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SHOULD PRESERVATIVES BE PARTLY MOBILE?

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Summary

CCA-treated wood with a thin shell of treatment has performed unexpectedly well for above ground construction, despite exposure of untreated check surfaces. It has been hypothesized that minor amounts of mobile CCA preservative components redistribute during weathering into checks, and that this 'surface treatment' prevents basidiospores washed into checks from germinating and causing decay. Research summarised here shows that CCA does redistribute onto check surfaces, basidiospores that arrive on the wood fail to colonise, spores of a copper-tolerant basidiomycete are not copper tolerant, and the colonisation sequence is an extended version of that found by other researchers for untreated wood. The ultimate failure of this material is caused by the same fungi commonly found on untreated wood and may be facilitated by detoxification of the redistributed chemical by the early colonisers. Work is underway to determine the relative importance of redistributed copper and arsenic and the levels required to prevent basidiospore germination on wood.

1. Introduction

Chromated copper arsenate (CCA) is the most widely used preservative in North America, representing more than 78.6% of wood treated in Canada (Stephens 1995). However, much of the CCA treated lumber placed in service as decking or landscape ties, during the late 1980's and early 1990's, had very thin shell treatment. That is because the heartwood of most Canadian wood species resists treatment, and requires incising to meet the CSA standard penetration requirement of 10 mm (CSA O80.2-M). However, treaters could not even try to meet this standard because most consumers prefer the look of unincised lumber. Although a revised standard with a reduced penetration of 5 mm for decking lumber has been developed (CSA O80.32), there remains a large volume of treated decking in service with a very thin shell of treated wood.

Due to the very thin shell of treatment, such materials might have been expected to fail within ten years. However, except for a few cases, CCA-treated wood, having a limited penetration, has performed surprisingly well (Morris and Ingram 2000), despite exposure of untreated checked surfaces. Although the reason for this unexpectedly good performance is unknown, several explanations have been suggested. The most pertinent one is that: the presence of mobile CCA components even after completion of the fixation process (normally greater than 98% fixed) provides protection of checked surfaces (Smith 1986). Minor amounts of mobile CCA preservative components may therefore redistribute into checks during weathering, and this 'surface treatment' may prevent fungal spores washed into checks from germinating and causing decay.

Environmental groups had taken issue with the usage of arsenic in preservatives, and the Pest Management Regulatory Agency and chemical suppliers have agreed that use of CCA on most residential treated wood products will be discontinued by 2004. Several new preservatives are being introduced to the Canadian market for above ground construction. In order to be confident in the long-term performance of an alternative preservative, its characteristics should be compared to CCA.

In this paper, the focus is on the role of mobile chemicals may play in explaining why CCA shell-treated wood exposed above ground performs well. As well, the information on wood-inhabiting fungi, especially wood-rotting fungi, associated with CCA-treated wood used above ground was developed. Such information will contribute to understand the eventual decay of those materials.

2. Chemical redistribution in CCA treated lumber

2.1. Materials and Methods

Commercially CCA-treated hem-fir lumber was exposed in order to get information on the early effects of exposure. For long-term exposure, due to the time limitation, CCA-treated materials in service for periods up to 10, 15 and 20 years were collected. The detailed information on these materials was described in Choi *et al*. (2001a).

The freshly exposed material was supported over containers from which leachate was collected monthly. After each sample collection, each container was washed with tap water and rinsed with distilled water. Atomic absorption spectroscopy (AA) based on the AWPA A9-99 standard was used to analyse for CCA in the leachate. In addition, the amount of hexavalent chromium in the leachate was analyzed by a spectrophotometer according to ASTM D1687-92 (1992).

To investigate chemical migration into exposed untreated check surfaces, thin sections were taken by hand from several locations (Figure 1). Each thin section was then digested using 70 % nitric acid and 50 % hydrogen peroxide according to AWPA A7-93. The chemical

content of the digested solution was measured by AA to quantify the amount of the CCA components on the exposed untreated checked surface.

