EFFECT OF TREATMENT POSTFIXATION PRACTICES ON COPPER MIGRATION FROM ALKALINE-COPPER-TREATED DOUGLAS-FIR LUMBER

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Abstract. The potential for preservative migration from treated wood exposed in or above aquatic environments has become a major concern in some parts of the United States. Best management practices (BMP) were designed to decrease the potential environmental footprint of treated wood, but there are few studies assessing the efficacy of these processes. The effects of applying various post-treatment BMP heating processes on loss of copper from copper azole Type B (CA) and alkaline copper quaternary compound Type B (ACQ)-treated Douglas fir were evaluated using a simulated overhead rainfall apparatus. This study examined the initial phases of wetting, which previous studies have shown to pose the highest risk to aquatic life. Immersion of CA-treated wood in hot water or a dilute ammonia solution was associated with lower levels of copper in rainfall runoff than steaming or kiln-drying, whereas steaming was associated higher copper levels. Similar trials with ACQ revealed that various heating treatments produced results that were similar to those found with air-drying. The results suggest that there might be opportunities for decreasing copper losses from CA-treated wood through further refinements in post-treatment BMPs. They also indicate that post-treatment heating processes that do not dry the wood still produce products that experience copper losses similar to those found with air-dried material.

Keywords: Douglas fir, metal migration, best management practices, copper azole, alkaline copper quaternary.

INTRODUCTION

Wood preservatives, by their nature, all have some degree of water solubility that allow them to be present in any free water in the wood cell lumens (Hunt and Garratt 1967; Zabel and Morrell 1992). This solubility makes them readily available for absorption by potential target organisms such as bacteria, fungi, and insects. There is, however, a delicate balance between availability of chemical required to protect wood for many decades and rapid solubilization and leaching into the surrounding environment. Chemical levels in wood treated with systems that lose biocide too quickly will become depleted, resulting in levels that are not capable of protecting the wood from degradation. This will result in premature failure.

For many years, the primary concern with preservative migration from treated wood was its potential to affect efficacy. However, there is increasing concern about the potential effects of migrating preservative on nontarget organisms outside the wood (Brooks 1998, 2004). As a result, the potential for preservative migration has become an increasingly important factor in deciding where these products can be used. This is a special concern in or near aquatic environments because many aquatic organisms are especially sensitive to preservative components such as copper (Brooks 2011). For example, there

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is evidence that copper can interfere with migratory behavior of some salmon species (Hansen et al 1999). One response to concerns about the use of treated wood in these applications has been the development of a series of post-treatment practices or best management practices (BMP) that are designed to help immobilize preservatives in the wood, decrease overtreatment, and limit the presence of surface deposits of preservative that can be readily solubilized into the surrounding environment (Lebow and Tipple 2001; WWPI 2006, 2011). Alkaline copper azole (CA) and alkaline copper quaternary compound (ACQ) are the two primary copper-based preservatives used to treat lumber for residual applications in the Pacific Northwest of the United States. Both systems use amine or ammonia to solubilize the copper along with a co-biocide to protect against possible copper tolerance (AWPA 2014). The majority of copper in both CA and ACQ precipitates as the ammonia evaporates from the wood, and the remaining copper complexes with amines and residual ammonia (Cooper 1991; Jin and Archer 1991; Lebow and Morrell 1995; Lebow 1996; Ruddick 1996, 2003; Jiang 2000; Zhang and Kamdem 2000; Pasek 2003; Ung and Cooper 2005; Yu et al 2009a, 2009b; Lee and Cooper 2012). There are a number of BMPs that accelerate copper deposition and decrease the risk of migration of CA or ACQ, with most using heat to drive off the amine or ammonia and immobilize the remaining metal components. Although BMP are increasingly specified by wood users, there are little data on their ability to limit preservative migration. This information will become increasingly important both for assessing current practices as well as for developing improved processes for decreasing preservative loss. In this study, we describe laboratory assessments of the ability of current BMP processes to limit copper migration from alkaline-copper-treated Douglas-fir lumber.

