

Min Ye for the degree of Master of Science in Wood Science presented on October 14, 2013.

Title: Effects of Best Management Practices on Copper Migration from Douglas-fir Lumber Treated with ACZA, CA or ACQ

Abstract approved: _____

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Copper is the most common ingredient in waterborne preservatives and provides excellent activity against most fungi and insects. However, issues associated with copper migration from treated wood have created increasing concerns about potential risks to non-target organisms in surrounding environments, especially those in sensitive aquatic environments. Various Best Management Practices (BMPs) that can help produce clean and residue-free wood have been developed to minimize potential chemical leaching into the surrounding environment.

The effects of various BMPs were assessed by examining the copper concentrations in runoff from boards subjected to a given BMP and exposed to simulated rainfall for up to 9 hours. The results suggested that BMP method markedly affected the rate of copper losses from boards treated with ACZA, CA or ACQ. Copper losses in runoff tended to be highest during the initial rainfall exposure and then decreased to background levels. Air seasoning or kiln drying were associated with lower copper losses from boards treated

with ACZA, while those steamed for 6 hours were associated with higher copper losses. Increasing ACZA retentions were associated with exponentially higher copper losses. Hot water or ammonia bathes were associated with lower copper losses from boards treated with CA or ACQ. Increasing hot water bath time from 1 to 3 hours or decreasing ammonia bath time from 3 to 1 hours tended to decrease copper losses. These results suggest that BMPs are not uniformly effective on all treatments.

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Effects of Best Management Practices on Copper Migration from
Douglas-fir Lumber Treated with ACZA, CA or ACQ

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I understand that my thesis will become part of the collection of Oregon State University. My signature below authorizes release of my thesis to any reader upon request. I also affirm that the work represented in this thesis is my own work.

Min Ye, Author

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CHAPTER 1 – INTRODUCTION

1.1 Background

Wood has long been a preeminent construction material in the United States, as well as in many other countries where timber resources are abundant. An important practice developed to improve the serviceability of wood is impregnation with preservatives (Hunt and Garratt, 1967).

Waterborne heavy metal preservatives are among the most commonly used chemicals for protecting dimension lumber employed in residential applications. The most common component in these systems is copper, which has excellent activity against most fungi and insects. Field studies have shown that copper-based preservatives provide decades of effective protection against deterioration.

For many years, chromated copper arsenate (CCA) was the dominant waterborne wood preservative and the most widely used system in the world. CCA was inexpensive, easy to handle, left the wood paintable and, most importantly, reacted with the wood to become leach resistant. However, the industry decision to remove CCA from residential markets resulted in a dramatic shift from this system to alternative copper systems.

Alkaline copper quaternary and alkaline copper azole both emerged as alternative systems for residential applications. These systems contain much higher proportions of

copper and, more importantly, use alkaline compounds instead of acids to solubilize the copper. As a result, copper in these systems tends to be more mobile in the wood.

While heavy metal-based preservatives provide excellent protection, they can also have potential negative effects. The active chemicals in the preservative can be toxic to non-wood-degrading organisms in the surrounding environment. Thus, there is increasing concern about preservative migration out of the treated wood and into the surrounding environment at levels that pose risks to organisms, especially those in sensitive aquatic environments (Lebow and Tipple, 2001). Leaching in small quantities into the soil surrounding the wood generally poses little problem because the metals are diluted with distance from the wood. However, these same metals can pose considerable risk when large quantities of treated wood are used in aquatic environments because aquatic organisms tend to be much more susceptible to heavy metals, notably copper.

Concerns about heavy metals in aquatic environments have led some regulators to restrict or ban the use of treated wood in or over bodies of water. The treating industry initially responded to these rulings through the courts, but quickly realized that they could produce products with lower environmental risk profiles through the development of improved treatment practices.

Various methods have been developed to immobilize the active ingredients in treated wood. In the western United States, the Western Wood Preservers' Institute (WWPI) developed a set of treatment and post-treatment guidelines called Best Management

Practices (BMPs) to reduce over-treatment, clean the wood surface of preservative residues and improve metals reactions with the wood. Methods specified by BMPs for reducing leaching of waterborne preservative include air-seasoning, steaming, kiln drying, vacuum and hot water baths (WWPI, 2011). These processes reduce the risk of using treated wood in aquatic and other sensitive environments.

Although the BMPs ensure better-fixed material, none of these approaches completely solves the leaching problem, because some active ingredients are always available in the cell lumen. While BMP procedures have become widely specified, they have largely developed empirically with few extended studies to determine the effects of various process variables on subsequent chemical loss. The absence of fundamental data on the effects of processing on leaching makes it difficult to develop improved BMPs.

1.2 Objective

To assess the effects of various post-treatment practices on mobility of heavy metal (copper) in wood treated with ACZA, CA or ACQ.

CHAPTER 2 – LITERATURE REVIEW

2.1 Purpose of preservative treatment

Wood is an exceptional structural material with a high strength-to-weight ratio along with good appearance and renewability (USDA, 2010). Wood also has some disadvantages, including a tendency to shrink and swell with moisture changes, combustibility, anisotropy and, most importantly, susceptibility to degradation by both living and non-living agents.

Non-living agents include physical and chemical agents, mechanical damage, weathering caused by ultraviolet light or erosion by wind or water. There are also a variety of living or biological agents that degrade wood. Most wood structures are designed to limit one or more requirements for these agents, including water, air, temperature or food. When water or moisture cannot be excluded, wood structures must be supplementally treated with wood preservatives (Morrell et al., 2011).

Wood is treated with preservatives to protect it from wood-destroying organisms, such as decay or stain fungi, insects or marine borers. This can increase the life span of the material in service, thus decreasing the overall cost of the product and avoiding the need for frequent replacements. Wood treated with commonly used preservatives can be used in service for 40 years or more. Therefore, preservative-treated wood is an economical,

durable, and aesthetically pleasing building material, that is a natural choice for many construction projects (Lebow, 1996).

2.2 Types of chemicals used for treatment

2.2.1 Oil borne-preservatives

The most commonly used oil borne-preservatives are pentachlorophenol, creosote and copper naphthenate. Oil borne-preservatives can have unpleasant odors and are generally not used in applications that involve human skin contact and inside dwellings. Moreover, unlike waterborne-preservatives, most oil borne-preservatives result in oily, unpaintable surfaces.

2.2.1.1 Creosote

Creosote is one of the oldest wood preservatives, and is a complex mixture of polycyclic aromatic hydrocarbons (PAHs) (Webb, 1990). It is made from coal tar which is a by-product of coking coal for steel production. Creosote is commonly used for utility poles and railroad ties. Creosote is effective against decay fungi, insects and most marine borers. The surface of creosote treated wood is very oily with a strong odor, making it difficult to paint and seal (Webb, 1990; Lebow and Tipple, 2001).

2.2.1.2 Pentachlorophenol

Pentachlorophenol (Penta) is a relatively pure, crystalline solid that dissolves in oils (Lebow and Tipple, 2001). Penta treated wood is a light or dark brown color, depending on the oil carrier. Like creosote, penta is mostly used for treating utility poles and railroad ties. Penta is often used in fresh water or soil applications, such as decking and foundation piling. Penta is a highly effective preservative with a broad range of uses against wood destroying organisms, but is not effective against marine borers (Simonsen et al., 2008).

2.2.1.3 Copper naphthenate

Copper naphthenate is an oil borne-preservative prepared by reacting naphthenic acids with copper salts (USDA, 2010). Copper naphthenate treated wood is used to a limited extent in aquatic applications and is used more in above water applications. It is not a restricted-use pesticide and is available in hardware stores. It is also commonly used for treating holes and field cuts made during construction with treated wood (Pilon, 2002).

