

DECOMPOSITION OF BASAMID IN DOUGLAS-FIR HEARTWOOD: LABORATORY STUDIES OF A POTENTIAL WOOD FUMIGANT¹

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ABSTRACT

Basamid (3,5-dimethyl-1,3,5,2H-tetrahydrothiadiazine-2-thione), a crystalline powder first used as a soil sterilant, has shown promise as a wood fumigant. This chemical decomposes to methylisothiocyanate (MITC), the primary active ingredient, as well as other products; but the rate of decomposition in wood is too slow to be effective unless certain catalysts are used. This study explored conditions and additives that accelerated Basamid decomposition in Douglas-fir heartwood. MITC production increased with increasing temperature and moisture content. Decomposition was also enhanced by a buffer powder formulated to reach pH 12 when mixed with 100 ml of water and, more efficiently, by copper sulfate. Carbon disulfide, a less fungitoxic compound, was the only other decomposition product detected in this study. Additional tests using a purge-and-trap system indicated that MITC was produced at a steady, moderate rate over a 28-day period. Addition of copper as a catalyst in these tests increased MITC production only during the first 7 days. Chemical analyses of residues at the conclusion of the tests indicated that most of the Basamid remained unchanged, providing a reservoir of chemical that should provide long-term MITC release.

Keywords: Basamid, fumigants, internal decay, utility poles, catalysis, Douglas-fir.

INTRODUCTION

Wood utility poles are routinely pressure-treated with preservatives to protect them against biological deterioration. However, many pole species, such as Douglas-fir (*Pseudotsuga menziesii*), in western North America contain a high proportion of heartwood, which is largely impermeable to liquid penetration. Although the heartwood of Douglas-fir is im-

pervious to liquids, it is permeable to gases (Hand et al. 1970; Graham 1973). Several volatile agricultural chemicals have been added as liquids to the interior of poles via downward-sloping holes, where they vaporize and move through the wood as gases to kill established decay fungi. Poles remedially 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 (Na-MDC), Vorlex (20% methylisothiocyanate, 80% chlorinated C-3 hydrocarbons), chloropicrin (96% trichloronitromethane), and MITC-Fume® (97% solid methylisothiocyan-

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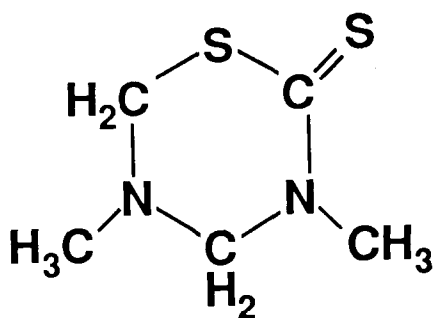


FIG. 1. The chemical structure of Basamid.

ate [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[®], a solid at room temperature, has proven highly effective as a wood fumigant; however, it is also very volatile, expensive, and not yet widely used.

Alternatives to the currently registered chemicals are crystalline solids that decompose to produce volatile fungitoxic byproducts. One such chemical is Basamid (United Agricultural Products, Greeley, CO), a soil sterilant. Because Basamid is a solid, it is not as readily absorbed through the skin as are liquids, and it is more easily stored and recovered in the event of a spill.

Chemically, Basamid is a heterocyclic ring containing carbon, nitrogen, sulfur, and hydrogen (Fig. 1). It was first prepared in 1897 by Delepine, who reacted carbon disulfide with trimethyltrimethylene triimine (Herschler 1953). 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, it has been prepared commercially by reacting carbon disulfide with methylamine and caustic soda (Merck and Co., Inc. 1989).

The 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. It has been used in agriculture as a fungicide, herbicide, nematocide, and insecticide (Keays and Zedler 1957; Hartley and Kidd 1987), as well as a slimicide in pulp and paper manufacturing (Herschler 1953) and as a preservative in adhesives and glues (Hartley and Kidd 1987).

Basamid decomposes slowly in wood and has successfully controlled decay fungi there after long exposures (Graham and Corden 1980; Eslyn and Highley 1985). Such slow decomposition could be useful if the chemical were applied before decay had to be eradicated. However, in pure form Basamid does not decompose rapidly enough to diffuse and kill actively growing decay fungi in wood (Highley and Eslyn 1986; Morrell et al. 1988). To be effective there, a chemical must be able to eliminate an actively growing fungal colony within 6 to 12 months after application.

Under dry conditions and ambient temperatures, Basamid is stable and not considered biologically active. Effectiveness against target organisms depends on the decomposition products formed and the rate at which they are released. 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; Hartley and Kidd 1987; Worthing 1987). MITC is considered to be the most important volatile toxicant produced (Munnecke et al. 1962; Goksoyr 1964; Spencer 1981) and has received the most attention in Basamid evaluations. MITC production is dependent on several environmental conditions including moisture, temperature, pH, and the presence of trace metals.

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; Hartley and Kidd 1987). Under neutral or basic conditions, the reaction shifts toward the production of MITC and hydrogen sulfide along with form-

aldehyde 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). In one of the first tests of Basamid in wood, 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). 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.

While there have been several studies of Basamid decomposition in soil, little information exists on how additives affect Basamid decomposition in wood. This paper describes tests designed to determine the effect of moisture and temperature as well as selected additives on the decomposition of Basamid in Douglas-fir heartwood. After an initial screening, two additives were selected for further study of their effects on both the rate of decomposition and the balance of decomposition products. Additional tests employing a purge-and-trap system were used in order to determine whether volatile products were escaping from the vials or reacting with the wood and to assess residual Basamid in the wood at the end of the test period.