MATERIALS AND METHODS

Lumber Preparation

Eighteen air-dried Douglas-fir boards (*Pseudotsuga menziesii* (Mirb) Franco) (nominally 50 mm ×

150 mm × 4 m [actual dimensions 38 mm × 140 mm × 4 m]) were commercially incised to a depth of 10 mm at a density of 800 incisions/m^2. The boards were conditioned to constant weight at 23°C and 65% RH before being randomly allocated to one of three treatment groups of six boards each (CA Type B at 1.7 or 3.3 kg/m^3 or ACQ Type B at 6.4 kg/m^3). These retentions correspond to the retentions specified in the American Wood Protection Association for aboveground and ground contact exposure listed as Use Categories UC3b and 4a for CA and the ground contact retention for ACQ (AWPA 2014). Each full-length board was end coated with a two-part epoxy to retard longitudinal preservative penetration.

Boards were commercially treated to target retention in accordance with AWPA (2014). The goal was to complete the pressure treatment cycle without proceeding to any post-treatment vacuums or heating that might accelerate loss of ammonia to hasten copper deposition.

Each treated board was immediately cut into ten 300-mm-long subsamples. Each subsample was weighed and labeled before being sealed in a plastic bag and frozen at −10°C until needed.

Post-Treatment with BMP

Frozen subsamples were defrosted before being subjected to 1 of 10 treatments listed in the Western Wood Preservers Institute BMP requirements as follows:

Air-drying: Boards were subjected to 4 wk of drying at 20-25°C to approximately 19% MC.
Fast kiln-drying: Boards were subjected to 3 da at 71.1°C with a 16.7°C wet bulb depression.
Slow kiln-drying: Boards were subjected to 7 da at 48.9°C with a 5.6°C wet bulb depression.
Steaming: Boards were steamed for 1, 3, or 6 h at 104.4°C.
Hot water soaking: Boards were soaked for 1 or 3 h at 100°C.
Ammonia bath: Boards were soaked for 1 or 3 h in 1% ammonia at 100°C.

Samples were placed in individual bags after being subjected to a given BMP and frozen until

needed. Each treatment was replicated on a sample cut from each parent board treated to a given retention. This resulted in end matching of materials receiving the same preservative treatment and retention but different BMP and was designed to help decrease the inherent variability among boards.

Simulated Rainfall Tests

Samples were warmed overnight to room temperature before the potential for metal migration was evaluated in a specially constructed overhead leaching apparatus that applied a controlled amount of simulated rainfall at a desired temperature. Previous studies (Simonsen et al 2008) showed that preservative migration was independent of both temperature and rainfall rate. Therefore, the device was operated at room temperature (20-28°C) and a rainfall rate ranging from 1 to 3 mm/h.

The apparatus (1.52 m wide × 0.61 m long × 0.91 m deep) was constructed with stainless steel and a plastic panel with eight sample holders on a 4.5° incline from horizontal to allow water to flow down the wood. Simulated rainfall was produced by four spray nozzles connected to a deionized water supply. Rate of water spray was controlled by a small pump and an electronic controller.

BMP-treated samples were placed into each holder and subjected to simulated overhead rainfall for periods up to 9 h. Runoff water was collected in tared 50-mL beakers that were weighed after the collection period to determine the total volume of water applied per board for each time period. The weight of water was recorded, and 10 mL of each water sample was placed into a vial. Water was collected after 0.25, 0.5, 0.75, 1.0, 1.5, 2.0, 4, 5, 7, and 9 h.

Chemical Analysis

Water samples were acidified by adding 0.25 mL of 1 M nitric acid into 4.75 mL of runoff water. The samples were stored at 3°C until they could be analyzed for copper using a PerkinElmer (Waltham, MA) Optima 3000DV inductively coupled plasma optical emission spectrometer with a diode array detector. Because most of the chemical migration happened at the beginning of water exposure, water samples collected during the first 2 h of simulated rainfall were tested for copper concentration, whereas the remaining samples were retained in case metal levels were still elevated after 2 h. Copper levels in the system during the 2-h period were used as the measure of BMP effectiveness.