2.2. Results and discussion

The cumulative amount of CCA components leached due to natural rain events from CCA is shown in Figure 2. The cumulative amount of hexavalent chromium (1.85 mg per square meter of deck surface until January in 2001) in the leachate was very small, less than 2% of total chromium (105.43 mg as cumulative amount per square meter of deck surface until January in 2001) in the leachate, suggesting that CCA was well fixed to the materials used in this study before exposure. Relatively high amounts of all components were leached for the first three months of installation. However, since then very little copper (less than 20 mg per square meter of deck surface at each month) and chromium were leached, while arsenic continued to be steadily leached.

The CCA-retention of the boards newly exposed for this study was 5.71 ± 2.93 kg/m^3 in a 5 mm assay zone, although the depth of copper penetration was 3.2 ± 2.3 mm. Since the boards were initially exposed during the summer, checks soon formed and developed beyond the chemically penetrated zone during the first month. Copper was still found in the leachate after checks formed. This suggested that surface run off from the boards carried some CCA components, and that this movement should also transfer chemical to the exposed wood in the check. This assumption was confirmed during analysis of the amount of chemical on exposed untreated wood surfaces.

Materials collected after long-term exposure had one or two very deep checks on each board. A significant amount of copper was found in checked surfaces of all materials collected from the field (Table 1). To confirm whether chemicals found on the checked surface redistributed from the treated wood, untreated wood close to the checked surface (untreated interior in Table 1), which was not exposed, was also digested and analyzed. A small amount of copper was found in the untreated interior in old materials. However, no chemicals were detected in the interior of 5 month-old boards and very little copper was found in 1 year-old boards. The amount of chemical found on the checked surface after 1year exposure was not statistically different from that after 5 months exposure. However, in general, the amount of chemicals found in checked surface and untreated interior increased with increasing time. This might be due to chemical accumulation in the checked surface after migration and the deeper chemical redistribution with water movement during service, although many factors limit a direct comparison of all materials.

3. Tolerance of basidiospores to copper

3.1. Materials and Methods

Cultures of two brown rot fungi, *Gleophyllum sepiarium* (14-7-3B), and *Oligoporus placentus* (PM7) were provided by Forintek Canada Corp. A variety of spores and

mycelium were used as inoculum sources (Choi *et al*. 2001b), but only data on basidiospores produced *in vitro* and mycelium stored in wood blocks are reported here.

Malt-extract agar (1.5%) containing $CuSO_4 \cdot 5H_2O$ at several concentrations were used. Small wood cubes (2mm × 2mm × 2mm) containing mycelia stored in wood, were inoculated at the center of the plate. Spore suspensions (1×10^6/ml) were spread onto each copper-medium. Plates were incubated at 25°C in the dark and cultured for three months to assess fungal growth and spore germination.

Mycelial growth was evaluated by measuring mycelial spread around the inoculum once every week for three months after inoculation. To evaluate spore germination, microscopic observation was applied.

3.2. Results and discussion

Minimum inhibitory concentration of copper for mycelial growth and spore germination is shown in Figure 3. *O. placentus* is known to be copper tolerant, while *G. sepiarium* is not. It has been hypothesized oxalic acid is involved in copper tolerance by forming insoluble copper oxalate which fungi cannot absorb. *O. placentus* is known to be an oxalic acid accumulator, while *G. sepiarium* is not. The strain of *O. placentus* used in this study showed much more tolerance to copper than *G. sepiarium,* based on mycelial growth.

In the case of spore germination, the copper concentration that inhibited germination of *O. placentus* was the same as that of *G. sepiarium*. This may be because spores of copper-tolerant basidiomycetes do not have their metabolism geared up to produce oxalic acid. If this phenomenon is common among copper tolerant decay fungi, it has major implications for the development of copper-based preservatives for above-ground applications.