2.2.2 Water borne-preservatives

Waterborne-preservatives have been increasingly used to treat wood for residential applications, such as decks and fences. The most commonly used waterborne preservatives are chromated copper arsenate (CCA), ammoniacal copper zinc arsenate (ACZA), alkaline copper quaternary compounds (ACQ), copper azole (CA) and borates

(USDA, 2010). Waterborne-preservatives are commonly used in residential applications because they leave a clean, paintable, and odorless surface after treatment. Moreover, water-borne systems are usually less costly than oil-borne systems and can pose a low fire hazard (Lebow and Tipple, 2001). Copper is used in most water-borne formulations because it is toxic to a variety of wood attacking organisms. Copper can cause membrane disruption and inhibit many important enzymatic reactions (McIntyre and Freeman, 2008; Rui and Morrell, 1994). Metal-based systems also have an advantage over oil-based systems because they react or are fixed to the wood. “Fixation” describes the chemical reactions between the active ingredient in the waterborne-preservative and the wood cell structure. Copper can form insoluble complexes that are less likely to leach from the wood (Cooper et. al., 1993; Lebow and Tipple, 2001). Different types of preservatives have different mechanisms and rates of fixation. Ideally, leaching risks would be mitigated if the preservative was completely fixed to the wood. Unfortunately, this is impractical because almost all preservatives function through direct contact and uptake by the target wood-destroyers (Morrell and Rhatigan, 2000). Although complete fixation is not feasible, adequate fixation can sharply reduce the risk of migration once the treated wood is placed into service.

2.2.2.1 Chromated copper arsenate

Chromated copper arsenate (CCA) was developed in India and was once the most commonly used waterborne preservative in the United States (Dahlgren and Hartford, 1972 a, b,c; Zabel and Morrell, 1992; Townsend et al., 2004). CCA contains chromic

acid, copper oxide and arsenic pentoxide. Copper can be effective against a variety number of species of wood destroyers (Hunt and Garratt, 1967). Arsenic is an insecticide that provides supplemental control against some wood attacking organisms and protects the wood from decay fungi, insects and marine borers. The chromium improves long-term weathering resistance to treated timber and helps fix copper and arsenic in wood through chemical complexes to the cellulose and lignin. CCA treated-wood has little or no odor (Lebow and Tipple, 2001). CCA was voluntarily withdrawn from residential applications at the end of 2003, but is still used in industrial applications.

CCA fixation has been investigated by researchers since the 1970's. The fixation process is a combination of precipitation, reduction – oxidation, adsorption, desorption, proton transfer, and ion-exchange. Initial investigations into CCA interactions with wood during and after the treating process were reported by Dahlgren (1974) and Dahlgren and Hartford (1972 a, b, c). They observed that a complex series of reactions occurred instantaneously after the wood was treated with CCA coupled with an increase in pH and a decrease in chromium content. They noted that the course of fixation had three phases: initial instant reactions; the main precipitation fixation period; and a final reaction or conversion period. The final products formed through ion exchange reactions include CrAsO_4 , Cu(OH)CuAsO_4 , and Cr(OH)_3 . Pizzi (1981, 1982) concluded that some copper reacts with chromium or arsenic to form copper chromate or copper arsenate and that the rest of the copper was associated with cellulose and lignin in wood, with the majority in the lignin. Arsenic reacts with both chromium and copper. Fixation reactions can

continue within the wood for weeks or even months after treatment, although some reactions occur during the first few hours (Pizzi, 1982). CCA fixation largely depends on the reduction of chromium from the hexavalent to the trivalent state along with the precipitation of chromium, copper and arsenic complexes into the wood. The rate of CCA fixation is highly temperature and time dependent, although wood species, pH, lignin structure, extractive content can also affect the rate (Dahlgren, 1974; Dahlgren and Hartford, 1972 a, b, c; Pizzi, 1982).

2.2.2.2 Ammoniacal copper zinc arsenate

Ammoniacal copper zinc arsenate (ACZA) is a waterborne-preservative primarily used in the Western U.S. ACZA contains 50% copper oxide, 25% zinc oxide and 25% arsenic pentoxide (AWPA, 2010). ACZA is a refinement of an early formulation, ammoniacal copper arsenic (ACA), that is no longer used in the United States (Lebow and Tipple, 2001).

The biggest benefit of ACZA is that it can penetrate into wood to a greater depth than most other preservatives (Lebow, 1992). The system is used to treat refractory western species such as Douglas-fir heartwood. ACZA is mostly used in industrial products, such as timbers, commercial decking for walkways and bridges or piling used in sensitive or aquatic environmental applications (WWPI, 2011).

The key factor in ACZA fixation is the volatilization of ammonia (Cooper, 1991; Ruddick, 1996). As ammonia evaporates from treated wood, arsenic is fixed by bonding with copper or zinc cations through ion exchange to form arsenic/metal complexes. Both copper and zinc are relatively leach resistant because of the low solubility of precipitates formed with arsenic or the wood substrate. Arsenic has high water solubility and is not readily adsorbed by the wood substrate. As a result, fixation of arsenic largely depends on the ratio of metal oxide to arsenic. Arsenic is precipitated by copper and zinc (mostly zinc) in treating solution in the form of zinc arsenate as the ammonia evaporates (Cooper, 1991; Ruddick, 1996; Lebow, 1992; Lebow and Morrell, 1995). Zinc precipitates more arsenic than copper and this knowledge was employed when a portion of the copper in ACA was substituted by zinc to produce ACZA (Lebow and Morrell, 1995). Copper and zinc fixation are independent of arsenic because of their ability to be adsorbed into the wood substrate. Copper and zinc not only react with arsenic, they are also readily absorbed to the phenolic hydroxyls found in lignin or extractives (Lebow, 1992).

2.2.2.3 Alkaline copper quaternary

Alkaline copper quaternary (ACQ) is another waterborne-preservative developed as an alternative to CCA. The formulation can be altered depending on wood species and end use (Lebow, 2004). All ACQ types contain copper oxide (62-71%), which is the primary fungicide and insecticide, and a quaternary ammonium compound (29%-38%), which provides additional protection against fungi and insects, as their primary active ingredients (AWPA, 2010). ACQ-B and ACQ-D have been used more often in the United

States (McIntyre and Freeman, 2008). ACQ-B was standardized by the American Wood Protection Association (AWPA) in 1992 and is primarily used for treating western wood species such as Douglas-fir, because it contains an ammonia carrier that improves penetration into refractory wood species. ACQ-B is formulated with 66.7% copper oxide and 33.3% quat as didecyldimethylammonium chloride (DDAC). ACQ-D, which uses ethanolamine instead of ammonia, is more often used by treating plants in other parts of the U.S (AWPA, 2010). ACQ contains more copper and tends to be more corrosive than CCA. The higher copper levels result in much greater potential copper losses in field exposure (Groenier and Lebow, 2006).

ACQ fixation mechanisms are similar to those of ACZA, although the copper adsorption is slower in amine systems (Jin and Archer, 1991). In general, the cupriammonium ion undergoes complex ion-exchange reactions with carboxylic and phenolic hydroxyl groups in lignin and hemicellulose in the wood substrate. These complexes then precipitate in the wood to form insoluble salts as the ammonia evaporates (Cooper, 1991; Pankras et al., 2009). DDAC rapidly adsorbs onto both lignin and cellulosic model compounds by cation exchange on carboxylic and phenolic hydroxyl groups or ion pair and hydrophobic effects (Preston et al., 1987; Jin and Preston, 1991). DDAC in the treating solution also competes with copper for ion-exchange sites in the wood substrate and may reduce copper fixation in wood (Jin and Archer, 1991). Pankras et al. (2009) reported that the relative proportion of copper in ACQ significantly affected leaching of copper. Copper to DDAC ratios of 2:1, 1:1, or 1:2 resulted in lower copper retentions in

the treated samples, substantially decreasing the amount of copper leached per unit area for the three species studied. Formulations with a 1:1 ratio of copper to quat appeared to be the most promising (Pankras et al., 2009).

2.2.2.4 Copper azole

Copper azole is another copper-based wood preservative that is mostly used in the United States, Canada and Europe. Copper azole type A (CBA-A) was standardized by the AWWPA in 1995 and contains 49% copper, 49% boron as boric acid and 2% azole as tebuconazole. Copper azole type B (CA-B) was standardized in 2002 and contains copper (96.1%) and azole as tebuconazole (3.9%). Wood treated with either type of copper azole has a greenish-brown color and little or no odor. CA can be used for the treatment of a variety of softwoods, including southern pine, red pine and hem-fir. The formulation may require addition of ammonia to the copper azole solution that helps increase penetration when treating Douglas-fir, although the formulation is listed as an amine system in AWWPA standard (AWWPA, 2010).

