

Dazomet: A Review of an Efficacious, Safe
And Cost-effective Fumigant for Wood Poles

By

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Abstract

This paper reviews the available information on the efficacy, toxicity, and safety and handling of the fumigant dazomet. Dazomet is a cost-effective, safe, and efficacious fungicide used for the elimination and prevention of decay fungi (basidiomycete) from wooden substrates, including utility poles and crossarms. Included in this review is the history of the use of fumigants in both agricultural and wood utility pole use, efficacy of MITC yielding fumigants and comparison of same, EPA Registration issues surrounding fumigants, including dazomet.

Also included in this work are current trends in the treatment of wood utility poles with fumigants, focusing on increasing use-trends for based chemistries and breakdown products of dazomet in use and in-service. This paper also reviews several current research projects associated with dazomet and predicts future trends in the wood utility pole maintenance and inspection arena.

Keywords: Fungicide, fumigant, dazomet, efficacy, decay fungi, wood poles, MITC, performance, toxicity, Basimid, mylone

Introduction-Fumigants

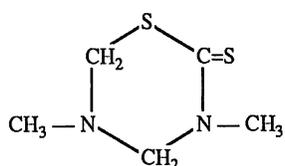
Fumigants are small biocide molecules that volatilize at relatively low temperatures or react to produce a gas. Most are highly penetrating and move rapidly through large masses of material, killing target pests. Because of the broad range of species controlled, fumigants have found uses on a wide variety of crops as a pre-plant soil treatment and in the wood preservation industry to control internal decay in large structural timbers (EPA 2005), as quarantine treatments for wood packing material and on logs infested with forest insect pests. Agricultural fumigants have been commercially used in the United States for over 20 years to control internal decay in utility poles and other timber structures (Ziobro et al. 2002). Large preservative treated timbers often develop internal decay when seasoning checks extend through the treated shell. Fumigants are used to control this decay *in-situ* when vapors diffuse through wood. A fumigant should be highly toxic to target organisms and be sufficiently mobile to protect entire at-risk zones and persist in wood at an effective concentration (Cooper 1986).

Alternative fumigants used include chloropicrin, mixtures of 1, 3-dichloro propene and chloropicrin, methyl isothiocyanate (MITC) and two MITC generators, dazomet and metam sodium (FAO/UNP 2001). Dazomet and metam sodium decompose within wood or soil to release MITC the primary fungitoxic component. Metam sodium introduced in the late 1970's is the oldest of the MITC based fumigants. It is usually sold and used as a 32.7% aqueous solution of sodium N-methyldithiocarbamate, buffered in caustic soda (NaOH). 97% MITC was introduced in the 1980's and is in a solid melt form. The third is the solid granular dazomet which was commercially introduced in the late 1990's under the trade names BASIMID™ and ULTRAFUME™. Dazomet decomposes within wood to release MITC at the stoichiometric conversion rate of approximately 45%. Addition of a copper naphthenate solution at the time of application to

accelerate the decomposition of dazomet is highly recommended when using dazomet in exterior wood substrates, such as poles (Ziobro et al. 2002).

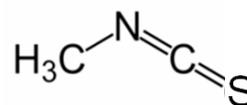
DAZOMET (Basimid®)

Dazomet is a cyclic dithiocarbamate biocide used in the control of annual and perennial weeds, soil-borne and wood fungi, bacteria and nematodes. It may also be used in salt form for example dazomet-sodium.



(3,5-dimethyl-1,3,5-thiadiazinane-2-thione) $C_5H_{10}N_2S_2$

DAZOMET



(Methylisothiocyanate , MITC)

C_2H_3NS
MITC

FIGURE 1. Example Fumigant Chemical Structures and Formulae

Formulated as microgranules, dazomet is off-white to yellowish solid of sulphurous odor. It melts in the range 103-105°C and is of low water solubility (3.5 g/l) at pH 5-9. Dazomet rapidly hydrolyses in water, the rate increasing with increasing pH, and is relatively prone to photodegradation (FAO 2001). It has a vapor pressure of 5.8×10^{-6} Pa at 20 °C (extrapolated), a decomposition temperature of 176 °C (with gas evolution) at 20 °C, octanol/water partition coefficient of $\log POW = 0.63$ at 20 °C. Its hydrolysis characteristics at 25 °C: half-life = 6-10 h at pH 5, 2-3.9 h at pH 7 and 0.8-1 h at pH 9.

Uses And Advantages Of Dazomet

Dazomet formulations are registered and sold in many countries throughout the world. It is not currently co-formulated with other pesticides (FAO 2001), with the

exception of one US EPA label, in which it is combined with NaOPP. Currently there are 32 US EPA Registrations for dazomet containing pesticides in the NPIRS database maintained by CERIS at Purdue University, but in addition, there also exists at least another “private label” sub-registrations maintained by companies in the wood treatment arena. It is mainly used in the agricultural sector used at a rate of up to 70 g / m² or 700 kg/ha for weed control, forest tree seed beds and turf seed beds. It is important in the control of fungi and insects especially in the stages when they are underground (army-worms, cut-worm etc). Dazomet is used by utility companies for remedial treatment of internal decay in wood poles, it is also used to eradicate internal decay in large poles, piling and large sawn timbers. Other minor uses are in the pulp paper manufacture and in leather as a preservative.

