ZINC BORATE - A PRESERVATIVE TREATMENT FOR COMPOSITES

MARK J. MANNING[1] and PETER E. LAKS[2]

[1]U.S. Borax Inc., Valencia, California.
[2]Michigan Technological University, Houghton, Michigan.

Termite testing is performed in cooperation with the Hawaii Department of Land and Natural Resources

ABSTRACT

Zinc borate, disodium octaborate tetrahydrate, and other borate chemicals are incorporated into wood composites to impart fungal and insect resistance to the final product. A number of publications have previously described some physical and biodegradation resistance properties of such materials. In this paper, the performance of borate-treated aspen waferboard in field testing is described. Results from above ground lap-joints, field stakes, and termite-specific testing performed in Hawaii and/or Florida are discussed. The potential for depletion in the ultimate end-use of the treated product is an important property of boron-based wood preservatives in general. Relative depletion rates of boron from waferboard specimens containing zinc borate or disodium octaborate tetrahydrate during field exposure are also discussed.

INTRODUCTION

The species, size and quality of standing timber available for harvest is changing worldwide. In North America, competing recreational and conservation uses for forests - especially those containing older, larger trees - is limiting the availability of larger dimension solid sawn lumber. These restrictions, coupled with technological advancements in the area of engineered wood products, have helped to increase the utilisation of structural wood composites. Besides substituting for solid lumber and plywood in protected applications, structural composites may be used in applications which require resistance to wood-destroying organisms such as fungi and various insects. When used in these applications it becomes necessary to treat the composite with a wood preservative.

In wood composites used in these situations, inorganic borates such as zinc borate and disodium octaborate tetrahydrate are particularly well suited as preservative systems (1-5). They can be added as a powder during the manufacture of the composite and both chemicals are stable under typical press (consolidation) conditions. In the case of zinc borate, there may be added benefits brought on by having a co-biocide in the form of the zinc ion - this is in addition to the relative leach resistance conferred by the lower solubility of this compound. The improved leach resistance of zinc borate over sodium borates such as disodium octaborate tetrahydrate makes this compound more suitable as a preservative for wood composites used in exposures where there may be a potential for depletion as result of continued wetting, such as painted exterior joinery and siding. Most of the studies described in this paper are evaluating the use of zinc borate as a preservative treatment for wood composites; disodium octaborate tetrahydrate was included in some of the studies to help evaluate performance differences as a function of preservative solubility.

The production of structural panels in the United States and Canada has continued to evolve over the last decade (6). In 1986, Canadian panel production broke down as 60% plywood and 40% Oriented Strand Board (OSB); by 1995, production of OSB accounted for 65% of the total in Canada. A similar, but less dramatic trend is seen in production figures from the United States: in 1995, OSB represented nearly 30% of the total - up from 20% in 1990. Increases in OSB capacity from 1994 through 1998, inclusive, have been calculated at 9.9 billion ft^2 - 5.7 billion in Canada and 4.2 billion in the United States. This projected surge in capacity (the 9.9 billion ft^2 represents 27% of the North American capacity at the end of 1994) is fueling concerns about operating ratios and profitability for some of the smaller mills. This probable over-capacity is driving the development of new OSB markets such as the Pacific Rim where there is a high insect and decay hazard. Utilization in these markets, along with the growth of value added products such as exterior siding and joinery (used in applications with significant hazards from wood destroying organisms) has necessitated the development of preservative treatment strategies for wood composites.

METHODOLOGY

Waferboard samples evaluated in this paper were prepared at Michigan Technological University (MTU) using Aspen (*Populus tremuloides* Michx.) as the wood species; this is a fast growing hardwood with no natural durability and is widely used commercially. Wax and polymeric diphenylmethane diisocyanate (pMDI) adhesive were used with target levels of 0.75% and 7.0%, respectively. Typical consolidation conditions were used to manufacture the boards to a density of 37 pcf. Field testing was carried out at the Michigan Tech field sites in Hilo, Hawaii (avg. annual rainfall of ~150" and mean temperature of 73 °F) and Gainesville, Florida (avg. annual rainfall of ~35" and mean temperature of 70 °F).

The antifungal and anti-insect properties of inorganic borates is primarily due to the BO_3^{-3} anion that is formed upon exposure of most inorganic borates to water. This is why the retention or loading of wood preservative systems containing borates is usually expressed as the boric acid equivalent (BAE) or the B_2O_3 equivalent. If a biologically active counterion is present in the borate salt, however, it may also contribute to the biological efficacy of the system.