Fixation of copper amine systems is relatively slow compared with ammonia copper systems (Jiang, 2000). Tebuconazole is an insoluble, non-leachable, light and heat stable organic co-biocide which functions to protect wood from wood destroying fungi that are tolerant to copper (Grundlinger and Exner, 1990). The reaction sites for copper in wood in the amine based system are the phenolic hydroxyl groups in lignin and carboxylic groups found in hemicellulose (Thomason and Pasek, 1997; Zhang and Kamdem, 2000;

Ruddick, 1996). The relatively high proportion of copper in the formulation and the limited reaction sites in wood results in higher leaching of copper from CA treated wood. Copper losses from CA are 3.5 to 17.9 times greater than those for CCA (Dickey, 2003).

2.2.2.5 Borate preservative

Borates are salts, such as sodium octaborate, sodium tetraborate or sodium pentaborate that are effective against insects and most fungi (Freeman et al., 2009). Borates also have low toxicity against non-target organisms. Borate treated wood is odorless and easily painted. Borates are not fixed in the wood and can leach into the surrounding water or soil. As a result, borate use is restricted to interior applications protected from wetting (Groenier and Lebow, 2006).

2.3 Concerns regarding the use of treated wood

While preservative treated wood has many benefits, potential risks and concerns still exist, especially when these materials are used in aquatic environments. It is widely acknowledged that chemicals are not completely fixed in the wood and they do migrate from the treated wood into the surrounding environments (WWPI, 2011; Lebow, 1996; Brooks, 1997a). The chemicals present in preservative treated wood can either immediately or over time pose a potential risk to other life forms in the environment (WWPI, 2006). A number of studies have shown that preservative components accumulate in the soil, sediment in fresh water and marine environments (Morrell et al.,

2003; Brooks, 1997a, b; Brooks, 1998; Stratus Consulting Inc., 2006). The risk is relatively low for the chemicals migrating into surrounding soil because most chemicals are confined within a limited distance that may range from 0.3 to 1m. Chemical levels decrease to a background level beyond this range (Morrell et al., 2003). However, there are concerns about preservative migration from treated wood into sensitive aquatic environments, especially into slow moving bodies of water (Brooks, 1997a, b; Brooks, 1998; Stratus Consulting Inc., 2006).

Preservative ingredients, such as copper, arsenic, chromium and zinc, are not only toxic to wood destroyers but can also be toxic to a wide variety of non-target organisms living in water. Copper is the prime concern and also the subject of much in-depth research because it is the most commonly used component in the metal based systems that have higher leaching rates (Stratus Consulting Inc., 2006). Proper management and control of copper generally reduces the risk of using waterborne preservative to levels under those that would be of concern (WWPI, 2006).

Invertebrates are among the most sensitive species to environmental contaminants in both freshwater and marine water environment. Cladocerans and larval forms of freshwater mussels in fresh water as well as embryonic and larval stages of mollusks appear to be among the most sensitive organisms in marine environments (Stratus Consulting Inc., 2006). Salmonids are affected at copper levels at or below critical values, depending on the species, and the effects including avoidance, growth, incipient lethal levels, olfaction, and physiology (Stratus Consulting Inc., 2006; Brooks, 2004). Some species of salmon or

trout have the ability to detect the copper at low levels and tend to avoid water with these levels (Hansen et al., 1999a). This avoidance may cause the displacement of habitat for salmonids or avoidance of environments that could serve as refuges from predators. However, prolonged exposure to sublethal copper concentrations can be toxic to the olfactory systems of salmonids, which affects a number of behaviors such as fright responses, predator avoidance, migration and reproductive synchronization (Stratus Consulting Inc., 2006).

The Pacific Northwest region is home to a number of native salmon species whose numbers have been declining due to a variety of factors including hydroelectric dams, overfishing and changing climate conditions. The Endangered Species Act (ESA) is a law designed to protect species from extinction. Among the 51 species of salmonids listed under the ESA, 30 are either listed as Threatened and Endangered (T&E), or are candidates for listing (Stratus Consulting Inc., 2006). According to the U.S. Environmental Protection Agency (EPA) database, a genus mean sensitivity of salmon to acute copper toxicity is 57.16 ug/L in freshwater and 498.8 ug/L for coho salmon in salt water (Stratus Consulting Inc., 2006).

2.4 Regulatory actions related to use of treated wood in aquatic applications

Restrictions on using treated wood in aquatic environments have encouraged wood producers to explore strategies for safely using treated wood, including environmental evaluation and risk assessment through empirical models, direct laboratory and field

studies and additional guidelines and standards for treated wood (Brooks, 1997a, 1998, 2003; Sinnott, 2000; Weis et al., 1998; Wendt et al., 1996; Lebow, 2002).

Knowledge about the levels of metal migration from treated wood and data from laboratory and field studies have allowed researchers to construct empirical spreadsheet models to assess the risk of using treated wood in aquatic environments (Brooks, 1997a, 2003; Sinnott, 2000). These models show that the risks of using treated wood are generally not likely to significantly impact aquatic lives in sensitive environments, including salmonids, unless the water in the environment is poorly circulated or the surface area of the treated wood represents a significant portion of the surface area of the water body (Brooks, 1996; Sinnott, 2000; Stratus Consulting Inc., 2006). A number of laboratory and field studies have been performed to assess the use of treated wood (Weis et al., 1998; Wendt et al., 1996; Brooks, 2003; Lebow, 2002). The rate of copper leaching is typically highest during the first several hours or days of exposure after installation and then drops dramatically with an exponential decay curve depending upon the exact product and environmental conditions (Brooks, 2003). The overall impact of using treated wood in aquatic environments appears to be minor in most situations, except in poorly flushed water bodies. The biological impact associated with using treated wood is confined to the areas the extremely close to the treated structures and this impact appears to decline with time after installation.

Although treated wood products used in aquatic environment are generally unlikely to cause detectable impacts to endangered salmonids and other life forms, some

uncertainties remain concerning the modeling and field studies. Many variables contribute to the concentration of toxic chemicals, including current speed of water, volume of wood installed, wood species and dimensions, preservative retentions, types of preservative, and degree of chemical fixation.

Guidelines for applying treated wood and using risk assessment models are intended to insure proper and safe use of the wood preservative by minimizing the potential risk in sensitive environments.

Wood products producers and industries contend that the potential adverse environmental impacts of using treated wood can be minimized when certain conditions are met including the use of minimum retentions along with the application of Best Management Practices (BMPs) with certification of inspection and proper field guidelines for installation (WWPI, 2006).

Best Management Practices (BMPs) are a set of standards and guidelines that supplement the AWP standards used for treated wood production and installation. The BMPs were developed by the Western Wood Preservers' Institute (WWPI) with the purpose of minimizing the amount of preservative applied to wood, while conforming to the AWP standards, maximizing fixation and immobilization of waterborne systems, and minimizing surface residues (WWPI, 2006).

The BMPs include simple recommendations for users of wood products, such as minimizing sawdust, shavings, dirt and other residues on the wood products as well as cleaning the retort prior to treatment. Limiting residues on the wood reduces the possibility of preservative losses into the water after installation. The BMPs provide a set of post treatment procedures that are intended to minimize the mobilization of the metals into the surrounding environments. The BMPs for oil-borne preservative systems help to minimize the amount of residues on the surface before installation by removing the internal pressure at the end of the treating process. These BMP processes include expansion baths, steaming, or final vacuums. The removal of internal pressure is critical for oil-type preservatives because internal pressure may cause excessive residues or bleeding on the surface after installation. The BMPs for water-borne preservatives are generally designed to produce stabilization of the chemicals in the wood. Evaporation of ammonia in the treatment solution through some form of heat, such as air-drying, kiln drying, steaming, hot water baths or combination of these accelerates stabilization. The process is a function of time, temperature and humidity for ammonia-copper based preservatives (WWPI, 2011).

CCA fixation is a function of time, temperature and also involves the reduction of hexavalent chromium to the trivalent state with the formation of a number of complexes of chromium, copper, or arsenic with the wood substrate. CCA fixation takes only a few hours at 66 °C, but takes weeks to even months at 18 °C (McNamara, 1989a; Cooper and Ung, 1992). BMPs for CCA stipulate that the wood be processed using hot water bathes,

air or kiln drying or steaming to accelerate fixation after treatment (WWPI, 2011). The volatilization and removal of ammonia is crucial for reactions between active ingredients in ACZA or ACQ and the treated wood to achieve stabilization. This can be accomplished by air or kiln drying. BMPs specify that wood treated with ACZA, ACQ or CA should be held for a minimum of three weeks at the ambient temperature (20-25 °C) or kiln dried to a maximum moisture content of 30% employing a kiln cycle of 50 °C - 70 °C dry bulb temperature. Other artificial heating methods can also be used for minimizing surface deposits and completing fixation, such as aqua-ammonia steaming at 88 °C - 93 °C for at least 1.5 hours (WWPI, 2011). Copper stabilization is generally slow in copper-amine systems; however, fixation is strongly influenced by temperature and time. The BMPs for CA require treated wood to be processed by air seasoning, kiln drying, steaming or other artificial heating to produce an acceptable level of chemical stabilization before the wood leaves the treatment facility (WWPI, 2011).