Statistical Analysis

Copper levels were analyzed using a randomized complete block design (RCBD) to fit a linear model to the data. BMP treatments were randomly assigned to experimental units such that each treatment occurred equally in each block. Ten different post-treatments were randomly assigned to each sample, and each single board was a block. The linear model for RCBD that explained each observation was

$$Y_{ijk} = \mu + \alpha_i + \beta_j + \gamma X_{ijk} + \varepsilon_{ijk}$$

where Y_{ijk} was the response (copper concentration in runoff) for which treatment $= i$, board $= j$; volume of cumulative water $= X_{ijk}$ under kth run of water collection, $k = 1, 2, \ldots, 6$; μ was the population mean; α_i was the effect of the post-treatment i, $i = 1, 2, \ldots, 10$; β_j was the effect of the board j, $j = 1, 2, \ldots, 6$; γ was the effect of the volume of cumulative water; and E_{ijk} was the random deviation associated with each observation.

After fitting the model, differences in copper levels among group means were subjected to analysis of variance (ANOVA) using R statistical software (R Foundation for Statistical Consulting, Wien, Austria). The primary interest was if any of the ten different posttreatments significantly affected metal losses. (H0: $\alpha_1 = \alpha_2 = \ldots = \alpha_{10}$)

A least significant difference (LSD) test was applied in conjunction with the ANOVA to assess differences. A Holm adjustment was applied along with the LSD test to adjust the p value and decrease the risk of Type I errors. The LSD test compared every pairwise treatment group mean for the first 80 mL of runoff collected and

identified differences between any two means. The 80 mL of runoff represented approximately 2 mm of rainfall and was selected to accentuate any surface copper dislodged during the initial precipitation events.

RESULTS AND DISCUSSION

Copper retentions in CA-treated boards averaged 1.31 and 2.28 kg/m^3 for the low and high retentions, respectively, whereas ACQ retention was 3.0 kg/m^3 as copper oxide (4.4 kg/m^3 accounting for the quat). The levels were somewhat lower than specified for CA and ACQ. As expected, there were large variations in retentions in individual boards, but there were no consistent relationships between initial board retention and subsequent copper losses (Ye 2013). This probably reflects a disconnect between the total amount of copper in the outer 10-mm assay zone and that available on the wood surface during rainfall exposure. However, higher retentions might be expected to influence long-term metal losses.

Copper levels in runoff tended to increase rapidly at the start of overhead wetting of both CA- and ACQ-treated wood, then declined with further rainfall (Figs 1–3). This pattern is typical of exposure of treated wood to wetting and is presumed to occur as residual copper on the wood surface is solubilized and released (Brooks 2011). Copper levels in the runoff decline once this readily available surface copper is depleted. One of the purposes of the BMP processes is to diminish the level of surface copper and thereby decrease copper concentrations in initial runoff.

Wood is a variable material in terms of density and receptivity to preservative treatment (USDA 2010). As a result, preservative retentions can vary widely between individual boards treated at the same time or even between locations on the same board. We attempted to account for interboard variation by subjecting one sample from each board to a given BMP process, but it was not possible to increase the replication to the extent required to completely account for the inherent wood variability. The potential for variability among individual lumber samples is illustrated by the much higher levels of copper in runoff from samples cut from Board 2 in both the low and high CA treatments and the very low copper levels in the samples cut from Board 1 in the high CA treatment (Figs 1 and 2). Similar results occurred with the single ACQ treatment. The results illustrate the difficulties of examining preservative migration from such a variable material. However, it was still possible to examine trends in migration with the various BMP processes.

It is generally presumed that immobilization of alkaline copper systems is a function of some initial copper reactions with wood polymers, notably the acidic groups on the carbohydrates and phenolic groups on the lignin, but these sites are extremely limited. These reactions are followed by evaporation of the ammonia and formation of insoluble copper-amine or ammonia complexes (Cooper 1991; Ruddick 1996, 2003). This process should replicate air-drying, which was considered the baseline BMP for comparison with other post-treatment processes.