Dazomet has advantages compared to other fumigants used on wood treatment. Other fumigant registered in the United States include metam sodium, vorlex (80% MITC in chlorinated hydrocarbons), chloropicrin (96% trichloronitromethane), and MITC-fume (100% MITC). Each of these has proven effective in controlling internal decay. The first three are applied as liquids making them easy to spill, difficult to recover and creating a hazard. Chloropicrin and pure MITC are acutely toxic and the vapors are highly poisonous if inhaled. Chloropicrin is a powerful irritant from the group of pulmonary agents, has a pungent odor and thus can be unpleasant to handle. MITC-fume is highly caustic and is commercially available for use only in insertable glass or aluminum vials. MITC-fume sublimates to a gas at 23°C. Dazomet’s solid formulation offers improved safety for remedial treatments and does not sublime or decompose when kept dry. Packaged as a slow release formulation, granular dazomet is relatively inert. It only decomposes to MITC within wood and MITC has a strong affinity for wood. The rate of movement and persistence of fumigant vapor is affected by its sorption characteristics with wood. Vapors with a high affinity for wood tend to diffuse into cell walls and be sorbed on the polar groups of wood resulting in slower diffusion but longer persistence. Other positive features of

dazomet are relatively low cost and provides moderate bactericidal/insecticidal control. Constraints in the use of dazomet may include ineffectiveness in the presence of high pathogen pressure, inconsistent control due to non-uniform distribution in soil or wood and effect of climate and meteorological unpredictability (FAO/ UNEP 2001).

Efficacy And Decomposition Rates To MITC

When applied to moist soils, or wood above 12% MC dazomet's active ingredient (tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione) breaks down into MITC, formaldehyde, carbon disulphide (CS₂) hydrogen sulphide (H₂S) and monoethylamine which interact, resulting in potent action (Pennington 1995; Forsyth and Morrell 1992). MITC is the major product of dazomet breakdown (98%). The threshold range for MITC against wood decay fungi is 20-40µg/g (ppm) of oven-dried wood sample (Morrell et al 2001; Morrell et al 2003).

Assuming the theoretical maximum decomposition rate for dazomet of 45%, a 210 gram application of dazomet would contain the equivalent of 94.5 grams of MITC. Like methyl bromide, dazomet is dependent on critical factors such as wood structure, temperature, and moisture (Pennington 1995). MITC generation and dissipation from dazomet depends on chemical and physical factors, especially temperature, moisture and pH. MITC generation increases at higher temperatures and the dissipation of MITC is faster at high temperatures and slower at low temperature. Thus environmental factors have an effect on performance of dazomet.

Because it decomposes too slowly dazomet has been thought not to be very effective as a wood preservative. Decomposition in wood is very slow for it to be effective in rapidly eliminating an actively growing fungal colony (Forsyth and Morrell 1992). After application MITC levels may be insufficient to pest control. However decomposition of dithiocarbamates including dazomet into MITC can be enhanced by the addition of certain metals and pH 10-12 buffers. Morrell et al

(1988) showed that pH 10-12 buffers increased MITC production from dazomet to rates capable of rapidly eradicating decay fungi in utility poles. Forsyth and Morrell (1992) investigated effect of temperature, moisture content and addition of pH 12 buffer, copper sulfate, copper chloride, manganese sulfate and magnesium sulfate to dazomet in ground wood (figure 2). Increasing temperature and moisture content enhances dazomet decomposition. At 12% MC in wood no MITC is detected. MITC production is greater in wood at 60% MC than at 30% MC. Copper had a much higher effect on dazomet decomposition than Mg or Mn salts and the valence state of copper seems to make no differences in performance. Because the presence of copper sulfate resulted in MITC production even in the absence of moisture, it is necessary to keep this additive separate from the fumigant until immediately prior to treatment. Copper sulfate enhances MITC production while reducing CS₂ evolution. CS₂ is not an effective fungicide as it volatilizes rapidly leaving the wood unprotected. MITC remains in wood providing long lasting protection. Addition of powdered pH 12 buffers enhances decomposition but favors CS₂ over MITC production. Addition of both buffer and copper sulfate enhances production of MITC while reducing CS₂ evolution (Forsyth and Morrell 1992). Furthermore, the addition of copper sulfate or copper naphthenate to dazomet enhanced MITC release, although greater enhancement was achieved with copper sulfate (Morrell et al. 2003). Diffusion of MITC occurs more rapidly in the longitudinal versus radial direction in wood (Zahora and Morrell 1989; Ziobro et al. 2002). It was later found that the use of waterborne or oil-borne copper naphthenate also resulted in the increased production of MITC than other compounds from dazomet, at a lower risk to workers than handling liquid, low pH, (acidic) copper sulfate solutions. Additionally, EPA labels for wood use list copper naphthenate as an accelerator.

Long exposures of dazomet are effective in controlling fungal growth. Slow decomposition could be useful if the chemical is applied to non-decayed wood at time of installation when immediate fungal eradication is not of concern

Comparison of efficacy of dazomet to other fumigants

Most studies on dazomet have compared its efficacy in moving through wood, and persistence in wood to fumigants. For example, after 12 years, OSU tests on Douglas Fir transmission poles demonstrates toxic threshold values of dazomet well above those needed to protect wood poles (OSU POLE CO-OP 2007 ANNUAL REPORT Figures 3-1, 3-2, 3-3, 3-4, 3-5.)