Although BMPs are increasingly specified, there is surprisingly limited research on the effects of BMPs on the extent of fixation and the absence of fundamental data on the effects of processing on copper losses makes it difficult to develop improved BMPs.

CHAPTER 3 – MATERIALS AND METHODS

3.1 Materials

Thirty Douglas-fir boards (*Pseudotsuga menziesii*) (nominally 50 mm × 150 mm × 4 m long [actually 38 mm × 140 mm × 4 m]) were commercially incised to a density of 800 incisions/m². The boards were conditioned to constant weight at 23°C and 65% relative humidity before being randomly allocated to one of 5 treatment groups of six boards each (ACZA at 4.0 kg/m³ or 6.4 kg/m³; CA at 0.96 kg/m³ or 2.4 kg/m³; or ACQ at 6.4 kg/m³). Each board was end-coated with a two-part epoxy to retard longitudinal preservative penetration.

The boards were commercially treated to a target retention in accordance with American Wood Protection Association Standards U-1 and T-1 (AWPA, 2010). The goal was to complete the pressure treatment cycle without proceeding to any post-treatment vacuums or heating that might have accelerated loss of ammonia or amine to hasten copper deposition.

Each of the treated boards was immediately cut into ten 300 mm long sub-samples. Each sub-sample was weighed and labeled before being sealed in a plastic bag and frozen at -10°C until needed.

3.2 Methods

3.2.1 Post-treatment with BMPs

The frozen sub-samples were defrosted before being subjected to one of nine treatments listed in the Western Wood Preservers Institute Best Management Practices requirements.

1. Air-drying: Samples were placed on stickers to encourage air-flow at ambient temperature (20-25°C) and conditioned to a target moisture content below 19% over four weeks.

2 - 3: Kiln drying: The samples were placed in a steam heated kiln on stickers to enhance air flow. Samples were either dried over a three-day cycle at a dry-bulb temperature of 71.1°C with a wet-bulb depression of 16.7°C or a one-week kiln schedule at a dry-bulb temperature of 48.9°C and wet-bulb depression of 5.6°C. The latter cycle limited drying, but the lower temperature should have encouraged ammonia or amine loss. Both of the schedules resulted in wood moisture contents below 19%.

4 - 6: Steaming: Samples were subjected to 1, 3 or 6 hours of steaming at 104.4°C in an autoclave with stickers in between samples.

7 - 8: Hot water bath: Samples were soaked in water at 100°C for 1 or 3 hours.

9 - 10: Ammonia bath: Samples were soaked in aqueous 1% ammonia at 100°C for 1 or 3 hours.

The 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 board treated with a given preservative.

3.2.2 Leaching tests

The samples were warmed overnight 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 (Figure 1). Previous studies (Simonsen et al, 2008) have shown that migration is independent of both temperature and rainfall rate- so the device was operated at room temperature (20~28°C) and a rainfall rate ranging from 0.1cm/h to 0.3 cm/h.



Figure 1 - Overhead leaching apparatus used to evaluate the effects of BMP procedures on copper migration from ACZA, CA or ACQ treated wood.

The apparatus (152.4 cm wide * 61.0 cm long * 91.4 cm) was constructed with stainless steel and a plastic panel and had eight 15.2 cm wide * 45.7 cm long * 5.1 cm high sample holders (Figure 1). Holders were placed on a shelf with a 4.5 °incline from the horizontal to allow water to flow down the wood. Simulated rainfall was produced by four spray nozzles connected to a deionized water supply. The rate of water spray was controlled by a small pump and an electronic controller.

Post - treated samples were placed into each holder and subjected to simulated overhead rainfall for periods up to 9 hours. Runoff water was collected in tared 50 ml beakers that were weighed after rainfall exposure to determine the total volume of water applied per board for each time period. The weight of water was recorded and 10ml of each water sample was placed into a vial. Water was collected at 15-minute intervals for the first hour then at 30-minute intervals for two hours and then after 4, 5, 7 or 9 hours.

3.2.3 Chemical analysis

Samples were acidified by adding 0.25ml 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 residual metal, mostly copper, at the Oregon State University Central Analytical Lab (CAL). The metals were analyzed using a Perkin Elmer Optima 3000DV inductively-coupled plasma optical emission spectrometer with a diode array detector (ICP). Since most of the chemical migration happens at the beginning of water exposure, water samples collected over the first two hours of simulated rainfall were tested for the copper concentration while the

remaining samples were retained in case metal levels were still elevated after 2 hours.

Copper levels in the system over time were used as the measure of BMP effectiveness.

3.2.4 Statistical analysis

Copper levels were analyzed using a Randomized Complete Block Design (RCBD) to fit a linear model to the data. An RCBD rather than Completely Randomized Design (CRD) was used because we were interested in the effects of a set of treatments, but needed to control for extraneous sources of variability that included the differences between boards in terms of wood variability and varying retentions among the 6 boards in each experiment. A RCBD assumes that a population of experimental units (samples) can be divided into a number of subpopulations or blocks (boards). Treatments were then randomly assigned to experimental units such that each treatment occurred equally in each block. In our design, ten different post-treatments were randomly assigned to each sample and each single board was a block.

In the case of our experiment, 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 k^{th} run of water collection, $k = 1, 2, \dots, 6$;

μ was the population mean;

α_i was the effect of the post-treatment i , $i = 1, 2, \dots, 10$;

β_j was the effect of the board j , $j = 1, 2, \dots, 6$;

γ was the effect of the volume of cumulative water;

ε_{ijk} was the random deviation associated with each observation.

After fitting the model, the differences in copper levels among group means were subjected to an Analysis of Variance (ANOVA) using R statistical software. In our experiment, we were mostly interested in whether or not any of the ten different post-treatments significantly affected metal losses. ($H_0: \alpha_1 = \alpha_2 = \dots = \alpha_{10}$)

A Least Significant Difference (LSD) test was applied in conjunction with the ANOVA to assess differences. The LSD test compared every pairwise treatment group mean and identified differences between any two means. However, the LSD test has the potential to inflate Type I errors (finding a difference between groups when it does not actually exist) when the p-value is not adjusted. Therefore, a Holm adjustment was applied along with

the LSD test to adjust the p-value and reduce the risk of Type I errors. In our analysis, we were interested in the difference between any two post-treatment mean effects.

The effects of various BMP treatments on copper losses over time were examined using box plots of average copper concentration for various BMP treatments after 80 ml (about 45-60min of collection) or 260 ml (about 2 hours of collection) of simulated rainfall exposure for a given preservative treatment. Tables comparing the copper levels for different post-treated samples in the system after 80 ml and 260 ml of rainfall collection were analyzed for each level of a treatment system. Plots showing trends of copper concentration over the volume of cumulative water and accumulated copper over the volume of cumulative water for each experiment were generated for each level of a treatment chemical.

CHAPTER 4 – RESULTS AND DISCUSSION

4.1 Effects of BMPs on fixation of copper in ACZA treated wood

BMP processes varied in their ability to limit metal losses from ACZA treated boards. Copper concentrations tended to be highest in the first two water collections for all treatments, and then declined with continued rainfall (Figure 2, 3, 4, 5). These results are consistent with numerous previous studies showing that the highest releases of copper occur during the initial exposures to wetting (Kumar et al., 1996; Brooks, 2003; Morrell et al., 2011). Copper concentrations in runoff from both ACZA retention groups were generally lowest in samples that were either air or kiln dried prior to exposure, although 1 to 3 hours of immersion in hot water was also associated with lower copper concentrations in the low ACZA retention (4.0 kg/m^3) group (Figure 6, 7, 8, 9). Conversely, steaming for 3 or 6 hours was associated with significantly higher copper levels in the low ACZA retention (4.0 kg/m^3) group (Figure 6, 7). As expected, cumulative copper in the runoff increased over time and BMP treatments varied in controlling the rate of copper release (Figure 10, 11). Air drying and kiln drying groups generally had lower rates of copper release compared with other BMPs. Copper release rates in steamed and ammonia bath groups were generally higher.