4. Microbial ecology of CCA-treated decking

4.1. Materials and Methods

Immediately after recovering samples as described earlier (Section 2.1), several wood sections (1 cm thick) were collected from each board. Each section from the end had seven points for isolation, while a section from the middle part was sampled at the checked surface, below the check, at the treated surface and below the treated surface. Four selective media suggested by Clubbe and Levy (1980), i.e. bacterial-inhibiting agar, copper sulfate agar, benomyl/steptomycine agar, and 2% malt extract agar were applied for isolation. Both classical taxonomy and modern molecular techniques have been used to identify fungal isolates.

To evaluate fungal tolerance to copper, all isolates were grown on media containing $CuSO_4 \cdot \bullet 5H_2O$ at concentration of 0.02M and 0.04M. Cultures were kept for at least 4 months to ensure fungal growth.

4.2. Results and discussion

The percent frequency of isolation from interior of the board is shown in Table 2. The succession of infection in CCA-treated decking; i.e. bacteria, mould and staining fungi, soft-rot fungi, and basidiomycetes, was similar that found from untreated wood above ground and from CCA treated wood in ground contact (Clubbe and Levy 1980). However, colonization was much slower than in these earlier studies. It is not possible at this stage to determine to what extent the slower sequence is due to the moisture conditions, the nutrient conditions or the chemical treatment.

Decayed boards were also collected from the 15-year-old decks. One board had a fruiting body on it; this fungus was tentatively identified as *G. sepiarium*. Most decay was associated with checks. In this study, *G. sepiarium* and *Gleophyllum. trabeum* were the only basidiomycetes isolated from inside of decayed decking. Other unidentified basidiomycetes, were isolated from the treated surface, checked surface or end cut of decking from both decayed and non-decayed boards. This shows that *Gleophyllum spp*. could colonize CCA treated wood exposed above ground after long-term exposure although many other basidiomycetes also existed in or on the material. *G. sepiarium* was previously reported as a dominant fungus found in CCA-treated exposed above ground in Vancouver area (Morris 1996).

Cephalosporium sp. and *Phialophora sp*. showed very strong tolerance to copper (Table 3), and accumulated copper in the centre of the plate. Butcher (1971) also reported that *Cephalosporium sp*. was highly tolerant to copper, and dominant among early colonizers. One unidentified, yeast-like isolate appeared to accumulate copper around the inoculum although it did not grow well on the media. The copper tolerant *Phialophora sp*. in our study possessed black pigment, which is melanin. It has been suggested in previous studies that fungal melanin binds heavy metals (Fogarty and Tobin 1996; Tonthat *et al*. 1995). *Cephalosporium sp*. and the yeast-like unidentified isolate do not produce any colour both in cell walls and in the media. They may have different mechanism to accumulate copper, e.g. oxalic acid as described above. Butcher (1971) mentioned that these very tolerant, and/or chemical releasing fungi had a role in modifying the effect of preservatives. This modification might allow non-tolerant basidiospores to germinate and colonize the treated substrate, and cause eventual decay. Further work is required to determine whether this is indeed the case.

5. General Discussion

The results in this study provide strong evidence that mobile chemical redistributes within wood, although some chemical leached from the samples, particularly at the beginning of exposure. When there was light rain, the water was absorbed by the CCA-treated board, rather than running off the board surface. This may allow the mobile chemicals to move around within wood instead of leaching out.

In our study, very small amount of copper on agar media stopped basidiospore germination even for a copper tolerant decay fungus. The copper concentration was much lower than that found on checked surface. However, it still remains to be determined whether the chemical content found on checked surfaces is sufficient to prevent spore germination of decay fungi since wood is much different substrate from agar media.

The succession of fungi in CCA-treated wood used above ground was similar to that in ground contact, except for the speed. The reason of slower colonization might be due to limited moisture content, limited nutrient and the amount of fungal inoculum to access above ground construction.