Chlorpiricin shows greater mobility and persistence than dazomet (Highley 1990; 1992). Highley (1990) determined the efficacy of chlorpiricin, MITC and dazomet to move through wood poles. 3 years after treatment, increment cores were taken at varying distances from fumigant holes and tested for residual fumigant in Douglas fir and southern Pine. No residual fungistatic effect was found in any of the timbers treated with MITC pellets most likely due to loss of the chemical from the wood. Fungistatic effect on dazomet was lost from all Southern pine timbers after 3 years. Dazomet moved slower in Douglas-fir and fungistatic effect was detected 0.61m from fumigation holes at 24 and 36 months after fumigation. Southern pine timbers contain a higher proportion of sapwood hence is more permeable than Douglas-fir. High permeability favors distribution of toxic vapors through wood but may reduce the duration of effectiveness. This probably explains the slower movement and greater persistence of dazomet in Douglas-fir than in Southern pine. Wrapping southern pine timber prior to application of all three fumigants enhanced movement and persistence. (Highley 1989; Highley 1992). In a similar study Highley (1992) used inhibition of brown rot *Gloeophyllum trabeum* as a measure of residual fumigant on chlorpiricin, MITC, metam sodium and dazomet treated red oak and white oak. Chlorpiricin moved furthest from point of application and was the most persistent fumigant. Fumigants were not as effective at greater distance from application point in white oak perhaps due to tyloses in vessels restricting the chemical movement. In Red oak which is more permeable movement was faster Highley (1992).

Morrell et al. (2003) further showed 12 months after treatment, MITC levels in metam sodium treated poles were higher than in the dazomet treated poles. However over time, the levels in dazomet treated poles continued to increase to levels exceeding those in metam sodium poles. MITC concentrations in dazomet treated Douglas-fir poles increased to levels higher than corresponding metam sodium treated poles after 36 months (Morrell et al. 2003).

Based on a MITC threshold value against decay fungi of 20 ppm, a 39 month chemical assay indicated that all three MITC-based fumigants effectively protect the zone of fumigant treatment, approximately 15.2 cm below to 15.2 cm above ground line, in southern pine pole stubs. Samples removed from the poles stubs treated with dazomet with and without accelerant, MITC or metam sodium, respectively contained levels above the minimum threshold levels after 39 months (Ziobro et al. 2002). However MITC provides greater protection in the short term.

Ziobro et al. (2004) used fumigant holes on PCP pressure treated pole stubs to incorporate MITC, metam sodium, dazomet and dazomet with copper naphthenate (containing 2% metal). Increment core samples taken 13 months after treatment showed that concentrations of MITC were greatest at all pole heights and core depths in pole stubs treated with 97% MITC. These poles had concentrations greater than corresponding levels in metam sodium poles by a factor of two and greater than levels in the two dazomet treatments by an average factor of five to six. Concentrations of MITC in the metam sodium poles were greater than levels in the dazomet poles by a factor of approximately two and half to three. During the 13-month exposure period, either a rapid decomposition of dazomet had not occurred or its decomposition efficiency is less than the stoichiometric rate of 45%. The addition of a copper naphthenate accelerant to dazomet resulted in an enhancement of fumigant decomposition. 39 months after treatment, and sampling 30.4 cm above the highest treatment hole, concentrations of MITC were in the 97% MITC pole stubs by an average

factor of twelve compared to corresponding levels in the metam sodium treated poles. Levels in the 97% MITC treated poles were greater than corresponding levels in the dazomet and dazomet plus copper naphthenate treated poles by an average factor of eleven and eight, respectively. These would indicate that a rapid decomposition of dazomet had not occurred during the 39-month exposure period (Ziobro et al. 2004). MITC concentrations remained relatively unchanged or increased only slightly within the zone of treatment in the dazomet and dazomet plus accelerant treated pole stubs, and decreased slightly above the zone of treatment between 13 and 39 months following treatment (Ziobro et al. 2002; Ziobro et al. 2002).

Ecological Effects And Mammalian Toxicity

Ecotoxicological effects of dazomet have been investigated using organisms from major ecotoxicological groups. Field studies have shown that the initially strong effects on populations of soil-dwelling organisms like earth-worms and soil arthropods are reversible. Dazomet is very toxic to aquatic organisms like fish, crustaceans and algae, and moderately toxic to birds. Due to the mode of application, which prevents exposure to bees, the product is rated harmless to bees. The half-life of dazomet in moist aerobic soil is less than 24 hours. The end products of degradation after complete mineralization are bicarbonate, nitrate and sulphate, which can be considered as plant nutrients (Fritsch and Huber 1995).

Dazomet is of moderate acute oral toxicity but of low dermal and inhalation toxicity. It is not irritating to skin and shows no skin-sensitizing properties (FAO 2001). It causes slight eye irritation (moderate conjunctival erythema and slight oedema). In rats oral toxicity LD₅₀ = 415 mg/kg bw, dermal= LD₅₀ > 2000 mg/kg bw, inhalation= LC₅₀ = 8400 mg/m³. No carcinogenic, mutagenic, teratogenic, genotoxic effects, developmental toxicity or impairment of fertility have been observed using rats and mice and rabbits (FAO 2001). Repeated doses cause haematological effects (predominately on red blood cells) and

another target organ is the liver (also a target organ of MITC). Increases in liver weights were consistently seen in repeat-dose studies in mice, rats and dogs. High dietary doses of dazomet cause nervous system effects. Doses of 540 -800 ppm and above (in 3- and 4-week studies) in rats caused strutting gait, foreleg paralysis, and paresis of hindlegs in rats.