Zinc Borate (ZB). Zinc borate ($2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$) is commercially available as a wood preservative under the tradenames *Borogard®* ZB or *Composibor™* (48.2% B_2O_3,U.S. Borax Inc.). In addition to its utility as a biocide, this compound is widely used as a flame retardant for plastics. Zinc borate is only sparingly soluble in water at room temperature (<0.28%, w/w) and could be considered "leach resistant". Because of its low solubility, it is impractical to pressure treat solid wood with an insoluble borate such as this; however, it is relatively simple to incorporate the powdered chemical into a wood composite during the blending process. In this paper ZB loadings are expressed as %BAE (Boric Acid Equivalent). For conversion of these numbers to actual ZB loadings, 1%BAE = 1.17%ZB by weight.

Disodium Octaborate Tetrahydrate (DOT). The composition of the commercially available sodium borate *Tim-bor®* wood preservative (67.1% B_2O_3, U.S. Borax Inc.) corresponds quite closely to a hypothetical compound disodium octaborate tetrahydrate, $Na_2B_8O_{13} \cdot 4H_2O$. This compound is the most water soluble of the commercially available borates; maximum solubilities range from 9.5% at 20°C to over 30% at temperatures above 50°C. This high water solubility, in combination with the broad spectrum biocidal activity of borates against all wood destroying organisms, have led to worldwide usage of *Tim-bor* in the dip or pressure treatment of solid lumber and plywood for interior or protected use. The inherent water solubility of disodium octaborate tetrahydrate limits the ultimate end-uses for wood products treated with soluble borates to applications where the wood is not in ground contact and, if exposed, is protected from liquid water. Aqueous solutions of disodium octaborate tetrahydrate range from mildly alkaline (pH 8.5 for a 1% solution) to practically neutral as concentration increases at room temperature (pH 7.6 for a 10% solution). The conversion equation to DOT weight loading from BAE loading is 1% BAE = 0.84% DOT by weight.

RESULTS AND DISCUSSION

Above ground lap-joints The purpose of this work is to evaluate the above-ground field performance of aspen waferboard composites containing ZB. Three performance factors were evaluated - biological resistance, leach resistance, and thickness stability. Depletion of ZB from above-ground exposure of waferboard is described in a section below. Thickness swell is not reported here. Previous work had shown that the standard L-joint test format is not suitable for composite evaluations because of the high thickness swell that may result. The lap-joint specimen used is in two parts with a total length of 11.75 inches, 4 inches wide, and 0.75 inches thick with a lap joint machined between the two parts. Nylon bolts with stainless steel springs are used to hold the joint together. The springs accommodate the thickness swell of these types of composites. Samples were treated with either ZB or

DOT at the target retentions (given in %BAE) shown in Table 1. The lap joints were mounted horizontally with the wide face up in aluminium racks and evaluated annually. No coating was applied to the specimens. Samples were exposed near Hilo, HI.

Visual ratings after 2.5 years of exposure are summarised in Table 1. The untreated controls are close to failure from decay after this time, while there is relatively little biodegradation in the treated specimens.

Above-ground termite test - Hawaii Aspen waferboards were made with target loadings of 0.0, 0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 5.0 %BAE zinc borate or disodium octaborate tetrahydrate and were exposed to the Formosan subterranean termite (*Coptotermes formosanus* Shiraki) in the Michigan Tech test site in Hilo, Hawaii. After the 48 month inspection, all the DOT specimens and the replicates with the highest ZB loading (5% BAE) were removed from the field for depletion analysis (results are described in the depletion section). Results for the ZB treated samples after 6 years exposure are graphically presented in Figure 1. An average rating of 10 indicates the sample was in perfect condition, while a 0 rating means the sample was essentially destroyed.

Zinc borate performed well in preventing termite damage to waferboard under these test conditions. All sodium borate containing samples with target loadings of 0.5% or less failed after 18 months exposure and there was substantial attack even at 5.0% after 48 months (termite rating of 6.9) in this high hazard test. In contrast, there is little or no damage to samples containing zinc borate at target levels of 0.5%, and most of the 0.2% ZB boards are still intact. Results from this rigorous test show that the improved leach resistance of zinc borate has resulted in less depletion of boron and a concomitant increase in performance (*vide infra*).