MATERIALS AND METHODS

Initial screening of additives

Several powdered additives were tested for their ability to enhance the decomposition of Basamid to MITC. On the basis of the weight of Basamid used, the following percentages of metals or other substances were added: 0.5, 1,

5, and 10% copper sulfate; 1% copper chloride; 1% manganese sulfate; 1% magnesium sulfate; and 5% of a buffer powder consisting of sodium phosphate (di and tri basic) formulated to reach pH 12 when mixed with 100 ml of water.

Douglas-fir heartwood was ground to pass a 3-mm screen. It was then adjusted to 30% moisture content (MC) in all tests except the ones in which only the buffer powder was added to it; in those cases it was adjusted to MCs of 12, 30, or 60%. In each test, 3 g (based on oven-dry wt) of sawdust was placed in each of three 40-ml glass vials and lightly tamped. In each of the three vials, 120 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 lightly tamped sawdust. All vials were then tightly capped with a Teflon-lined silicone septum and stored at 23 C.

Basamid decomposition was determined 1, 3, 5, 7, 10, and 14 days after treatment by removing an air sample through the septum of each vial with a gas-tight syringe. Those sample volumes ($<250 \mu\text{l}$) provided enough air for detection of MITC without creating a significant negative pressure within the vial. The samples were 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 concentrations were quantified by comparison with injections of known amounts of MITC dissolved in ethyl acetate.

Effect of additives on decomposition

On the basis of the initial screening, tests were run to determine the effects of wood and of promising additives on the rate and efficiency of Basamid decomposition into MITC and other products including primary amines and carbon disulfide. Glass vials (40 ml) equipped with Teflon-lined silicone septa were

again employed. Each vial received 100 mg of Basamid either alone or amended. Three vials received 2 drops of water. Three vials received 50 mg of Douglas-fir heartwood sawdust ground to pass a 20-mesh screen and adjusted to an MC of 9%. Another three vials received 50 mg of sawdust to which 2 drops of water had been added. The following additives were tested without sawdust, each in three vials; 5 mg of buffer powder (alone and with 2 drops of water), 2 drops of buffer solution at pH 12, 2 drops of NaOH in water at pH 12, 2.5 mg of copper sulfate (alone and with 2 drops of water), and 2 drops of 1N acetic acid. All vials were stored at room temperature (20–24 C) for the duration of the experiment.

After 4, 24, and 48 h, two headspace samples were removed through the septum of each vial with a gas-tight syringe. Each sample was injected into one of two Varian 3700 gas chromatographs. The chromatograph used for amine analysis operated at the following conditions: injector temperature, 200 C; oven temperature, 75 C; flame ionization detector temperature, 240 C; column 6 ft long by 2-mm inner diameter, glass, packed with 4% Carbowax 20M on 0.8% KOH 60/80 Carbowax B (Supelco, Inc.); nitrogen carrier flow rate, 30 ml/min. The chromatograph used for sulfur analysis operated as follows: injector temperature, 150 C; oven temperature, 100 C; flame photometric detector temperature, 240 C; column, 6 ft long by 2-mm inner diameter, glass, packed with 10% Carbowax 20M on 80/100 Supelcoport (Supelco, Inc.); nitrogen carrier flow rate, 30 ml/min. Standard amine solutions were made with distilled water as the solvent; MITC and carbon disulfide solutions were made in ethyl acetate. Concentrations of all detected compounds were determined by comparison with appropriate standards.

Effects of buffer and copper on decomposition

Tests were run in the presence of wood to determine the decomposition products of Basamid either alone or amended with 5% buffer powder or 1% copper sulfate or both, with the

powdered additives being measured as percentages of the weight of Basamid used; the additives were mixed thoroughly before treatment. For each test, 120 mg of Basamid with or without additive(s) was placed in an evenly distributed layer in each of three 40-ml vials and covered with 1 g (based on oven-dry wt) of sawdust that had been adjusted to an MC of 6 or 30%. A fine-meshed plastic screen was then placed on top of the sawdust, and an additional 2 g (based on oven-dry wt) of sawdust adjusted to the same MC was placed on top of the screen. 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. Control vials containing either sawdust but no chemicals or chemicals but no sawdust were assembled in sets of three to detect the volatile components from untreated wood and the stability of Basamid with additives in the absence of moisture.

Two air samples were removed from each vial after 5, 10, 20, and 30 days. One of these samples was injected into a Varian 3700 gas chromatograph and analyzed for sulfur-containing compounds as described above. The other sample was injected into a second Varian 3700 gas chromatograph and analyzed for non-sulfur compounds by a flame ionization detector. Operating conditions were the same as described above except for the following: column temperature, 110 C; column, 4% Carbowax 20M on 0.8% KOH 60/80 Carbowax B (Supelco, Inc.).

Total chemical analyses

The chemical collection method was modeled after those previously used to study various fungicides in soil (Munnecke et al. 1962; Munnecke and Martin 1964) by solvent scrubbing of air that had been slowly passed through glass cylinders packed with Basamid-treated sawdust. Chemical analyses of the solvent allowed identification and quantification of trapped volatile decomposition products.