Figure 2 - Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with ACZA to a target retention of 4.0 kg/m^3 and subjected to one of the BMP procedures. Each figure represents data from a given board.

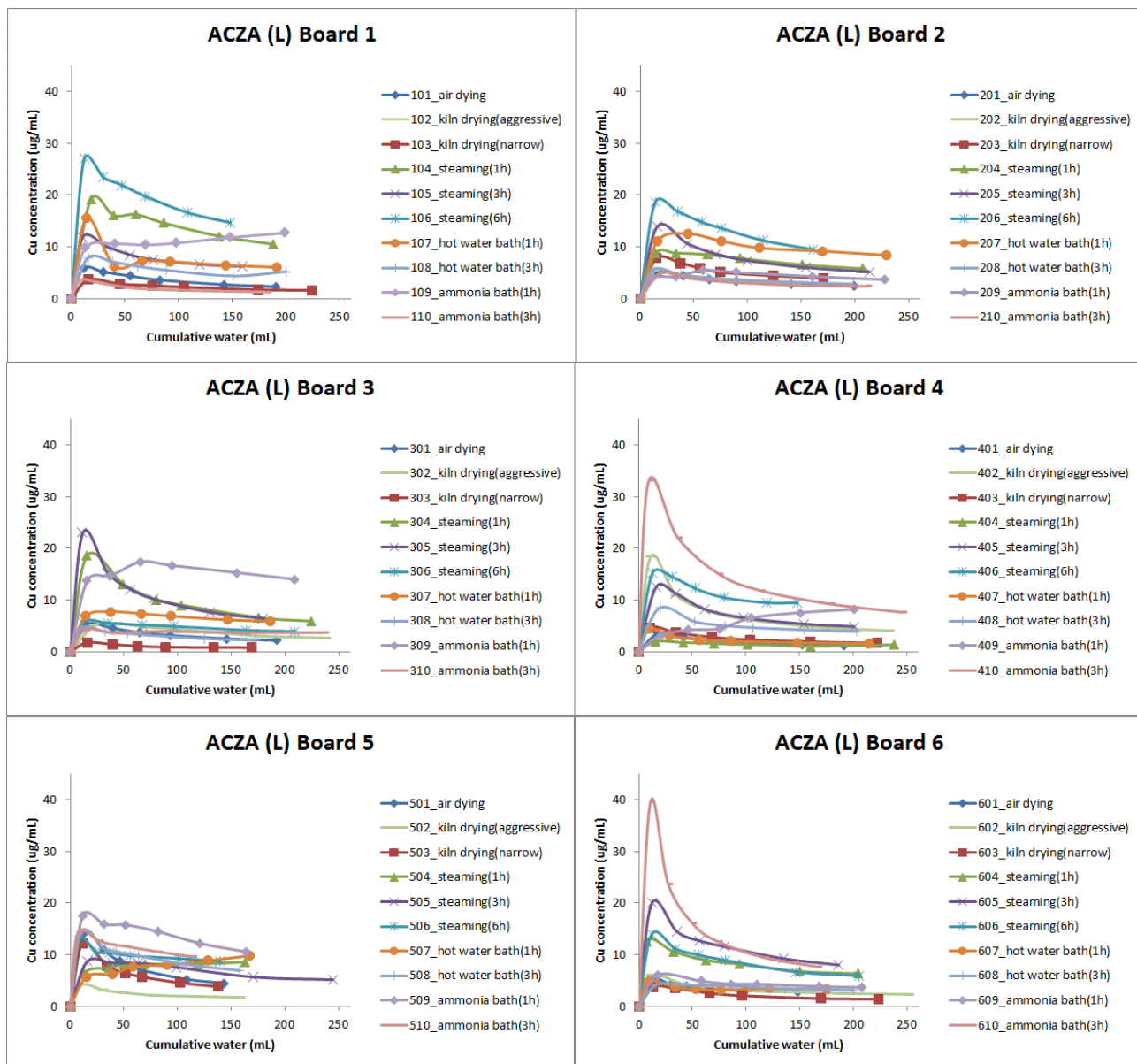


Figure 3 - Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with ACZA to a target retention of 4.0 kg/m^3 and subjected to one of the BMP procedures. Each figure represents data from all of the runs for a given BMP process.

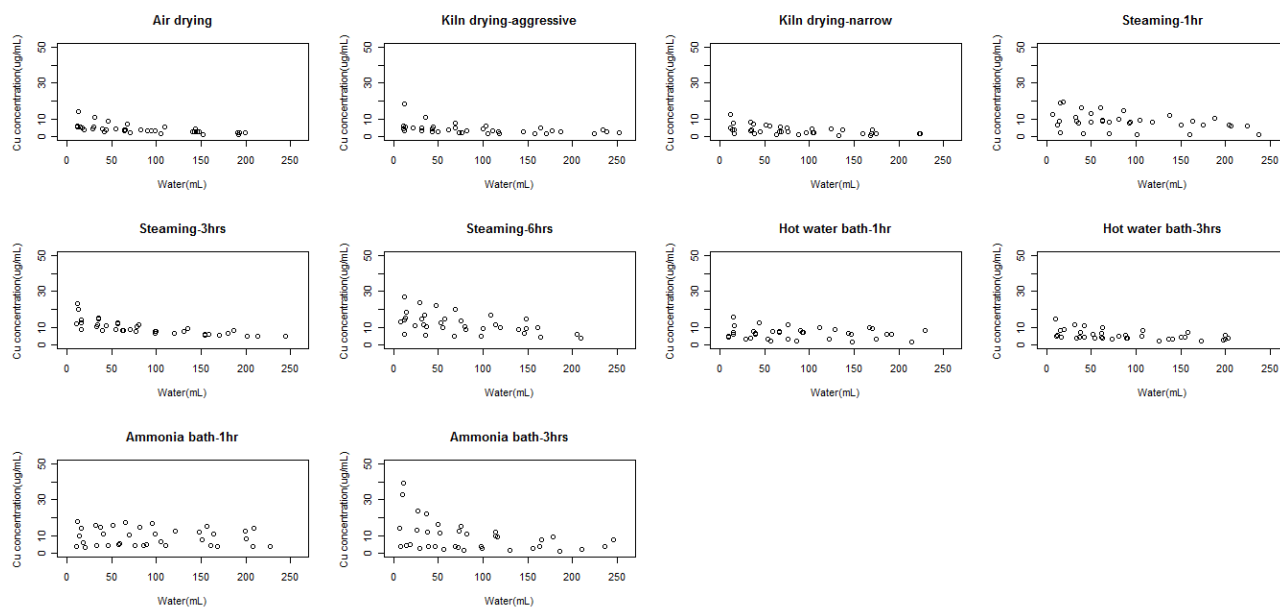


Figure 4 - Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with ACZA to a target retention of 6.4 kg/m^3 and subjected to one of the BMP procedures. Each figure represents data from a given board.