After long-term exposure, the CCA-treated materials used above ground did show some decay. Copper tolerant fungi were isolated from both non-decayed and decayed boards. These fungi accumulated copper around their hyphae. However, it took over 6 months for this to occur on the artificial media. Therefore, we can expect this process takes much longer in treated wood, especially when exposed above ground. Most decay was associated with checks, and this supports the premise that checks provide the access route for fungi to penetrate into treated-wood used above ground.

Taken together, these results provide considerable support for Smith's (1986) hypothesis and suggest that some mobility may be essential for performance of preservatives as thin shell treatments on Canadian species. It is recommended that the new preservatives now being introduced be investigated using some of the techniques described above.

6. Literature

American Standard Test Methods. 1992. ASTM D1687-92. Standard test methods for chromium in water.

American Wood Preservers' Association. 1995. A7-93. Standard for wet ashing procedures for preparing wood for chemical analysis. AWPA Granbury TX.

American Wood Preservers' Association. 1996. A9-99. Analysis of treated wood and treating solutions by atomic absorption spectroscopy. AWPA Granbury TX.

Butcher, J.A. 1971. Colonization by fungi of *Pinus radiata* sapwood treated with a copper-chrome arsenic preservative. J. Inst. Wood Sci. 4:16-25

Canadian Standards Association. 1988. CSA O80.2-M Preservative treatment of lumber, timber, bridge ties and mine ties by preservatives by pressure processes. CSA. Rexdale, ON.

Canadian Standards Association. 1997. CSA O80.32. Preservative treatment of decking lumber with waterborne preservatives by pressure processes. CSA. Rexdale, ON.

Choi, S.M., J.N.R. Ruddick and P.I. Morris 2001a. The possible role of mobile CCA components in preventing spore germination in checked surfaces, in treated wood exposed above ground. Internat. Res. Group on Wood Preserv. Document No. IRG/WP 30263 15p.

Choi, S.M., J.N.R. Ruddick and P.I. Morris 2001b. The effect of storage and subculturing on *in vitro* fruit body formation and spore production in *Gloeophyllum sepiarium* and *Oligoporus placentus*. Internat. Res. Group on Wood Preserv. Document No. IRG/WP 20232 10p.

Clubbe, C.P. and J. F. Levy 1980. The colonization and succession of fungal in wood. Internat. Res. Group on Wood Preserv. Document No. IRG/WP 1107 8p.

Fogarty, R.V. and J.M. Tobin 1996. Fungal melanins and their interactions with metals. Enzyme Microbial Tech. 19:311-317

Morris, P.I. 1996. Observations on the condition of treated landscape timbers in southwestern B.C. Report prepared for Timber Specialities Ltd. and Hickson Building Products Ltd. Forintek Canada Corp. Vancouver, BC. 10p

Morris, P.I. and J.K. Ingram 2000. Nine-year inspection of a field test of incised and unicised decking. Report prepared for Canadian Institute of Treated Wood. Forintek Canada Corp. Vancouver, BC. 12p.

Smith, R.S. 1986 Personal communication to Paul Morris.

Stephens, R.W. 1995. The management of post-use treated wood. Proc. Can. Wood Pres. Assoc. 16:89-94

Tonthat, C.C., F.V.O. Kloeke, G.G. Geesey and J.M. Henson 1995. Melanin production by a filamentous soil fungus in response to copper and localization of copper sulfide by sulphide-silver staining. Appl. Environ. Microbiol. 61:1968-1975.

TABLE1: CCA component measurement on exposed untreated surface and treated surface from collected decking materials.