Douglas-fir heartwood was ground to pass a 3-mm screen and adjusted to 30% MC by adding an appropriate amount of distilled water

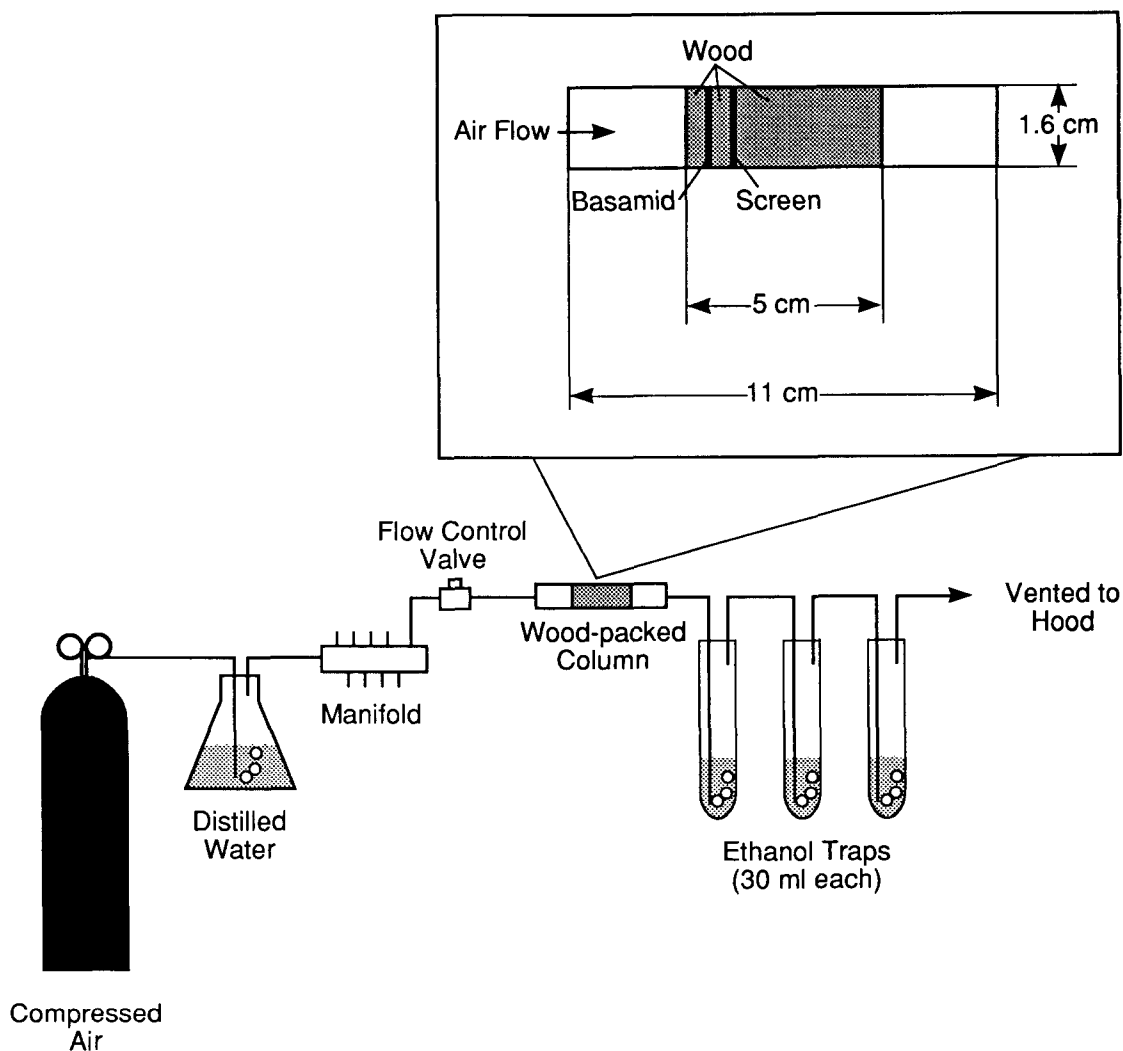


FIG. 2. Purge-and-trap system used to collect volatile decomposition products from Basamid or Basamid amended with copper sulfate over a 28-day period.

and allowing it to equilibrate for at least 48 h at 5 C. A 1.75-g (oven-dry basis) aliquot of this wood was packed into a glass column (11 cm long by 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 an evenly distributed layer of Basamid was added. The chemical layer was then covered with an additional 0.125 g of wood. The entire as-

sembly was tamped with the wooden dowel, resulting in 5 linear cm of wood in the glass column (Fig. 2).

The columns received 100 mg Basamid or Basamid amended with CuSO_4 (1% as copper per weight of Basamid). Control columns with no chemical treatment were also tested to determine whether 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 10–20 ml/min. Before passing through the columns, the air was humidified by bubbling through distilled water to prevent desiccation of the wood. The effluent air stream from each column was bubbled through three consecutive solvent traps, each containing 30 ml of 95% ethanol. Ethanol was chosen as a solvent because of the solubility properties of the majority of compounds expected to be produced (Weast 1984; Merck and Co., Inc. 1989). The ethanol in each trap was completely exchanged after 1, 2, 3, 5, and 7 days, and then every 3 days through day 28.

The trapping solvents were analyzed by injecting 5 μ l of each into one of two Varian Model 3700 gas chromatographs equipped for sulfur or amine analysis as described earlier, 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 min, then increasing at 80 C per min to 120 C for 2 min; and (2) amines—50 C for 2 min, then increasing at 80 C per min to 150 C for 4 min. Compounds detected were quantified by comparisons with chromatograms of injected standards.