Consideration must be given to the rapid decomposition of dazomet when it comes in contact with water or humid air, generating MITC. The threshold limit value for MITC gas set by the American Conference on Government Industrial Hygienist is 0.02 ppm which is an extremely low concentration. MITC can damage by inhalation, ingestion and contact in quantities as low as 0.4 ppm. Conflicting assessments may arise from the difficulty of assessing dazomet characteristics when MITC is almost inevitably generated under the conditions of test. The toxicology/ecotoxicology data refer to dosing with dazomet, and the observed effects may have been caused by dazomet, MITC or both. Apart from conducting parallel studies with dazomet and MITC, there is no way to distinguish between their effects (FAO 2001). There is an underlying difficulty in separating 'dazomet data' from 'MITC data', when reviewing the literature in the public domain and in the US EPA files, as well as MedLine.

Commercial Products, Current and Future Trends

Over the past decade, the commercial use of dazomet as a wood pole fumigant has increased dramatically in the North American pole inspection and treatment market. Initially, CSI/Pole Care registered the product under their proprietary tradename as UltraFume™. Latter, Copper Care Wood Preservatives, Inc, registered the chemical under the tradename Super-Fume™. Osmose also markets the fumigant under the trade name Dura-Fume™. Currently the product is available in 1-gallon HDPE/HDPP durable dispensing containers, but occasionally may be also supplied in larger containers. Efforts to control dose

amount have centered on application and delivery devices that pre-measure and dispense the particulate granules. Example of these devices are “Tip and Poor Jugs,” “The Applicator,” funnels and other simple measuring devices. While much experimentation has gone into simplifying the application of dazomet fumigant granules the overwhelming number of applications are made by simply filling the pre drilled hole to the top, less two inches from the uppermost opening for the plug. This system of filing the hole is dependent on the treaters ability and precision drilling equipment to consistently drill the proper sized reservoir hole and proper depth. Application charts usually spell out, in detail, the size and depth for the treaters/inspector to follow to administer the correct and effective amount of dazomet fumigant.

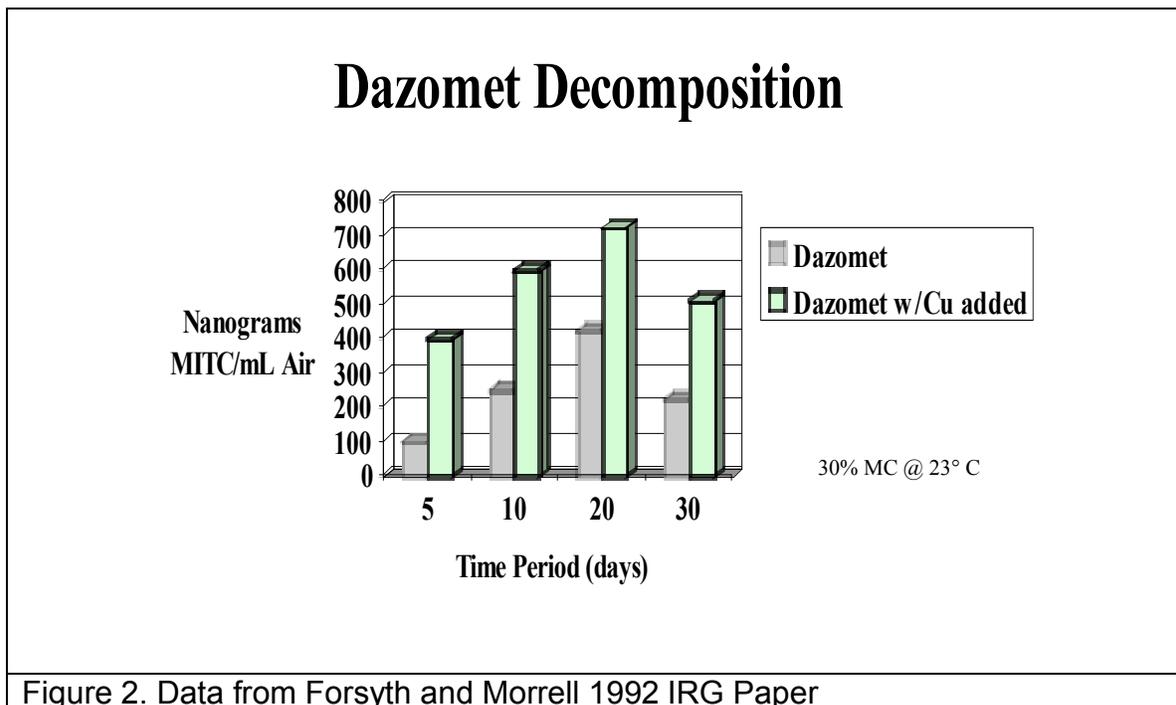
Oregon State University reports testing of a solid “Basamid” rod in their 1999 OSU Pole Co-op report. A commercial rod product could possibly eliminate some of the undesirable handling characterizes of a granular formula such as dust, spills, dose measurement, clumping etc. Encapsulated MITC and solid borate rods have enjoyed commercial success as easy to use pre-measured dose products but have demonstrated some inherent limits such as extreme volatility or lack of the ability to travel a far enough distance, vertically and radially in the wood, especially at lower MC’s. An “easy-to-use” dazomet rod product could fill the market void as a substitute for the above listed systems. While efficacy results have been more than acceptable on the solid rod, no serious efforts to commercialize them have taken place thus far. This may be due to the difficulty in producing a compressed rod that will hold together during normal inspection and treating crew handling operations.

