3	E
None	6	23	12	85.8	E
Both	30	5	12	76.1	E
None	30	5	12	41.2	E
Buffer	30	5	12	21.4	E
Both	6	23	12	20.6	E
Buffer	6	23	12	18.9	E
Copper	6	5	12	7.4	E
None	6	5	12	6.7	E
Copper	6	23	12	5.1	E
Buffer	6	5	12	1.5	E
Both	6	5	12	0.6	E

*Means with the same letter are not significantly different at alpha = 0.05.

APPENDIX A.6

ANOVA Table

Source	DF	Sum of Squares	Mean Square	F-value	Prob > F
Model	26	8731.4	335.8	4.6	0.0001
Error	261	18940.3	72.6		
Total	287	27671.7			

LSD Groupings

Additive	MC(%)	Temp.(°C)	N	Mean	Grouping*
None	30	32	12	21.2	A
None	30	23	12	17.2	A
Copper	30	32	12	9.1	B
Buffer	6	32	12	6.9	B C
Copper	6	32	12	6.7	B C D
Copper	30	23	12	5.6	B C D
Buffer	30	23	12	4.7	B C D
Buffer	30	32	12	3.2	B C D
Both	30	32	12	2.7	B C D
Both	30	23	12	2.1	C D
Both	6	32	12	1.6	C D
Copper	30	5	12	1.4	C D
Buffer	6	23	12	0.8	C D
Buffer	30	5	12	0.8	C D
Copper	6	5	12	0.4	C D
Both	30	5	12	0.4	C D
None	6	5	12	0.3	C D
Both	6	23	12	0.2	C D
Copper	6	23	12	0.1	C D
Both	6	5	12	0.0	D
None	6	32	12	0.0	D
Buffer	6	5	12	0.0	D
None	30	5	12	0.0	D
None	6	23	12	0.0	D

*Means with the same letter are not significantly different at alpha = 0.05.

APPENDIX A.7

ANOVA Table

Source	DF	Sum of Squares	Mean Square	F-value	Prob > F
Model	12	12375623	1031301.9	6.7	0.0001
Error	86	13273946	154348.2		
Total	98	25649569			

LSD Groupings

Additive	N	Mean	Grouping*
Copper/water	9	1289.8	A
NaOH	9	389.8	B
Copper	9	317.6	B C
Buffer powder/water	9	287.5	B C
Wood/water	9	231.9	B C
Water	9	215.6	B C
Buffer solution	9	215.0	B C
Acetic acid	9	168.7	B C
Buffer powder	9	3.3	C
None	9	0.0	C
Wood	9	0.0	C

*Means with the same letter are not significantly different at alpha = 0.05.

APPENDIX A.8

ANOVA Table

Source	DF	Sum of Squares	Mean Square	F-value	Prob > F
Model	12	5913314	492776.2	26.5	0.0001
Error	86	1597904	18580.3		
Total	98	7511219			

LSD Groupings

Additive	N	Mean	Grouping*
Copper/water	9	754.7	A
Acetic acid	9	399.3	B
Wood/water	9	310.4	B
Buffer powder/water	9	5.2	C
Buffer solution	9	3.9	C
NaOH	9	1.5	C
Water	9	0.1	C
Copper	9	0.0	C
None	9	0.0	C
Buffer powder	9	0.0	C
Wood	9	0.0	C

*Means with the same letter are not significantly different at alpha = 0.05.