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 downstream side of the plastic screen was extracted in 95% ethanol for 48 h 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 by 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 min on a rotary shaker. The extract was then filtered through a 0.45- μ m syringe filter and analyzed with a Shimadzu LC6A high-performance liquid chromatograph. Analysis conditions were as follows: liquid phase—95%

dichloromethane : 5% hexane; flow rate—3.5 ml/min; column—Nucleosil 100 silica 5 micron (250 mm long by 4.6-mm inner diameter) (Alltech Associates, Inc., Deerfield, IL); UV detector—280 nm; injection volume—10 μ l. Basamid residues were quantified by comparison with chromatograms of injected Basamid standards in dichloromethane. Percent recoveries were calculated by spiking 0.25 g of the same Douglas-fir wood with measured amounts of Basamid and comparing chromatograms with those of Basamid with no wood.

Statistical analysis

All tests were subjected to a repeated-measures analysis of variance (ANOVA) with an alpha level of 0.05 (SAS Institute, Inc., Cary, NC). This analysis was chosen because each specimen was sampled several times over the test period. The statistical procedure included 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 of additives

Moisture greatly enhanced the decomposition of Basamid to MITC (Fig. 3). No MITC was detected in any vial containing wood at 12% MC. MITC production from Basamid was significantly greater in wood at 60% MC than in wood at 30% MC. As in previous results (Morrell et al. 1988), using a buffer powder also enhanced MITC production, although the resulting levels were still quite low. It is possible that much of the released MITC was bound to the wood (Zahora and Morrell 1988), although no effort was made to confirm this possibility.

MITC production from Basamid was significantly greater with either copper sulfate (Cu^{+2}) or copper chloride (Cu^{+1}) than with manganese or magnesium. Copper chloride produced significantly higher MITC levels than did copper sulfate. MITC production also increased significantly as the amount of added

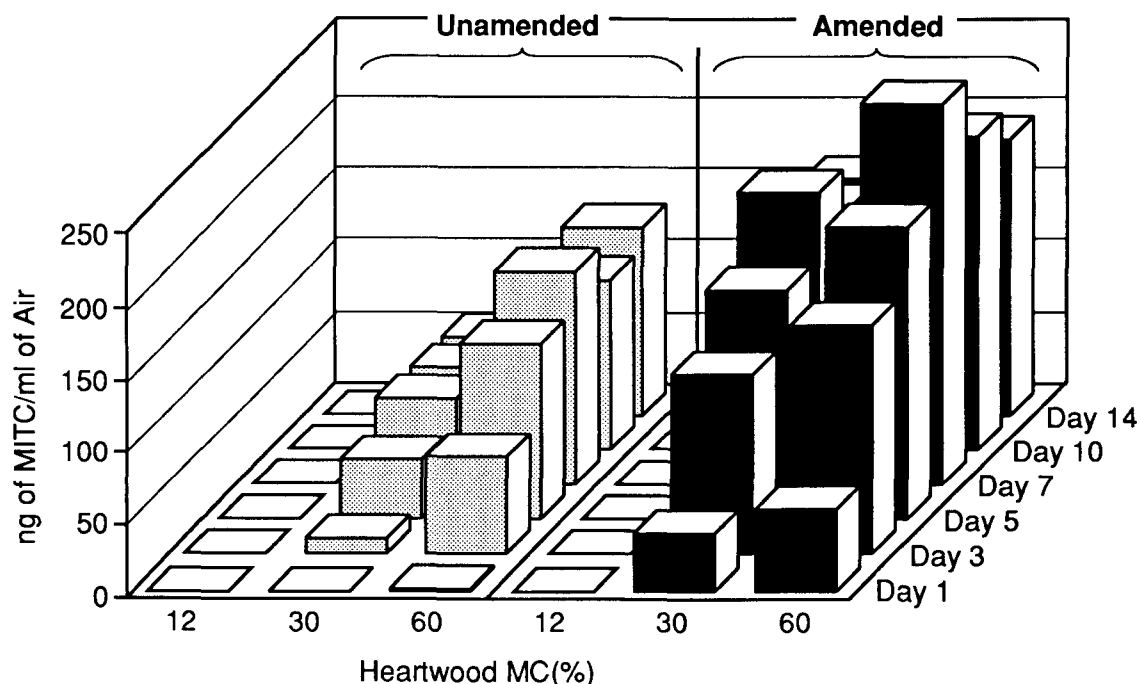


FIG. 3. MITC levels at selected times in the headspaces of sealed vials containing Douglas-fir heartwood at various MCs as well as Basamid either unamended or amended with a buffer powder.

copper increased. These results confirm field tests with Basamid amended with various additives (Forsyth and Morrell 1993). In those tests, copper sulfate with the same buffer powder used here outperformed other additives in elevating MITC production in Basamid-treated Douglas-fir poles over a 2-year period. The initial screening in the present tests also indicated that copper warranted further study: copper sulfate was chosen because the results could be more directly compared with previously established field tests in which this additive was used.

Effects of additives on decomposition

Unamended Basamid did not decompose into detectable volatiles during the test period (Table 1), an indication that the chemical was very stable when kept dry at room temperature. Wood at 9% MC also had no effect on decomposition. However, adding water to unamended Basamid or to Basamid plus wood had a significant effect on MITC production.

Decomposition into MITC when wood plus water was added to Basamid did not increase significantly over that obtained when only water was added to Basamid, indicating that wood was not a major catalyst in this reaction. However, when wood plus water was added to Basamid, levels of carbon disulfide increased dramatically over those produced when only water was added.

It should be noted that there were two overlapping sulfur peaks on the chromatograms, one being carbon disulfide (retention time ca. 0.41 min) and the other being unidentified (retention time ca. 0.36 min). The unidentified peak, probably either carbonyl sulfide or hydrogen sulfide, often overshadowed carbon disulfide, preventing the peak of the latter from being integrated. Further experiments will be needed to fully separate, identify, and quantify the more volatile sulfur-containing compounds.