Furthering the need for a more efficient way of applying dazomet, Super-Fume Tubes have been developed. Based on the same effective and safe granular formula that is applied from jugs (HDPE/HDPP Containers), the tubes use a perforated or gas- permeable outermost packaging material to contain a pre-set dose of the granular dazomet product. These tubes may be applied in a similar

fashion to that of a solid borate rod, solid NaF rod, or of a gel fumigant vial. The advantages of a self-contained, pre-measured dose are appealing. Tests were experimentally installed at Southern California Edison in 2004 (figure 4) Additional Super-Fume Tube efficacy testing is currently underway at the OSU Peavey Arboretum site, through the OSU Pole Co-Op, and managed by Dr. Jeff Morrell (Figure 5.)

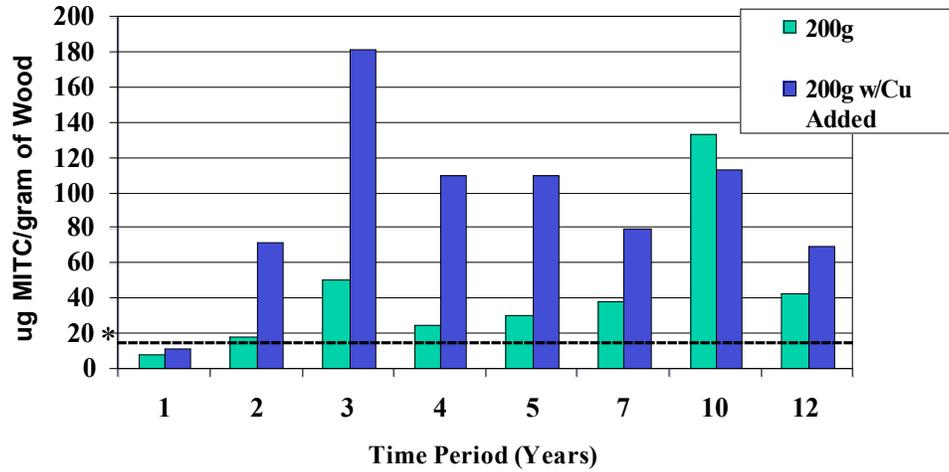
Field and Lab Efficacy Data

Early efficacy test at OSU, and reported to the IRG, identified the need for the addition of an accelerant like Copper.



OSU Co-op 12 Year Dazomet

DF Transmission Poles, Corvallis, OR



* Threshold = 20 ug/g

Sample from G.L., Inner Segment

Figure 3. MITC from Dazomet in DF Transmission Poles and Effective Loadings in Years 1-12

Long-term data demonstrate that MITC loadings spike with the addition of an accelerant, but level out over time. In addition, those threshold levels of MITC remain well above the amount that is needed to protect the wood after 12 years.

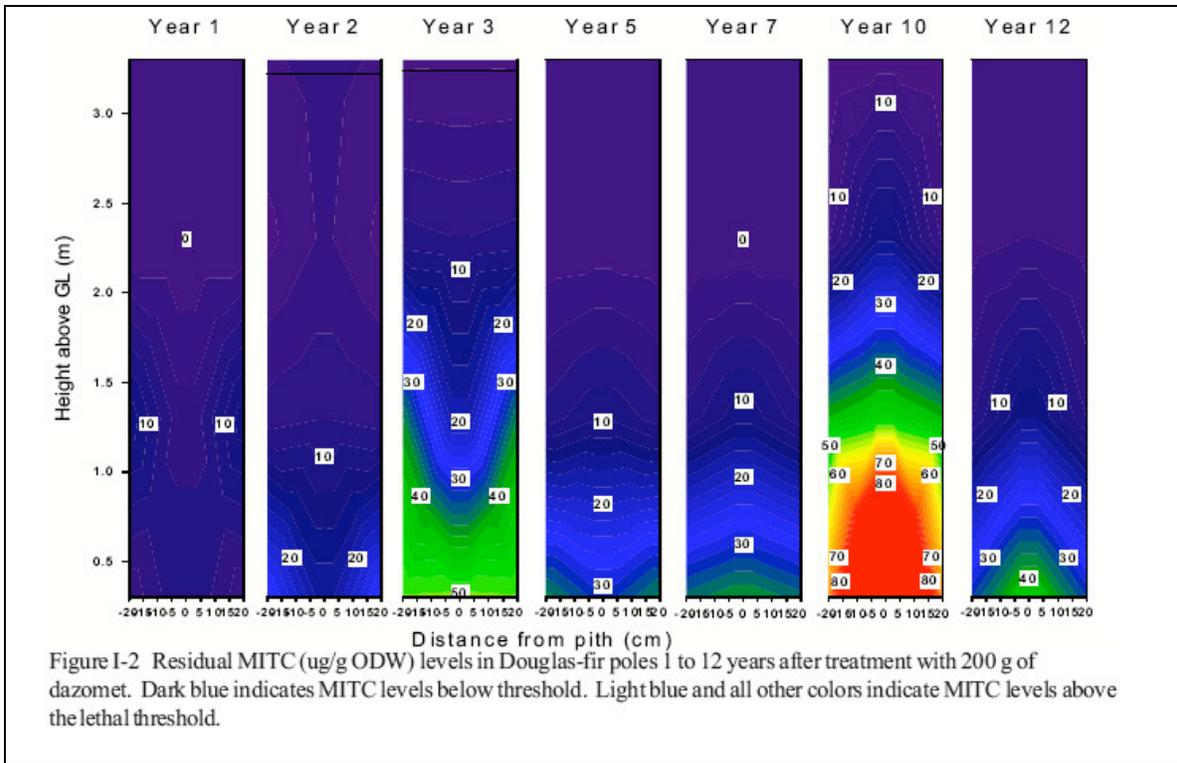


Figure 3-1. (Morrell/OSU Co-op)