In the termite test methodology used, the specimens, along with untreated wood attractor stakes, are placed in a horizontal array on hollow core concrete blocks approximately 10 cm thick (7). The assembly is then covered with a wooden box to prevent direct contact with rain. This test format was designed to simulate wood building components in above-ground situations that are subject to a damp environment (e.g., sill plates, exterior millwork, and siding). The concrete blocks will wick water up to the test blocks when the soil substrate is damp. The termite site also has heavy rainfall (approximately 150 inches per year). The test blocks have a relatively high moisture content throughout most of the year. It seems likely that blocks will be exposed to a significant leaching hazard, potentially causing depletion of boron from the blocks containing sodium octaborate tetrahydrate and reducing their termite resistance. Because of its lower water solubility, much less of the zinc borate would be expected to leach under these conditions. To investigate this hypothesis, all remaining sodium octaborate samples and the zinc borate specimens with a target borate content of 5% BAE were removed from the field after 4 years exposure and assayed for boron content; these results are discussed in the section on depletion.

Field stakes in Hawaii and Florida Stakes (0.75 x 2.0 x 16 inches, 10 replicates) of aspen waferboard containing ZB or DOT at the following target retentions (ZB: 0.0, 1.0. 2.0, 3.0, 5.0 and 8.0% BAE; DOT: 3.0% BAE only) were installed in the MTU field test site near Hilo, Hawaii and Gainesville, Florida. These stakes were buried to half their length in the ground and evaluated on an annual basis. Both sites are in areas with high rainfall and decay hazard from soft rot and Basidiomycete fungi. Visual ratings after two years exposure are summarized in Figure 2 for Hawaii and Figure 3 for Florida. Field stakes like this are normally rated for both decay and termite damage. There is little termite activity at the Hawaiian field test site so the termite ratings are relatively high.

There are obvious performance differences between the stakes installed in Hawaii and those exposed in Florida. These variations are most likely caused by the significant differences in precipitation at the two sites. The higher rainfall at the Hilo site would be expected to increase the potential for depletion of the ZB, thereby leading to a reduction in performance. Chemical analysis of the depletion stakes installed at the Hilo site support this explanation (see section on depletion, below). The data displayed in Figure 2 illustrates the differences in performance in going from the first to the second year of exposure at the Hilo site. Figure 3 displays the visual ratings after two years exposure at the Austin Carey field site near Gainesville, Florida. The decay rate is substantially slower at the Florida site and this is reflected in the ratings.

The comparative performance of ZB- and DOT-treated waferboard (both treated to a target retention of 3% BAE) is illustrated by the results after two years exposure. The average decay ratings for the DOT-treated stakes was 0 in Hawaii and 6.7 for the stakes installed in Florida; corresponding results for the ZB-treated stakes were 6.8 and 10.0, respectively. This performance differential, particularly the results from the Hawaiian exposure, effectively demonstrates the aforementioned solubility differences. In a relative sense, the ZB is acting as a "fixed borate" wood preservative.

Depletion results As described above, some of the field termite specimens were removed after 48 months exposure in an effort to investigate any possible boron depletion. Samples were chemically analyzed for boron using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Analytical results showed that an average of approximately 85% of the boron had leached from the DOT specimens, while 41% had been depleted from the ZB replicates treated to a target retention of 5% BAE.

Ground contact depletion was investigated using the same ZB-treated aspen waferboard manufactured at MTU and containing a target loading of 3% BAE. Depletion stakes (2.0 x 0.75 x 16.0 inches) were installed at the MTU field site near Hilo, Hawaii. The stakes were vertical with ca. two-thirds of the length buried in the ground. Thirty replicate stakes were installed. Ten stakes were removed after 1 and 2 years exposure. After removal, the stakes were cut into four segments. The first cut was made at the groundline, then the above and below ground segments cut again into upper and lower sections to give four segments per stake. These were coded as follows:

1 - Above ground, upper
2 - Above ground, lower
3 - Below ground, upper
4 - Below ground, lower

The sections were chemically assayed and the results for boron are illustrated in Figure 4. There is a clear progression in boron depletion from year 1 to year 2, and moving from the upper half of the stakes to the lower portions. In this rigorous ground contact exposure the boron component of the zinc borate is mobile and has depleted from the below ground segment of the stake after two years. The only significant zinc depletion was from the lower quarter of the stake (29% loss after two years); the rest of the stake showed no clear change, supporting the concept that the zinc component of the ZB is more highly fixed than the boron.