The effect of pH-altering additives on MITC production was evident, but moisture ap-

TABLE 1. MITC and CS₂ concentrations over a 48-h period in the headspaces of vials containing 100 mg of Basamid amended with selected additives.

Additive	Concentration (ng/ml of air) of:					
	MITC			CS ₂		
	4 h	24 h	48 h	4 h	24 h	48 h
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
Buffer powder	5	6	0	0	0	0
Buffer powder plus water	108	421	334	2	14	0
Buffer solution at pH 12 (from powder)	64	340	242	2	5	4
NaOH solution at pH 12	324	546	299	3	1	0
Copper sulfate	539	306	108	0	0	0
Copper sulfate plus water	2,895	705	270	323	1,091	850
Acetic acid	223	193	90	288	537	373

T = trace.

peared to be necessary for this increase. NaOH solution at pH 12 was more effective than the buffer solution at pH 12 from powder, indicating that 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 did the additives at a higher pH.

In addition, acetic acid enhanced the production of carbon disulfide—to levels similar to those induced by wood plus water. This similarity was not surprising as Douglas-fir heartwood has a pH almost as low as does acetic acid. However, the effects of pH on decomposition are poorly understood.

Copper sulfate clearly affected MITC production more than did any other additive tested. The addition of water was not necessary to induce this reaction but significantly enhanced the effect. Conversely, copper sulfate induced no carbon disulfide until water was added. Chromatograms indicated that an unidentified sulfur compound was produced in the absence of water and that the presence of water shifted the production of early-eluting sulfur compounds exclusively to carbon disulfide.

Surprisingly, neither mono- nor dimethylamine was detected in these tests, even when high levels of carbon disulfide were produced. When carbon disulfide is removed from the Basamid molecule (presumably as sulfur from position 1 and carbon along with its double-bonded sulfur from position 2; see Fig. 1), the only remaining atoms are carbon, nitrogen, and hydrogen. It seems likely that at least some amine component would be produced in detectable quantities from this residue. Because this was not the case, further tests are needed to determine the fate of the nitrogen-containing residues.

Effects of buffer and copper on decomposition

Analyses for both methylamine and dimethylamine in the headspaces of the test vials were inconclusive. If present, these compounds were below the limits of detection. There were, however, several unidentified compounds produced in small quantities in the tests conducted at higher MCs and temperatures. The presence of copper sulfate resulted in MITC production from Basamid even in the absence of wood or added moisture. Thus,