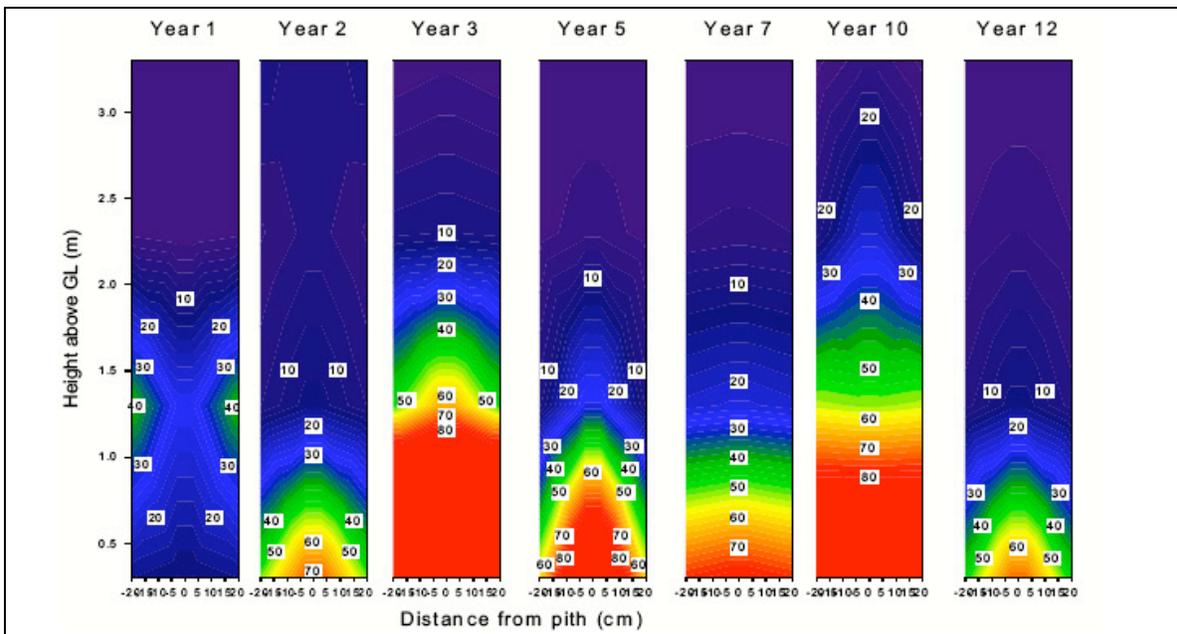


Figure 3-2. (Morrell/OSU Co-op)

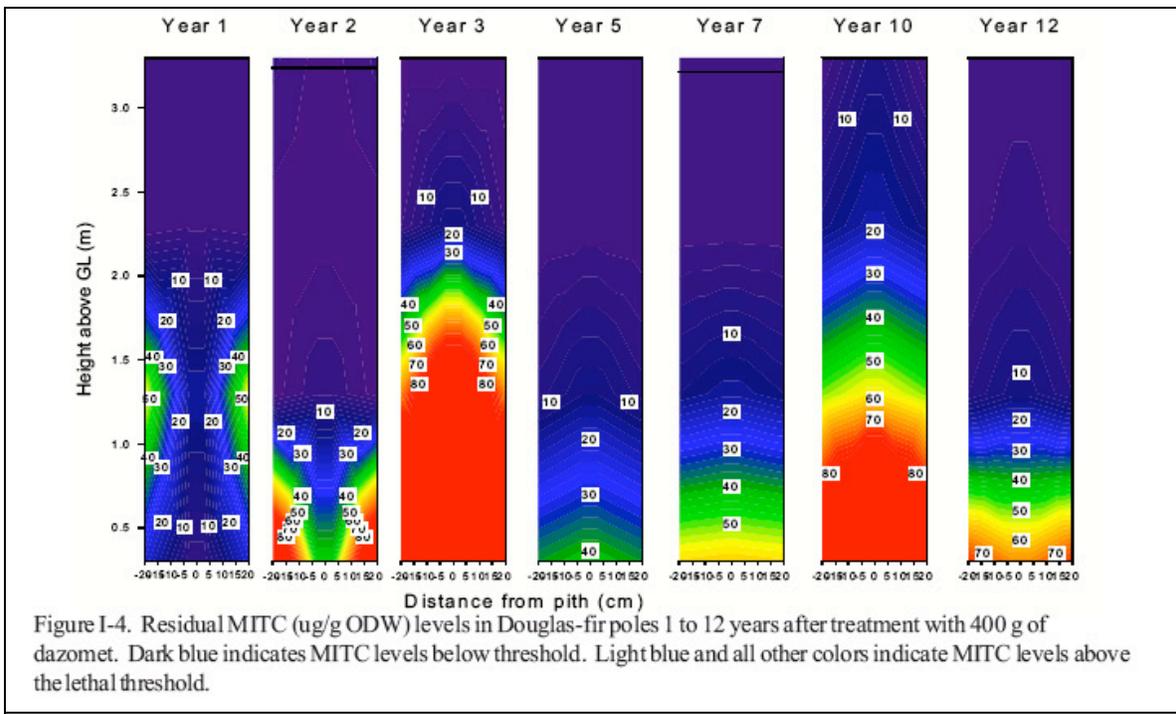


Figure 3-3. (Morrell/OSU Co-Op)