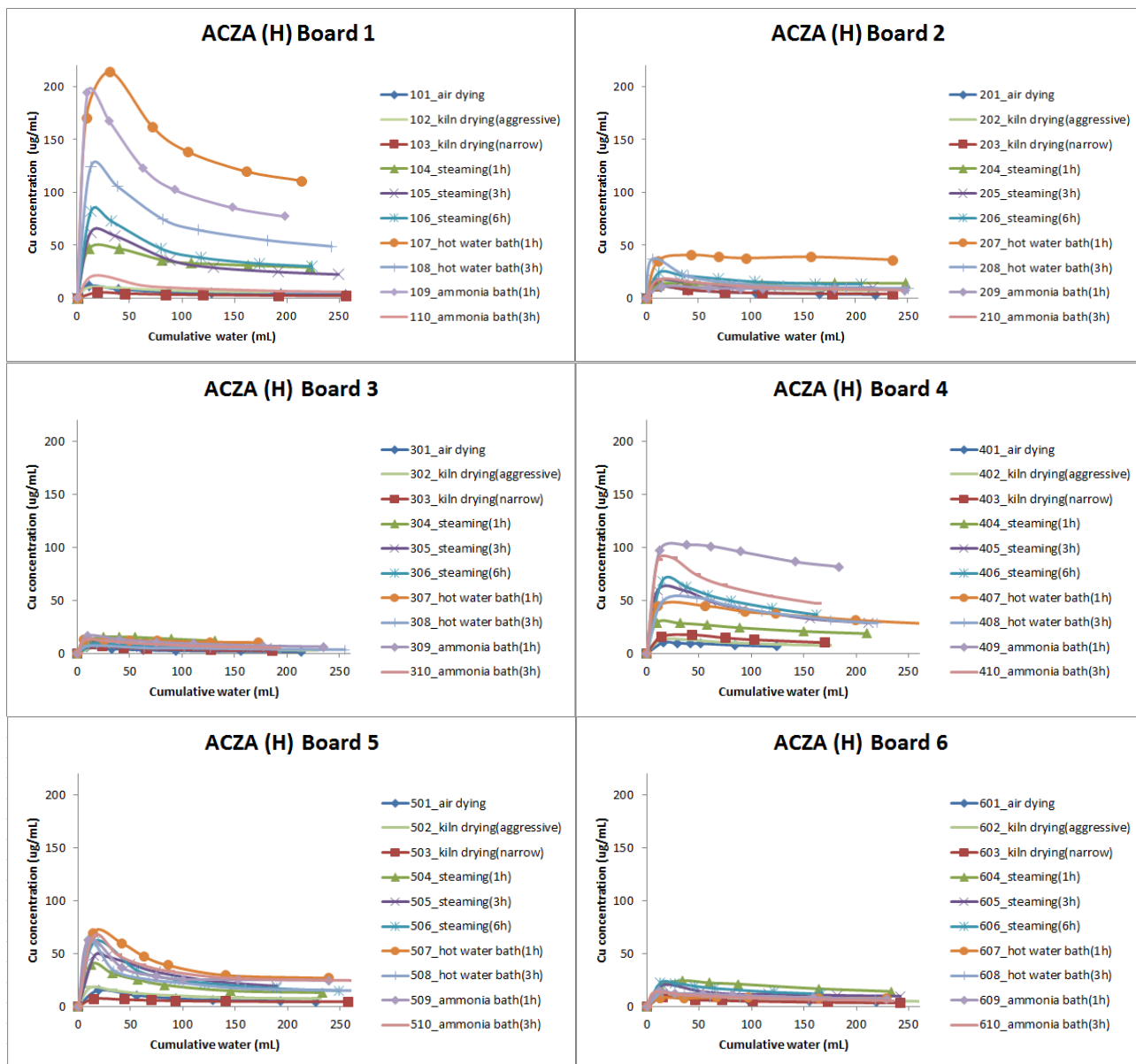


Figure 5 - Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with ACZA to a target retention of 6.4 kg/m^3 and subjected to one of the BMP procedures. Each figure represents data from all of the runs for a given BMP process.

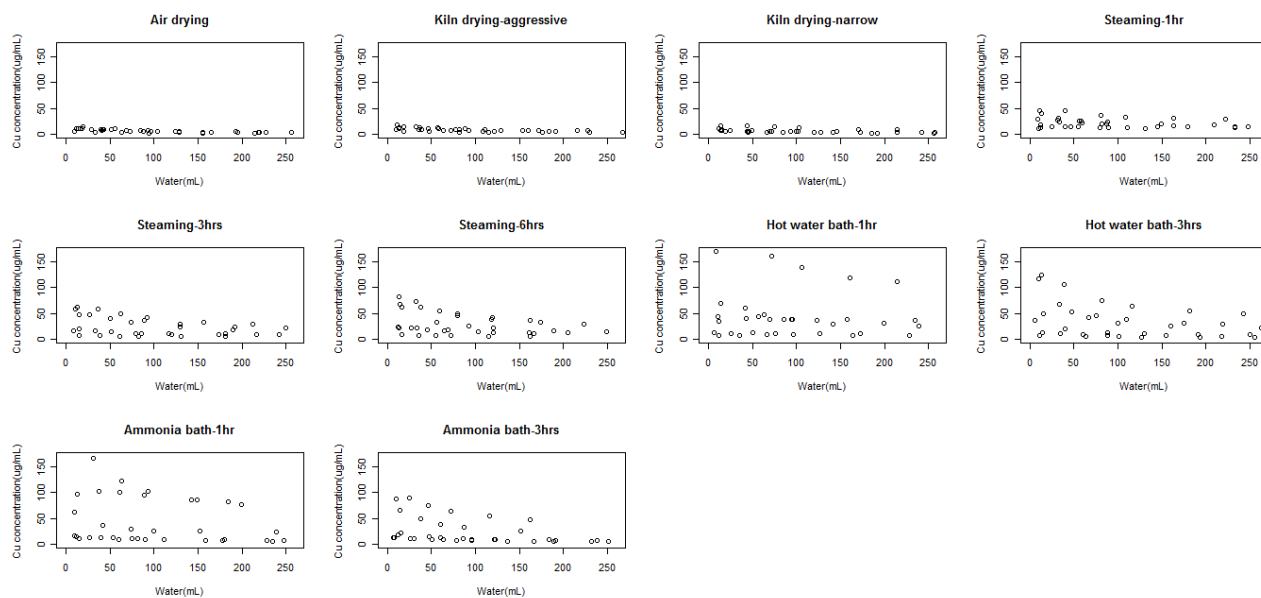


Figure 6 - Box and whisker plots showing copper concentrations in 80 ml (45-60 min of collection) of runoff from Douglas-fir lumber treated with ACZA to a target retention of 4.0 kg/m^3 and subjected to one of the BMP procedures.

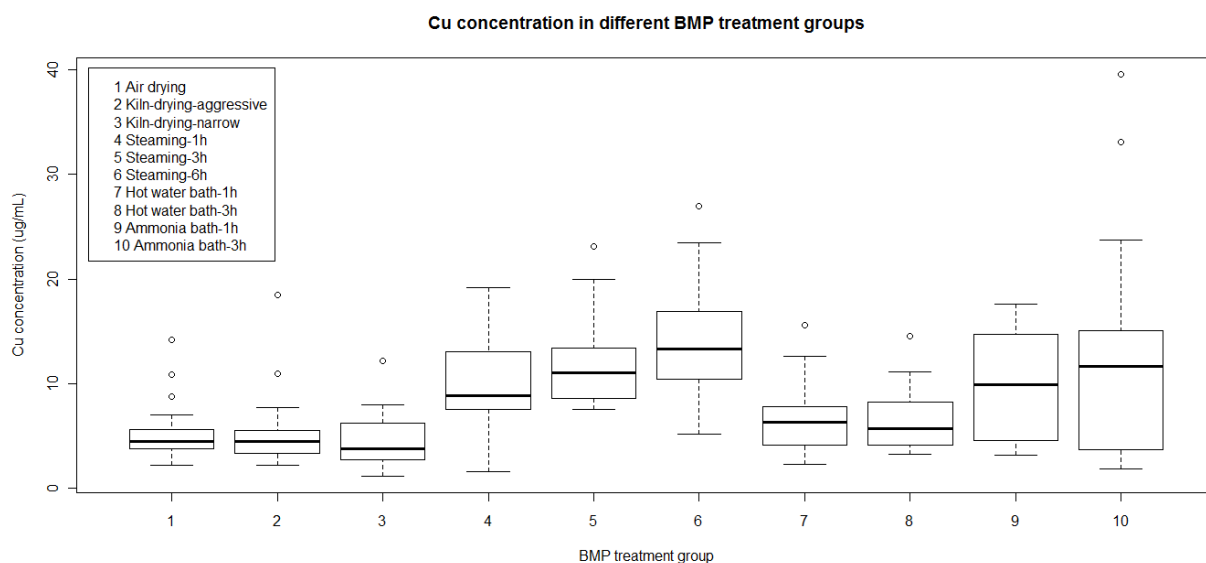


Figure 7 - Box and whisker plots showing copper concentrations in 260 ml (about 2 hours of collection) of runoff from Douglas-fir lumber treated with ACZA to a target retention of 4.0 kg/m^3 and subjected to one of the BMP procedures.