Above ground depletion was investigated using ZB-treated aspen waferboard (target loading of 2% BAE) cut into 4.0 x 4.0 inch depletion specimens and installed horizontally in above-ground racks at the MTU field site near Hilo, Hawaii. Thirty replicate specimens were installed. Ten replicates were removed after 1 and 2 years exposure. The 4 x 4 x 0.75 inch specimens were first cut into top and bottom 4 x 4 x 0.37 inch portions, then a center 2.0 x 2.0 inch segment cut out of each board. This cutting scheme yielded four samples per exposure specimen - top center (TC), top outer (TO), bottom center (BC), and bottom outer (BO). The results are summarized in Figure 5.

The boron and zinc components depleted at different rates with very little zinc being lost over the two year length of the test. There was also a pronounced position effect with more boron being depleted from the top as compared to the bottom, and more boron lost from the outer sample zones compared to the center segments. Intuitively, this is what would be expected. There is some additional loss in boron during the second year of exposure, but the changes are relatively small, especially for the bottom outer segment. This can be at least partially explained by movement of boron from the center and upper sections of the specimens to the outer and lower portions - the core is acting as a reservoir for the edges where most of the depletion is occurring.

CONCLUSIONS

The data presented in this paper demonstrates that zinc borate is an effective preservative for aspen flake composites when used in appropriate exposure conditions. The greater the leaching hazard, the more boron is depleted and lower long term visual ratings are observed. As expected, the depletion rate was greater from composite in soil contact compared to treated material above ground. In larger ZB-containing specimens exposed above ground, there is more depletion from the edges and the upper rain-exposed surfaces compared to the inner and lower regions. Zinc is depleted at a much lower rate than the boron. Some of the depletion data indicates that a "reservoir" effect can occur with ZB-containing composites. Boron from low depletion rate regions (e.g. the center of a specimen) can diffuse into high depletion rate regions (e.g. the edges or ground-contact area) to replenish the boron content of these areas. Comparison of results from ZB and DOT treated composites shows that zinc participates in protecting the wood product from fungal and insect attack.

The affect of leaching hazard is easily seen in the comparison of field stake results from Hilo, Hawaii and Gainesville, Florida. After two years exposure, the fungal ratings at the two sites for 2% BAE boards are 4.4 and 10, respectively. An important factor influencing these results is the much higher annual rainfall in Hilo (~150 inches) compared to Gainesville (~35 inches). The difference in performance between ZB and DOT is also apparent from these results. In Hilo, the DOT stakes treated to 3% BAE have failed at two years exposure, while the ZB stakes treated to 3% BAE have fungal and insect ratings of 6.8 and 9.8, respectively. A similar difference in performance can be seen in the matching stakes installed in Florida, and long-term termite testing in Hawaii.

Much of the test data given here is from methods designed to evaluate preservative systems for ground-contact use. This is a much more severe exposure than an above-ground application such as painted exterior joinery or siding. The functional and performance difference between a 2 x 0.75 x 16 inch field stake and a typical ZB-containing commercial product such as a 4' x 8' sheet of composite siding is large. The stake has a higher surface to volume ratio making its preservative loss rate higher than the sheet, but more importantly the entire stake is exposed to a leaching/decay hazard, while this is not the case with the siding.

As a treatment for wood, inorganic borates combine a unique set of characteristics - efficacy against both fungi and insects, fire retardancy at higher loadings, low cost, ease of handling and treatment, low mammalian toxicity, and minimal environmental impact. Among the borate chemicals available, zinc borate seems especially well suited for use as an above-ground preservative for aspen flake wood composite systems.

REFERENCES

1. Laks, P.E. and Manning, M.J. 1995. Preservation of wood composites with zinc borate. International Research Group on Wood Preservation. IRG/WP 95-30074.

2. Laks, P.E. and Manning, M.J. 1994. Inorganic borates as preservative systems for wood composites. Proceedings of the Second Pacific Rim Bio-Based Composites Symposium. November 6-9, 1994. Wood Science Department, Faculty of Forestry, University of British Columbia, Canada; pp. 236-244.