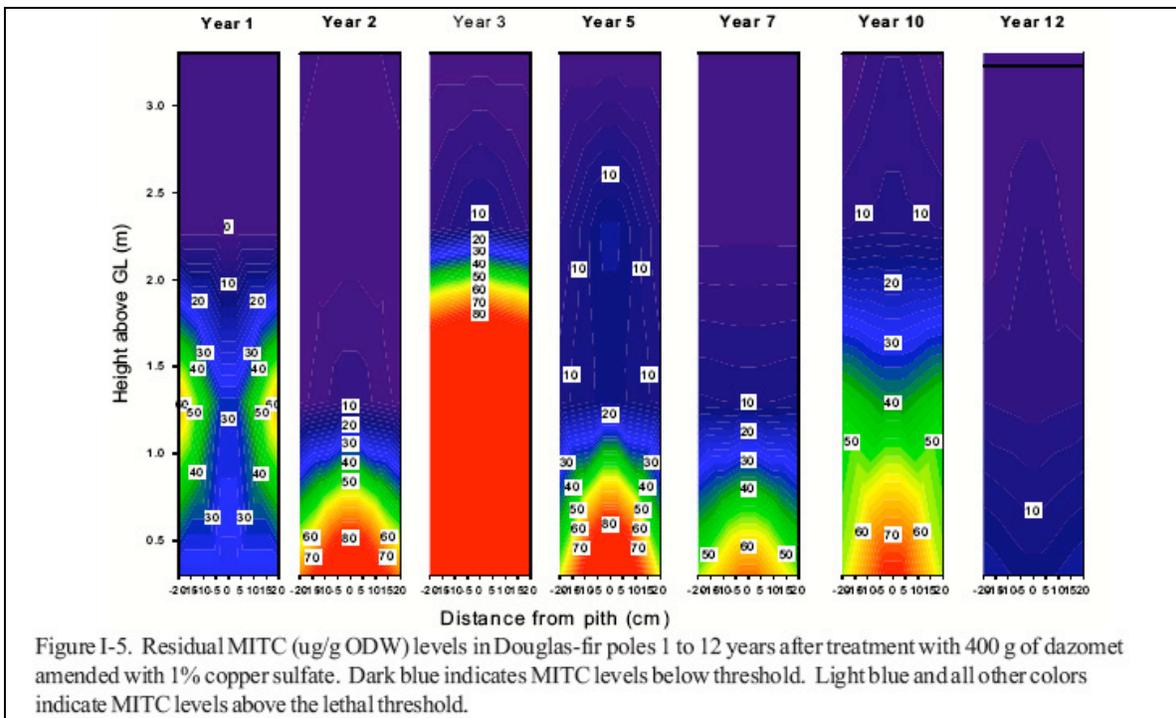


Figure 3-4. (Morrell/OSU Co-Op)