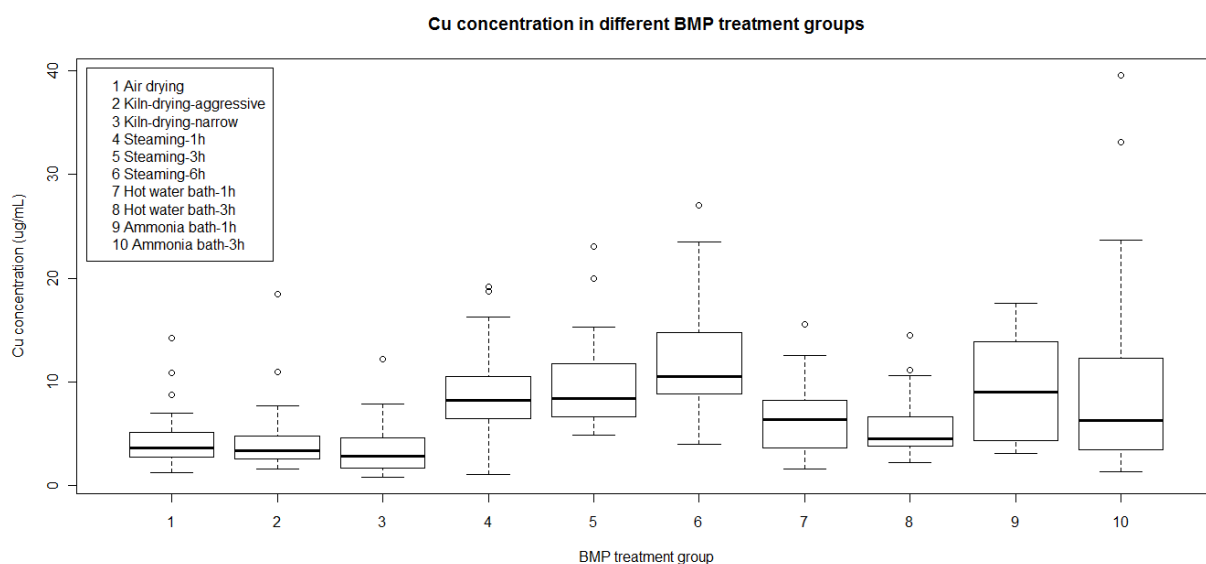


Figure 8 - Box and whisker plots showing copper concentrations in 80 ml of runoff from Douglas-fir lumber treated with ACZA to a target retention of 6.4 kg/m^3 and subjected to one of the BMP procedures.

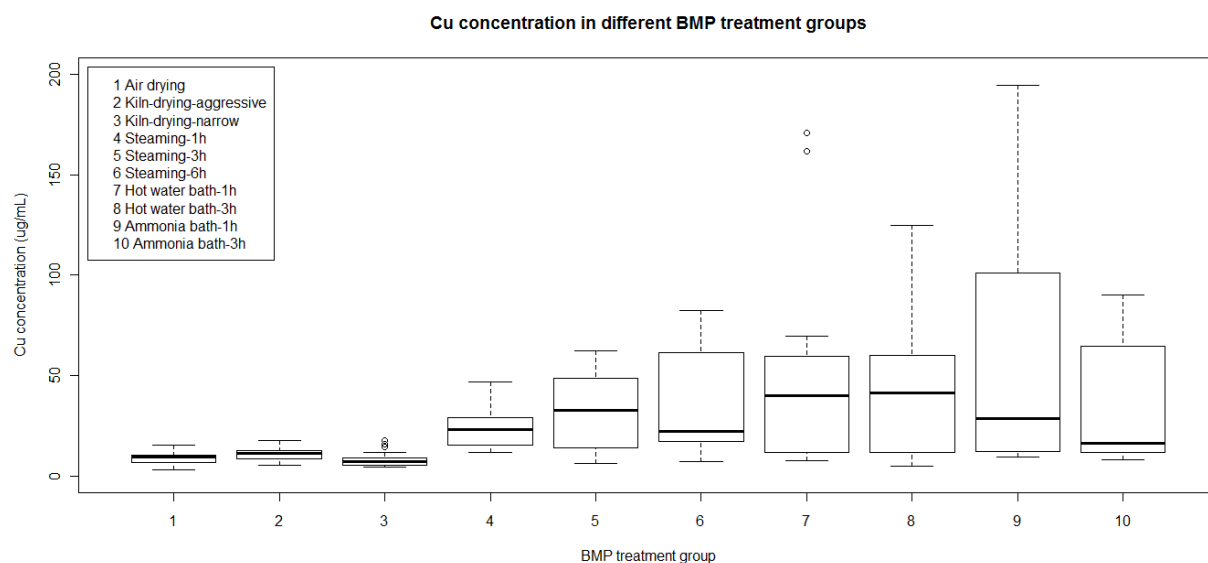


Figure 9 - Box and whisker plots showing copper concentrations in 260 ml of runoff from Douglas-fir lumber treated with ACZA to a target retention of 6.4 kg/m^3 and subjected to one of the BMP procedures.

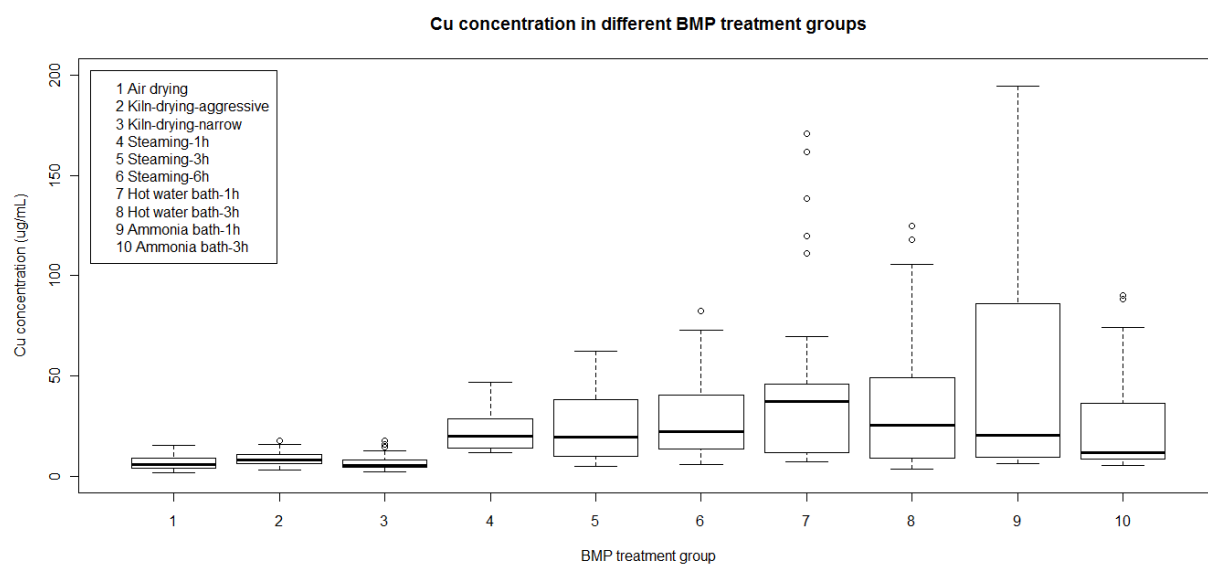


Figure 10 - Cumulative copper losses in runoff from Douglas-fir lumber treated with ACZA to a target retention of 4.0 kg/m³ and subjected to one of the BMP procedures. Each figure represents data from a given board.