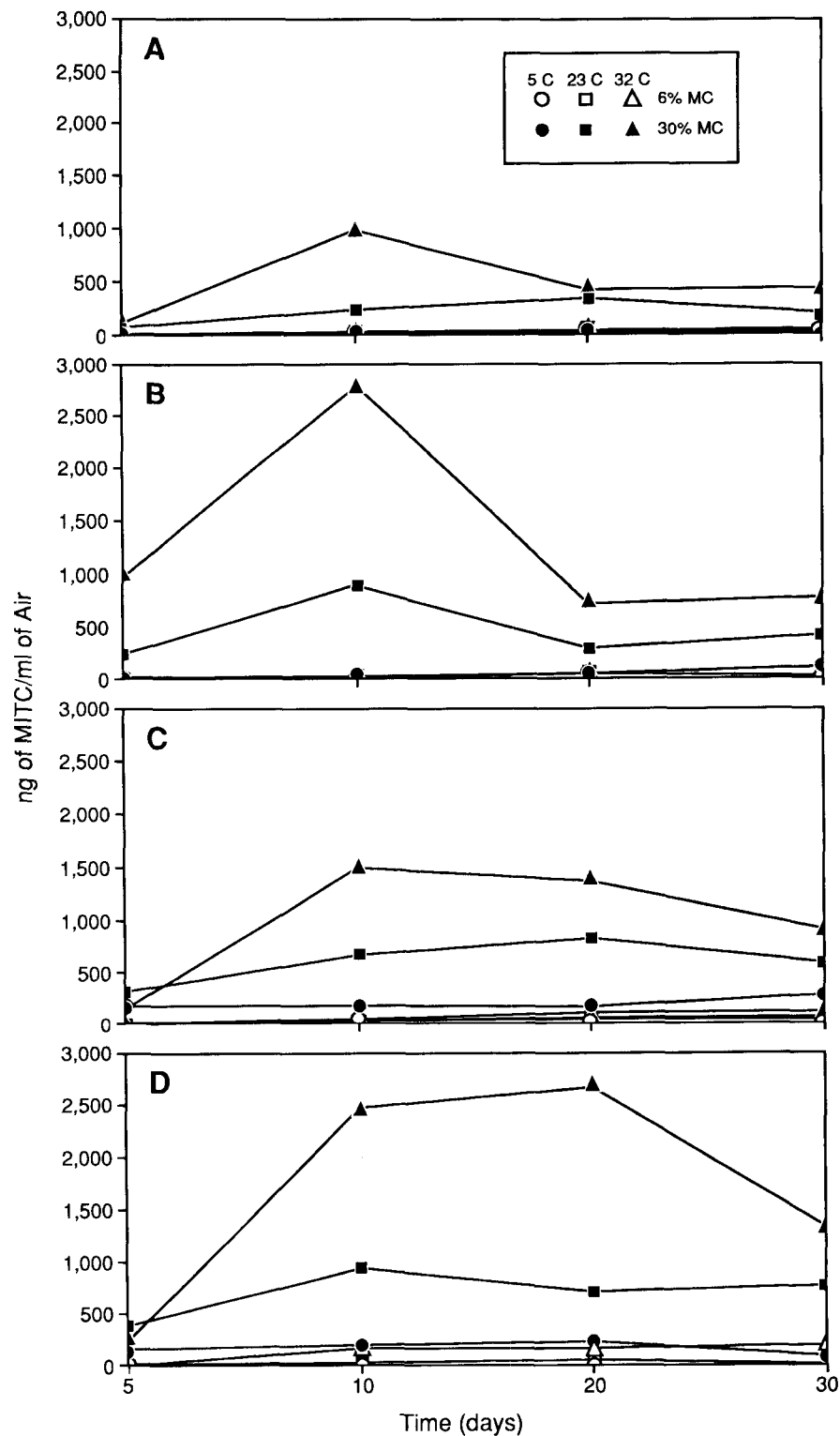


FIG. 4. MITC levels over a 30-day period in the headspaces of sealed vials containing Douglas-fir heartwood that had been conditioned at 6% or 30% MC, treated with Basamid either (A) alone or amended with (B) buffer powder, (C) copper sulfate, or (D) both buffer powder and copper sulfate, and stored at 5, 23, or 32 C.

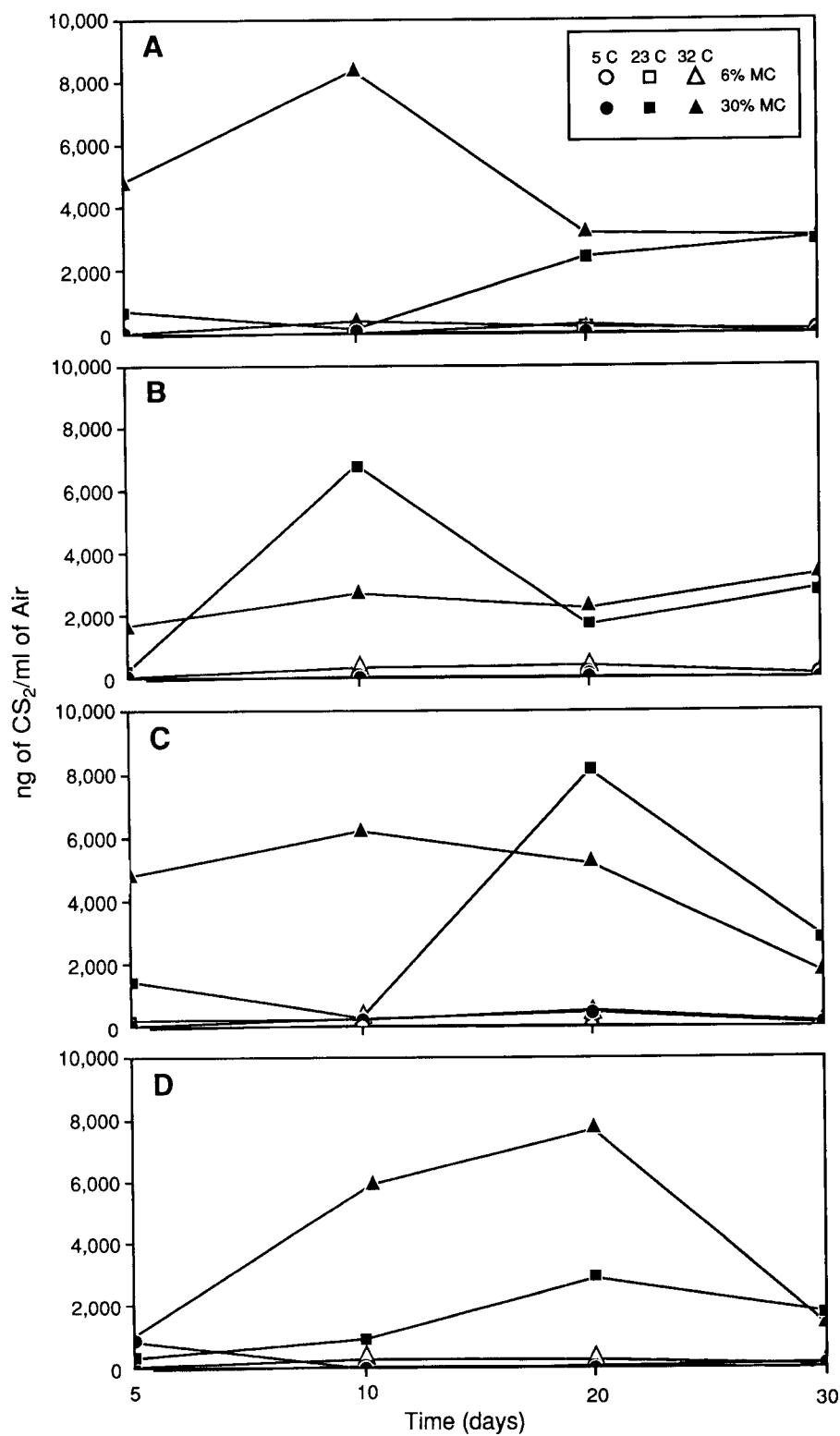


FIG. 5. CS₂ levels over a 30-day period in the headspaces of sealed vials containing Douglas-fir heartwood that had been conditioned at 6% and 30% MC, treated with Basamid either (A) alone or amended with (B) buffer powder, (C) copper sulfate, or (D) both buffer powder and copper sulfate, and stored at 5, 23, or 32 C.

in field applications it may be necessary to delay mixing this additive with Basamid until just before treatment in order to prevent premature decomposition of the fumigant.