Migration of Copper from Copper-Azole-Treated Wood

Copper levels in runoff from boards treated to the lower CA retention that were air-dried or subjected to one of the two kiln-drying processes did not differ significantly from one another. Copper levels in runoff from boards subjected to 1, 3, or 6 h of steaming were all significantly greater than those from the air-dried boards, suggesting that steaming increased copper levels near the surface. Copper levels in runoff from boards subjected to immersion in hot water or ammonia water did not differ significantly from the air-dried control or were slightly lower.

Copper levels in runoff from boards treated to the higher CA retention followed similar trends although the differences were not always significant. For example, copper levels in runoff from boards that were air-dried did not differ significantly from those of boards subjected to
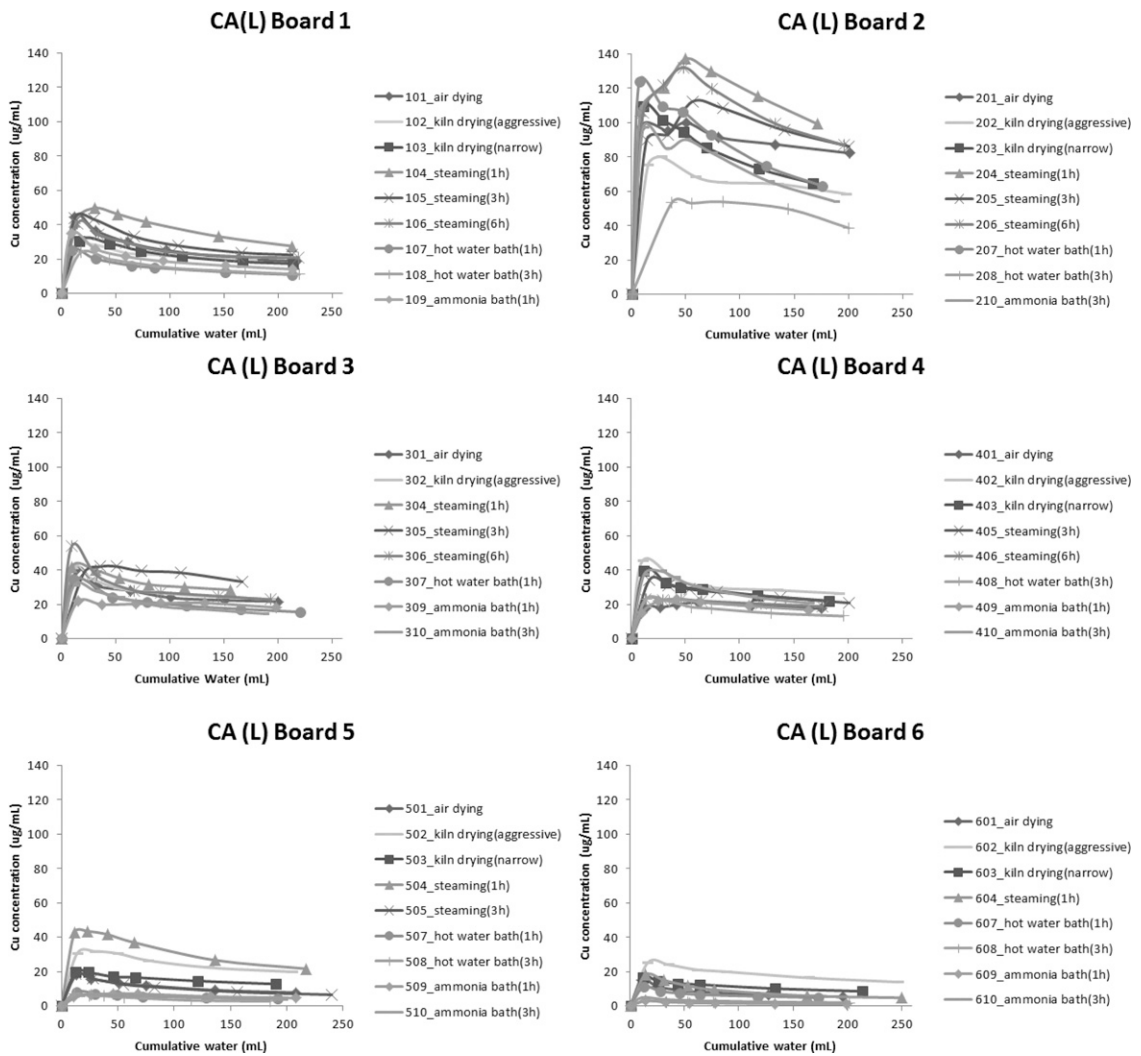
Figure 1. Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with CA to a target retention of 0.96 kg/m^3 and subjected to one of the best management practice procedures. Each graph represents data from a given board.