Time of exposure	Position	CCA (mg chemical/g wood) Cu	Cr	As
20 years	treated surface	3.80 (1.67)[a]	10.23 (4.26)	6.05 (0.81)
	check surface	0.61 (0.13)	0.30 (0.02)	0.52 (0.41)
	untreated interior	0.10 (0.07)	0.12 (0.04)	0.10 (0.05)
15 years	treated surface	3.48 (0.62)	18.28 (1.40)	7.42 (1.79)
	check surface	0.43 (0.26)	0.36 (0.43)	0.77 (0.39)
	untreated interior	0.12 (0.09)	0.08 (0.11)	0.09 (0.03)
10 years - exposed in Vancouver	treated surface	1.73 (0.17)	6.36 (1.43)	6.21 (1.70)
	check surface	0.32 (0.06)	0.59 (0.38)	0.21 (0.10)
	untreated interior	0.05 (0.02)	0.07 (0.07)	0.01 (0.01)
1 year	treated surface	5.63 (1.67)	16.99 (4.26)	5.18 (0.82)
	check surface	0.35 (0.12)	0.16 (0.08)	0.12 (0.03)
	untreated interior	0.04 (0.02)	0.01 (0.01)	0.01 (0.00)
5 months	treated surface	7.30 (2.31)	11.56 (0.56)	5.47 (0.97)
	check surface	0.29 (0.11)	0.07 (0.05)	0.11 (0.10)
	untreated interior	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)

[a] Values in parentheses represent one standard deviation.

TABLE 2: Percent frequency of isolation from interior of the board

Exposure time	Bacteria	Mould or Staining fungi	Basidiomycete	Total Isolation rate
0.4	33	6	0	39
1	13	18	0	31
10	2	73	0	75
15	2	66	5	73
20	5	73	0	78

TABLE 3: Copper tolerant fungi

Cu concentration	
0.02M*	0.04M
Phialophora spp.	*Phialophora sp.*
Cephalosporium sp.	*Cephalosporium sp.*
Penicillium spp.	*Unidentify isoalte*
Phoma spp.	
Fusarium sp.	
Cladosporium sp.	
Unidentified isolate	

* The number represents copper concentration that allowed fungi to grow.

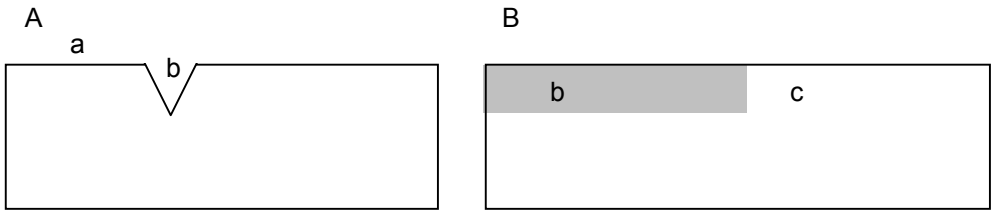

Figure 1: Areas of chemical analysis. A: Cross-section of end-cut, B: Longitudinal-section of board split along check. Analysis was conducted at a: treated surface of the board, b: checked surface, and c: untreated interior beyond end of check.