Both MITC and carbon disulfide were identified in the headspaces of the test vials. As in the screening tests, higher MCs resulted in increased MITC production regardless of the temperature or additive used (Fig. 4). Higher temperatures also enhanced MITC production, as has been previously noted with metham sodium (Turner 1962; Turner and Corden 1963; Morrell 1992). Similar trends were noted for carbon disulfide production (Fig. 5), although these levels were much higher than those found for MITC. In most treatments, levels for both compounds were decreasing after 30 days. The decline may have resulted from various decomposition products recombining into nonvolatile compounds or from loss from the vials.

Both buffer powder and copper sulfate affected decomposition in the same way as in the initial screening tests. Although trends in MITC production were nearly the same regardless of whether buffer powder was added to Basamid, the levels with the buffer were much higher. Addition of copper also enhanced production, but the effects were delayed and the levels of MITC did not decline as rapidly as in those treatments without copper. Once again, these results paralleled those in Basamid field tests (Forsyth and Morrell 1993). Combining the buffer and copper sulfate boosted both initial and long-term MITC production, especially at 30% MC and 32 C. In some tests, carbon disulfide production was also increased by the addition of buffer powder or copper sulfate; however, the proportion of carbon disulfide to MITC was not as great when copper sulfate was added.

One goal of this research was to identify additives that will enhance Basamid decomposition to effective fungicides. The fungicides must interact with wood and not immediately volatilize, leaving the wood unprotected. One way to measure the efficiency with which Basamid decomposes to form MITC, the most

important fungitoxic product, is to determine the ratio of carbon disulfide to MITC formed. While copper increased carbon disulfide levels slightly, it increased MITC levels markedly, often causing the ratio of carbon disulfide to MITC to decrease by an order of magnitude. These decreases were statistically significant, especially when both additives were used in tandem.

There are two possible pathways for MITC production through cleavage of the Basamid ring. One involves the same carbon atom involved in the evolution of carbon disulfide, perhaps explaining why the latter's production rate falls when that of MITC rises. Although carbon disulfide is fungitoxic, it is less effective than MITC and volatilizes rapidly, providing no residual protection to wood. MITC, conversely, has been shown to remain in and to protect wood for long periods (Zahora and Morrell 1988). Thus, it is crucial that both the decomposition products and their rates of breakdown be controlled if Basamid is to serve as a fungitoxicant in wood.

Total chemical analyses

MITC was always produced in higher amounts when Basamid was amended with CuSO_4 (Fig. 6A), confirming the results of previous tests (Forsyth and Morrell 1992). These production rates, however, were higher only during the first 7 days. After this time, rates were comparable for the two treatments. For instance, total MITC production between 7 and 28 days from Basamid alone was 216 μg ; production from the copper-amended treatment was 238 μg , a difference of only 22 μg . This similarity indicated that although copper effectively catalyzed an initial burst of MITC production from Basamid, it played no significant role in prolonged production. After 28 days, the total production of MITC in the air effluent of the copper-amended treatment was approximately twice that of the Basamid alone treatment. Similar trends were observed by Munnecke et al. (1962) in Basamid-treated soil, although the MITC production levels were higher. This difference was probably due to the