the slow kiln-drying but were significantly lower than those from boards subjected to the faster kiln process. Copper runoff from boards subjected to any length of steaming did not differ significantly from levels in runoff from the air-dried controls. As with the lower retention samples, runoff from boards subjected to either hot water or ammonia water immersion was lower than that from air-dried boards, and these differences were significant for the longer immersion periods (3 h in hot water or ammonia water). Immersion would be expected to remove copper residues near the wood surface, thus decreasing the amounts of metal available for movement during subsequent rainfall exposure. The ammonia solution should solubilize some copper from the surface, further decreasing the likelihood of copper migration in rainwater runoff. However, these processes also have the potential to encourage migration of copper deposited deeper into the wood toward the surface and this could increase copper loss. These immersion methods merit further study to determine if they can consistently decrease subsequent copper losses in service.
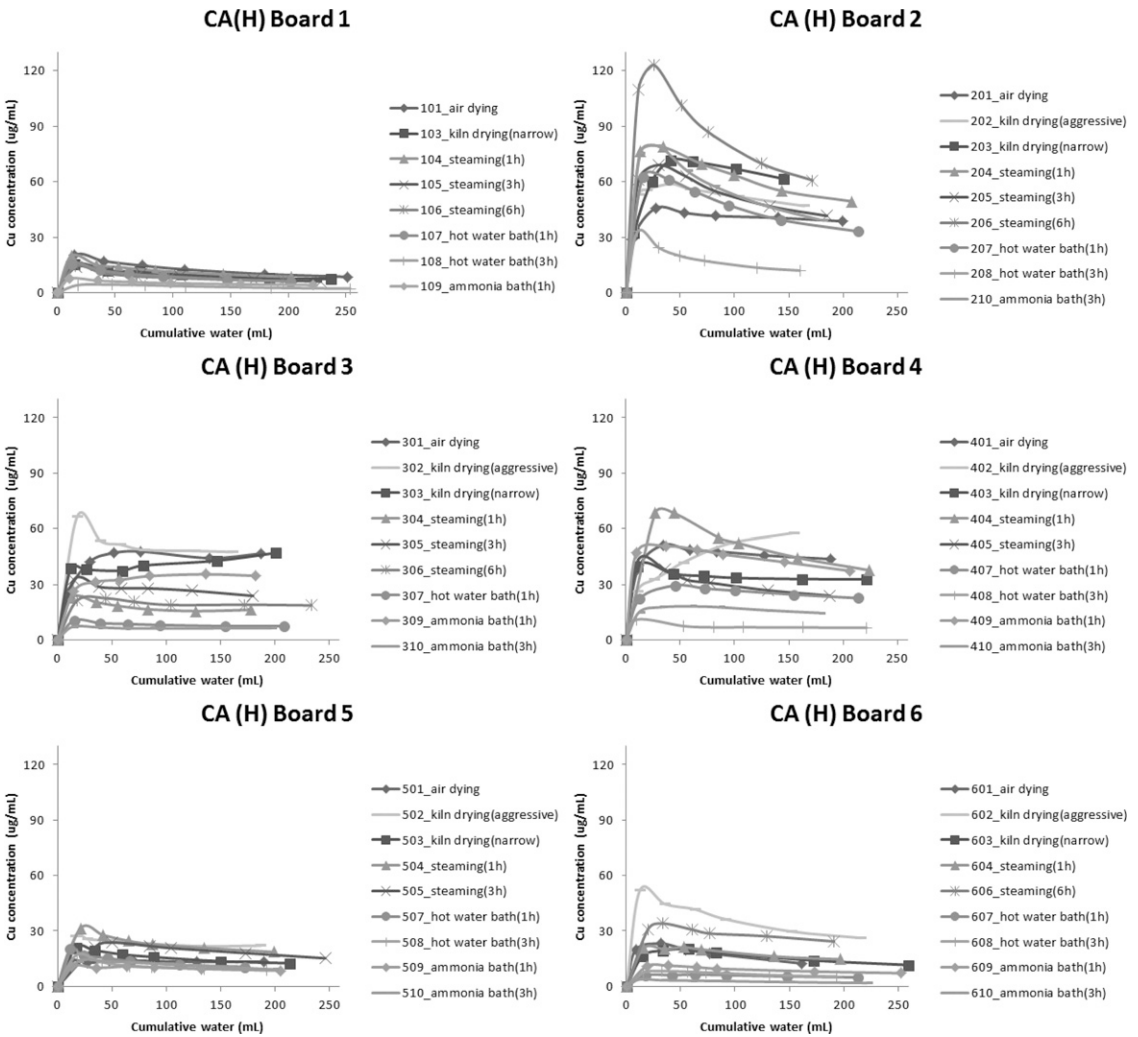
Figure 2.   Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with CA to a target reten-
tion of 2.4 kg/m^3 and subjected to one of the best management practice procedures. Each graph represents data from
a given board.