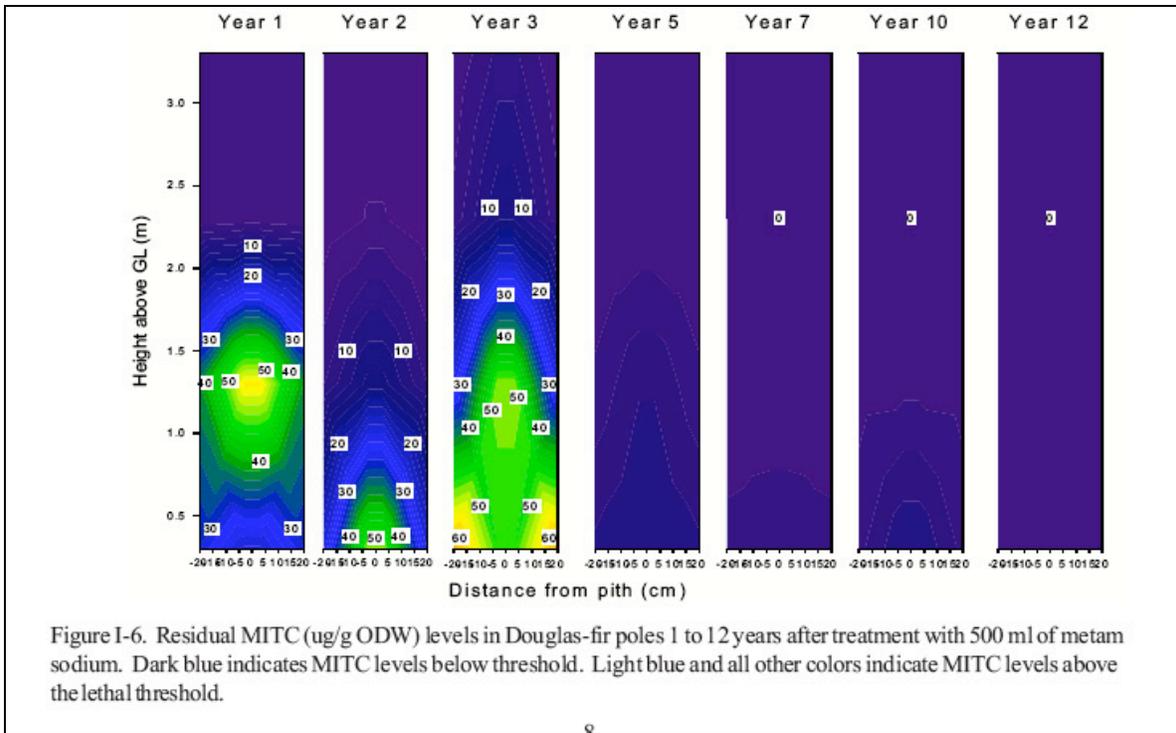


Figure 3-5. (Morrell/OSU Co-op)

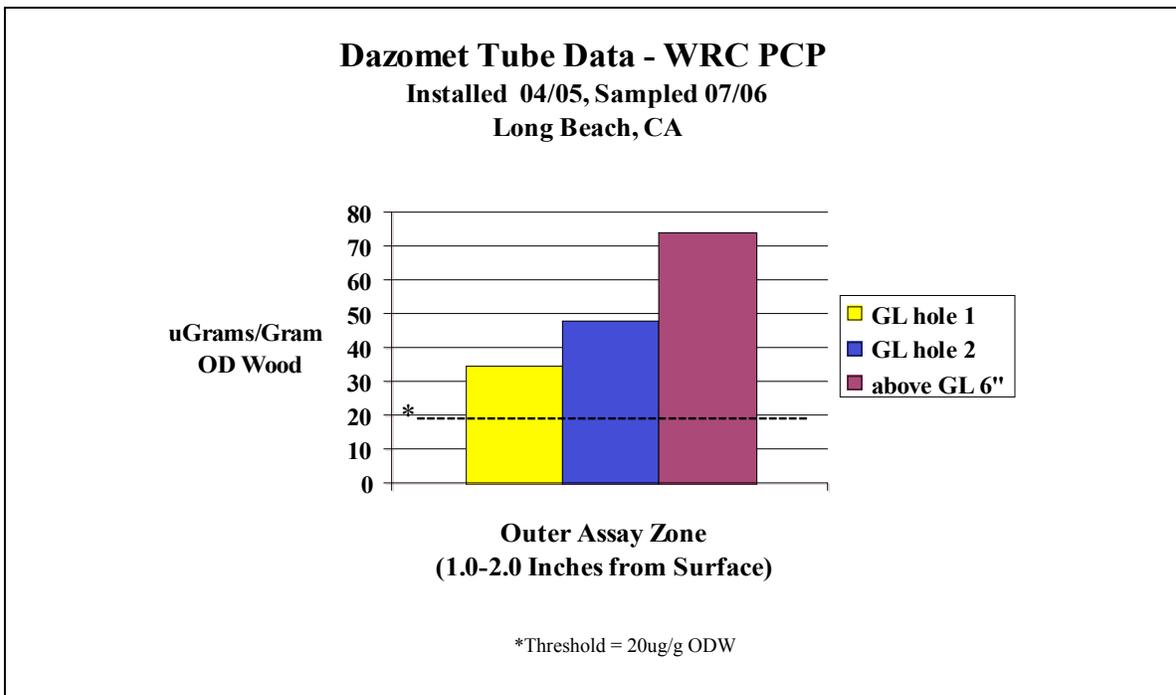


Figure 4. MITC Levels from Dazomet at Multiple Sampling Locations

Pre - packaged tubes are releasing enough fumigant to offer acceptable levels of protection at SCE. (Figure 4)

Initial “Dazomet Tube” testing at OSU demonstrates above threshold performance even at lower loadings, at multiple sampling depths.

Table I-6. MITC levels in Douglas-fir poles 1 year after application of dazomet as a granular system or in cardboard tubes with or without supplemental copper naphthenate.

Treatment	Dosage (g/pole)	Supplement	Residual MITC (ug/g of wood) ^a											
			-15 cm		0 cm		30 cm		45 cm		60 cm		90 cm	
			Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer
Granular	210	CuNaph	108	53	114	19	79	45	47	39	27	10	21	1
		None	144	48	108	15	63	32	34	27	17	2	17	2
Tube	180	CuNaph	133	66	158	53	81	53	39	19	22	5	12	2
		None	108	16	112	21	72	10	51	14	20	9	7	1
Control	0	None	0	1	8	0	1	0	0	0	2	0	0	0

^aValues represent means of fifteen analyses per position. Numbers in bold represent MITC levels above the toxic threshold.

Figure 5, Data from 2007 OSU Pole Co-Op Annual Report by Morrell and Love

Summary and Conclusions

Long-term test results have demonstrated the excellent efficacy of dazomet as a wood pole fumigant. The addition of an accelerant, such as copper naphthenate, increases the release of fumigant early in the treating cycle, thus eliminating concerns from earlier testing that the product was not breaking down fast enough to deliver a lethal dose to the inhabiting fungi. Commercial use of dazomet has been increasing and ease of application is improving. The use of dazomet as a wood pole fumigant will continue as an accepted and preferred tool in wood pole maintenance programs.

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