3. Laks, P.E. and Palardy, R.D. 1990. The development of borate-containing flakeboard. Proceedings of the First International Conference on Wood Protection with Diffusible Preservatives. November 28-30, 1990. Forest Products Research Society, pp. 76 -79.

4. Laks, P.E., Quan, X., and Palardy, R.D. 1994. Preservative systems for OSB panels. Proceedings of the Technical Research Forum. Structural Board Association. March 30, 1994.

5. Laks, P.E., Quan, X., and Palardy, R.D. 1994. The effects of sodium octaborate tetrahydrate and zinc borate on the properties of isocyanate-bonded waferboard."Adhesives and Bonded Wood Symposium" Proceedings. (C.-Y. Hse and B. Tomita, eds.), FPRS, pp. 144-157.

6. 1996-97 North American Factbook, published by *Wood Technology*. Pease, D.A., Blackman, T. and J.A. Sowle, eds. Miller Freeman Inc., 1996.

7. Laks, P.E. and Pruner, M.S. 1994. Wood preservative properties of chlorpyrifos. *Forest Products Journal,* 45(2):67-71.

		1 Year		2 Years		2.5 Years	
Treatment	Loading	Decay	Termite	Decay	Termite	Decay	Termite
	- % -	---------------------- Average Visual Rating ----------------------					
ZB	0.5	10	10	9.8	9.8	9.8	10
	1	10	10	9.4	9.9	9.7	10
	2	10	10	9.9	9.9	10	10
	3	10	10	10	10	9.9	10
	5	10	10	10	10	10	10
DOT	3	10	10	9.8	9.8	9.0	10
Untreated	---	9.9	10	3.4	10	3.3	3.6

[a]Average of 10 replicates. A rating of 10 indicates no deterioration, 0 indicates failure.

Table 1. Average visual decay and termite ratings for above ground test specimens (lap-joints) exposed for 2.5 years in Hilo, Hawaii.[a]

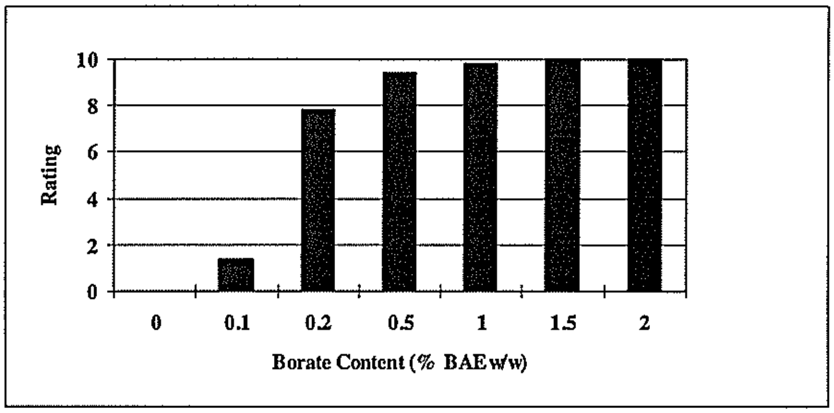


Figure 1. Average termite ratings for borate waferboards after 6 years exposure to *Coptotermes formosanus* in a covered, aboveground test chamber in Hawaii.

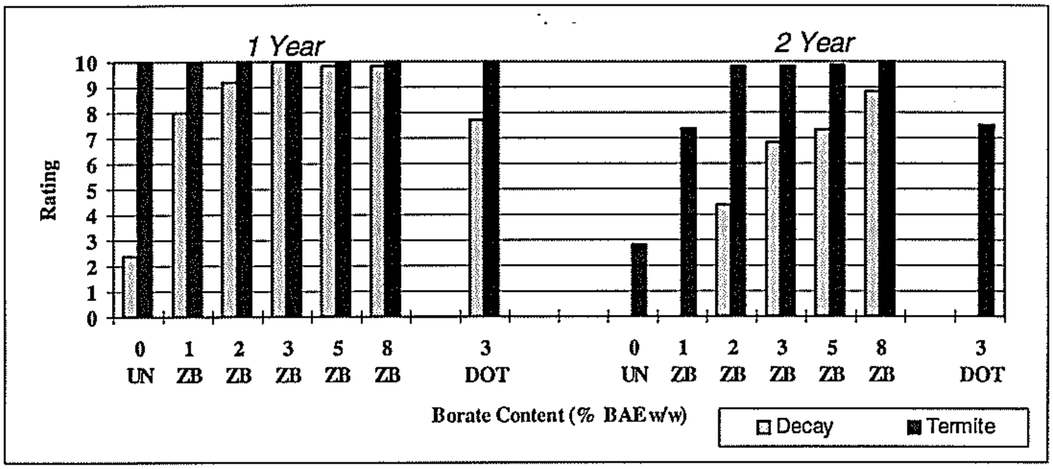


Figure 2. Average decay ratings for Aspen composite field stakes containing ZB after one and two years exposure in a field site near Hilo, Hawaii.