With the exception of the air-dried and kiln-dried
samples, the other boards were still wet when
exposed to the simulated rainfall. The results
suggest that BMPs generally produced boards
with copper migration behavior that was at least
similar to that found with air-dried material.
However, the results also suggested that some
BMPs, notably the hot water and ammonia water
treatments, have the potential to further decrease
the risk of metal migration from CA-treated
wood, and these merit further study.

The lack of differences in copper levels in runoff
from samples treated to low and high retentions
was also interesting. CA Type B primarily con-
sists of copper (96.1%) with a small amount
of a triazole compound (tebuconazole) (AWPA
2014). Although small amounts of copper react
directly with the wood, the majority of copper
forms complexes with residual amine and is
immobilized. The results suggest that increas-
ing levels of copper were not associated with
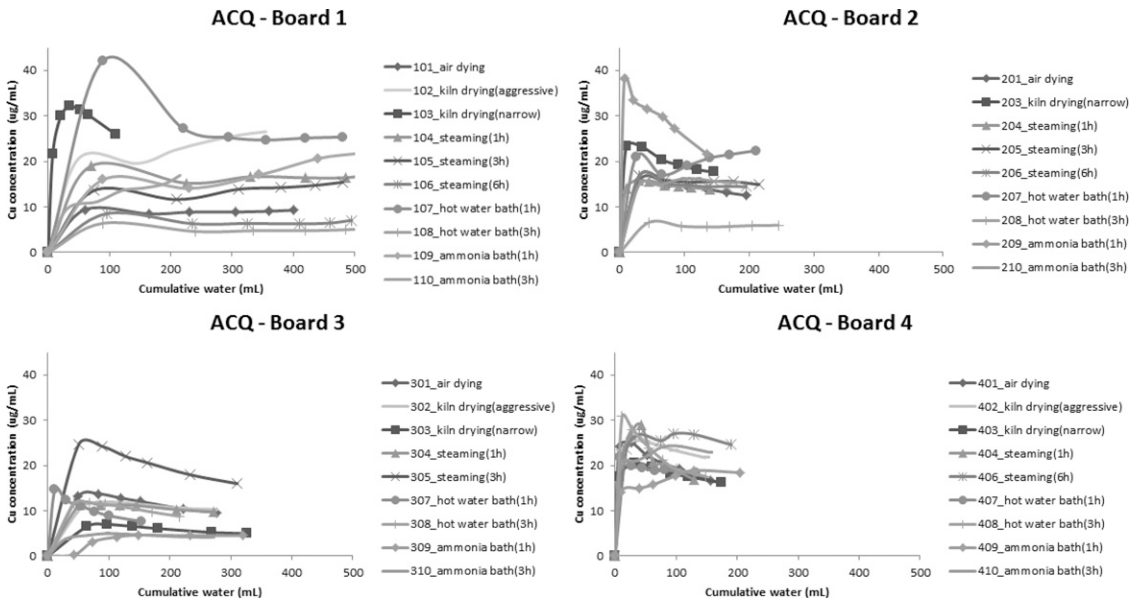proportional increases in copper losses in these