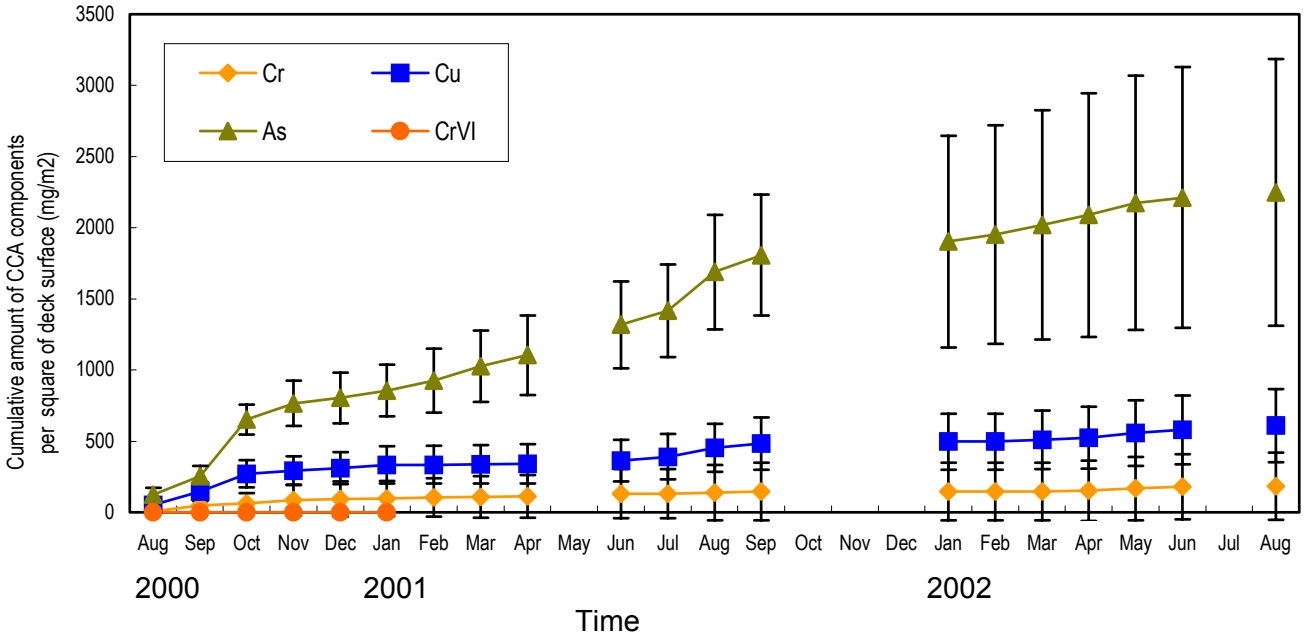

Figure 2: Leaching of CCA components due to natural rain events. (bars are standard deviation.)

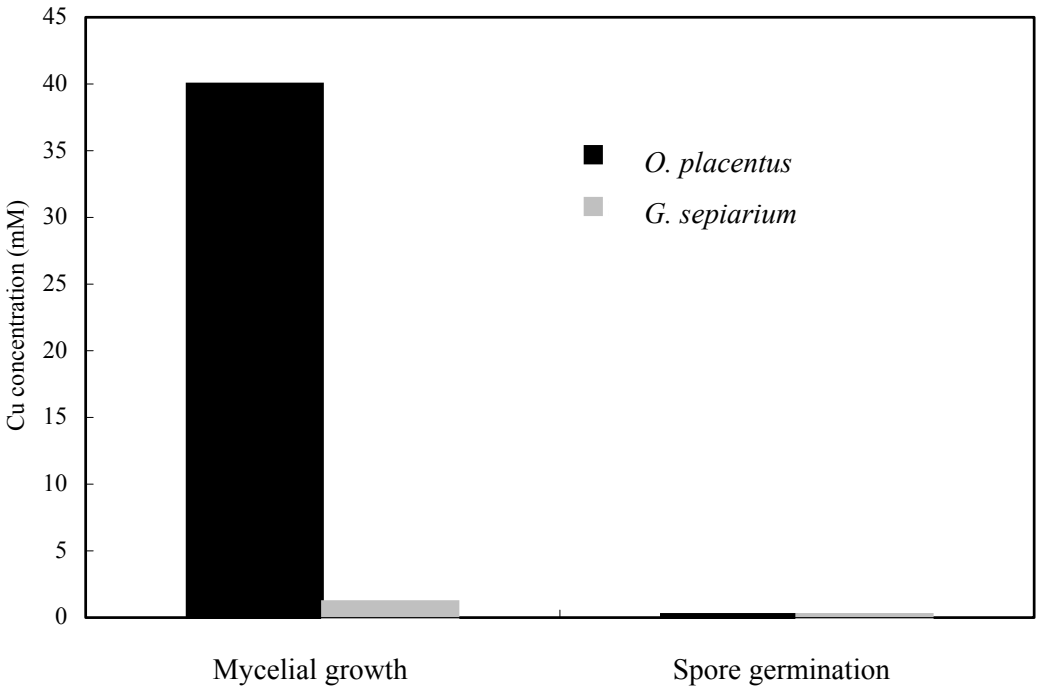

Figure 3: Minimum inhibitory of copper concentration