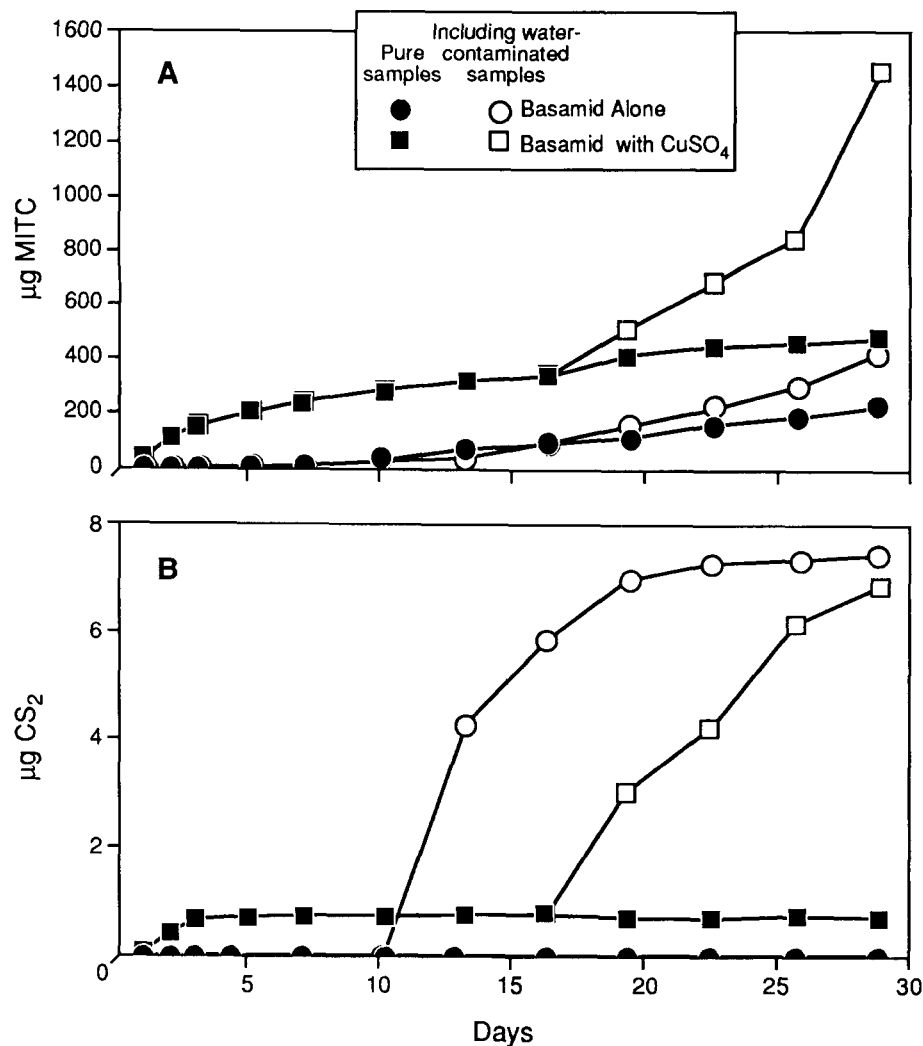


FIG. 6. Average cumulative production of (A) MITC and (B) CS₂ from 100 mg of Basamid or Basamid amended with copper sulfate in Douglas-fir heartwood at 30% MC as determined by purging and trapping in 95% ethanol over a 28-day period. Values that include water-contaminated samples are averages of all three samples in the treatment, including one in which water condensed.

complete mixing of the chemical with the soil in a water suspension as well as the more reactive nature of soil. Munnecke's higher initial rates of MITC production may have been caused by early catalytic effects of soil minerals, as suggested by Chandra and Bollen (1961).

Only one specimen treated with Basamid alone produced carbon disulfide, and then only at one time point. Carbon disulfide was pro-

duced from copper-amended Basamid at very low levels and was detected only during the first 3 days of the test, reflecting the early production of MITC (Fig. 6B).

It should be noted that one glass column assembly from each treatment was excluded from the final calculations because of water condensation inside the air lines and glass columns, an event that further illustrates the effect of moisture on Basamid decomposition. Fig-

TABLE 2. Volatile and residual chemicals produced from 100 mg Basamid or Basamid amended with copper sulfate as determined by a purge-and-trap method with 95% ethanol over a 28-day period.

Sample	Volatile MITC (μg)	Volatile CS ₂ (μg)	Volatiles (% total)	Residual MITC (μg)	Residual CS ₂ (μg)	Residual Basamid (mg)	Total % recovered
Basamid							
4 ^a	808.7	22.4	0.83	370.5	0.509	81.0	82.2
5	200.2	0.0	0.20	134.7	0.0	97.5	97.8
6	262.9	0.0	0.26	148.4	0.397	89.5	89.9
Basamid + CuSO₄^b							
7	429.9	1.0	0.43	42.1	0	93.0	93.5
8	536.9	0.4	0.54	11.5	0	97.1	97.6
9 ^a	3,359.4	19.3	3.38	1,431.2	5.999	69.3	74.1

^a Samples were contaminated by water condensation.^b 1% copper sulfate (% copper per weight of Basamid) was added.

ure 6 includes data from these water-contaminated columns and clearly shows the immediate catalytic effect of water on Basamid.

MITC residues in the extracted wood averaged 141.5 μg for Basamid alone and 26.8 μg for Basamid amended with copper (Table 2). This distribution was unexpected because total production of volatile MITC was far greater in copper-amended samples. Carbon disulfide residues for both treatments were very low.

Recoveries in the Basamid-spiked wood samples ranged from 95.7% to 100.9% (data not shown). These values were much higher than those reported by Elzner (1980), whose highest recovery was 82.2%. Elzner's lower recovery rates probably were due to the added sample cleanup and concentration required in soil samples, resulting in loss of chemical.

Residual Basamid levels were quite high for both treatments, 93.5 mg for Basamid alone and 95.05 mg for copper-amended Basamid (Table 2). These levels indicate a large reservoir of Basamid remaining that can provide long-term MITC release. Total carbon, nitrogen, and sulfur were similar for all samples following extraction and were not above expected background levels.

CONCLUSIONS

Raising the temperature and moisture content enhanced Basamid decomposition, as did adding buffer powder. The latter, however,

greatly favored the production of carbon disulfide over that of MITC. Copper sulfate, on the other hand, enhanced the production of MITC from Basamid while reducing the evolution of carbon disulfide. This was especially true when buffer powder was added to the copper sulfate. Basamid was unstable in the presence of copper sulfate, even without added moisture. Thus, in field applications it will be necessary to keep this additive separate from the fumigant until just before treatment. Although amines are potential products of Basamid decomposition, none were detected in these studies; consequently, their possible role in the process remains unknown.

Total chemical analyses indicated that increased MITC production due to copper sulfate catalysis was confined to the first few days following treatment; however, during later measurements, rates for non-amended and amended Basamid were similar. This suggests that copper sulfate boosts MITC production to levels necessary for fungal control soon after treatment. Accidental contamination by water had an immediate catalytic effect on the decomposition of Basamid. High Basamid residues remaining in the wood at the end of the test suggest that this chemical decomposes slowly enough to provide a long-lasting reservoir of chemical for future MITC release.

These studies indicate that Basamid amended with appropriate additives produces significantly higher levels of MITC in Douglas-fir

heartwood than does Basamid alone. Field tests with wood poles have shown that Basamid amended with additives produces moderate levels of MITC that protect against internal decay for at least 3 years (Forsyth 1993; Forsyth and Morrell 1993). Further laboratory and field trials with this chemical should produce an internal treatment that is both safe to apply and lastingly effective.

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