Figure 3. Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with ACQ to a target retention of 6.4 kg/m^3 and subjected to one of the best management practice procedures. Each graph represents data from a given board.

short-term tests, although greater copper loadings may have effects during longer exposures.

Copper Migration from Alkaline-Copper-Quaternary-Treated Wood

ACQ was only evaluated at ground contact retention (6.4 kg/m^3), and only four boards were examined. ACQ contains 67% copper oxide and 33% didecyldimethyl ammonium chloride (DDAC). DDAC reacts relatively quickly with wood and was not considered in this evaluation (Jin and Archer 1991). The amount of copper in this system is much greater than that found in even the high or ground contact CA treatment. Copper levels in runoff followed the same trend as CA, with increasing levels of copper for the first three or four water collections followed by a decline with continued rainfall (Fig 3). Copper levels were generally similar in runoff from the four boards tested, but the effects of the BMP processes on losses varied between boards. Average copper losses tended to be similar for all BMP processes, although steaming for 3 h was associated with much greater variation in concentrations (Fig 3). Copper tended to fix fairly rapidly in ACQ-treated

wood subjected to heating (Yu et al 2009b), and the results in this study supported that premise. Copper levels in runoff did not differ significantly among the BMP processes evaluated except when boards were subjected to immersion in 1% ammonia. This process resulted in significantly lower copper levels in the runoff (Table 1).

Table 1. Average copper concentrations in runoff from Douglas-fir lumber treated with CA to target retentions of 0.96 or 2.4 kg/m^3 or ACQ to retention of 6.4 kg/m^3 and exposed to simulated rainfall until 80 mL of cumulative rainfall (approximately 45-60 min of rainfall) was collected.

	Average copper concentration in runoff (μg/mL)[a]		
BMP treatment	CA (0.96 kg/m^3)	CA (2.4 kg/m^3)	ACQ (6.4 kg/m^3)
Air-drying	24.3 cd	25.6 bc	17.4 ab
Kiln-drying (rapid)	33.2 abc	41.2 a	20.7 ab
Kiln-drying (slow)	29.7 bc	28.3 ab	21.5 ab
1 h steaming	41.0 ab	29.4 ab	18.4 ab
3 h steaming	37.1 ab	29.2 ab	35.5 a
6 h steaming	44.5 a	32.5 ab	24.3 ab
1 h hot water	19.6 d	16.3 cd	16.0 ab
3 h hot water	11.2 e	10.3 d	16.9 ab
1 h ammonia bath	10.0 e	16.2 cd	11.1 b
3 h ammonia bath	17.6 d	13.1 d	12.6 b

[a] Values followed by the same letter(s) do not differ significantly from one another in a given column by a LSD test at α = 0.05 with a Holm adjustment.

The remaining processes produced results similar to those found with air-drying, suggesting that they would be appropriate for decreasing the need to hold treated wood prior to installation. It was also interesting that copper levels in runoff from ACQ-treated wood were similar to those found with either CA treatment despite the presence of nearly twice as much copper in ACQ-treated wood.

CONCLUSIONS

BMP processes produced variable results on subsequent availability of copper to migrate in simulated rainfall. Heating in either water or dilute ammonia solutions was associated with less copper in runoff from boards treated with CA or ACQ, and this merits further study. The results illustrated the differences in responses to BMP processes with initial treatment and suggest the need for additional research to better develop the BMP processes and improve the understanding of how each process affects copper immobilization.

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