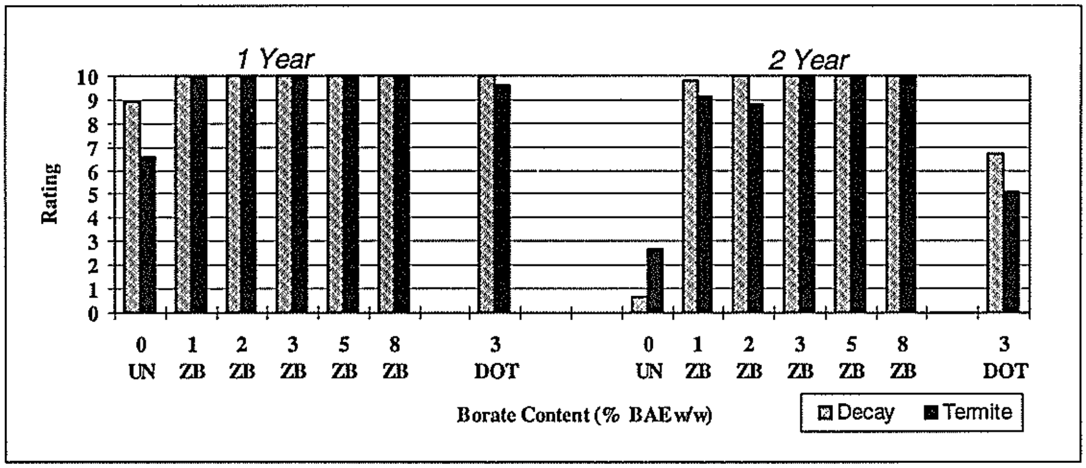
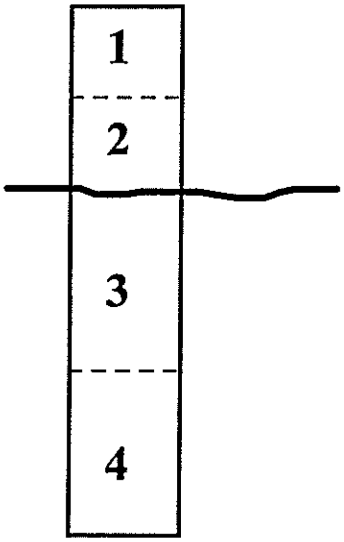
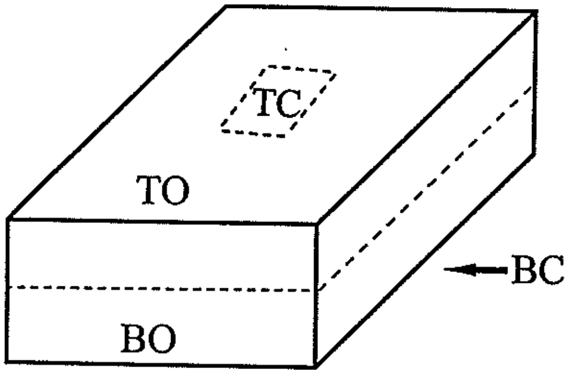


Figure 3. Average decay and termite ratings for aspen composite field stakes containing ZB after one and two years exposure in a field site near Gainesville, FL.



Zone	% Boron Remaining 1 year	2 year
1	68	55
2	68	56
3	22	5
4	3	1

Figure 4. Chemical assay results from field stake depletion specimens after one and two years exposure in Hilo, HI. Boron results are given for each of the four zones: zones 1 and 2 from the above ground portion while zones 3 and 4 are below ground.



ZONE	% Boron Remaining (one year data)	% Boron Remaining (two year data)
TO	37	20
TC	69	68
BO	44	31
BC	86	81

Figure 5. Chemical assay results from depletion blocks after one and two years exposure in Hilo, HI. Boron results are given for each of the four zones described above.