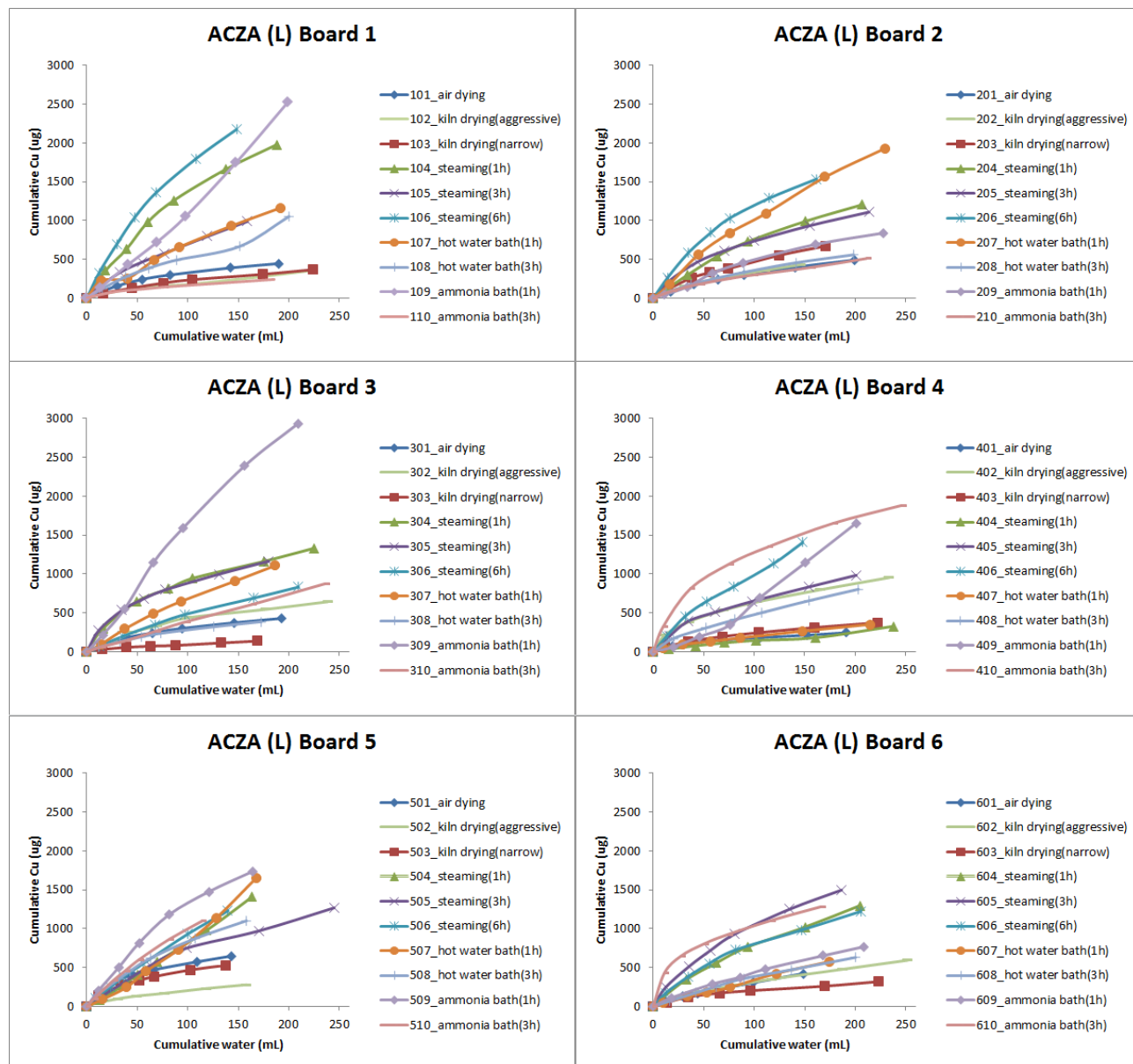
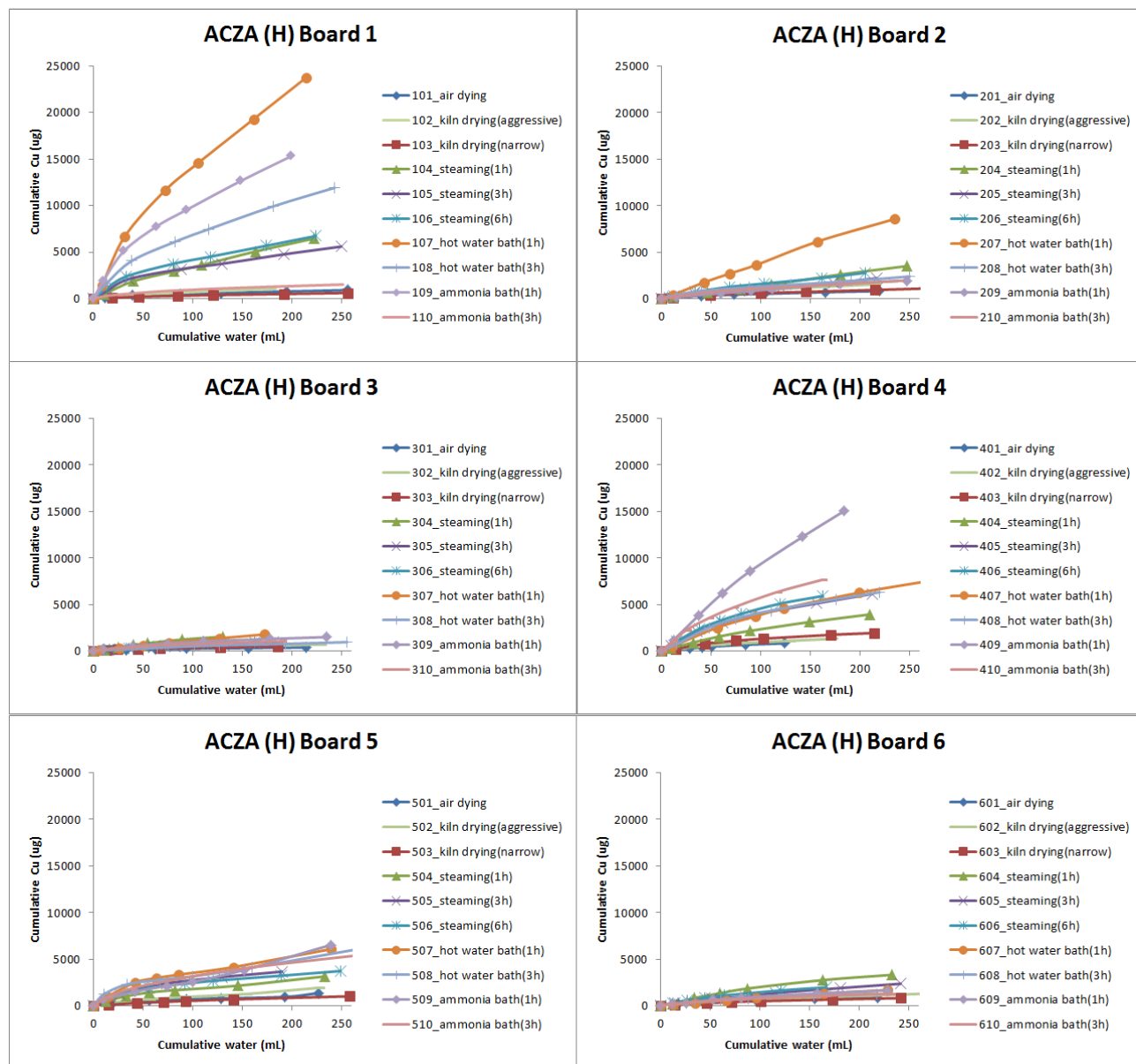


Figure 11 - Cumulative copper losses in runoff from Douglas-fir lumber treated with ACZA to a target retention of 6.4 kg/m^3 and subjected to one of the BMP procedures. Each figure represents data from a given board.



Multiple comparison tests of copper concentrations in the runoff after 80 ml or 260 ml of cumulative rainfall exposure were performed using a Least Significant Difference (LSD) test (Table 1, 2). Pairwise comparisons showed that 6 hours of steaming was associated with the highest copper levels with a mean copper concentration of 11.8 ug/ml in 80 ml of cumulative rainfall and 10.7 ug/ml in 260 ml of cumulative rainfall, while slow kiln drying was associated with the lowest copper levels with a mean copper concentration of 3.2 ug/ml in 80 ml of cumulative rainfall and 2.9 ug/ml in 260 ml of cumulative rainfall for the low ACZA retention (4.0 kg/m^3) group (Table 1). Copper concentrations in runoff from boards steamed for 1 hour were significantly lower than those from boards subjected to 6 hours steaming for both durations of water collection. This result suggests that longer exposure to steam may have moved more copper to the wood surface where it was more available for migration. Kiln drying tended to stabilize more copper than steaming or ammonia bathes. Changing the kiln drying cycle from slow drying to rapid drying had no significant effect on copper concentrations in the runoff for both durations of collection. Increasing hot water or ammonia bath time from 1 to 3 hours had no significant effect on copper levels in runoff.

Table 1 - Average copper concentrations in runoff from Douglas-fir lumber treated with ACZA to a target retention of 4.0 kg/m ³ and exposed to simulated rainfall until 80 ml or 260 ml of cumulative rainfall was collected.		
BMP Treatment	Average Copper Concentration in Runoff (ug/ml)	
	80 ml (45-60 min of collection) of Cumulative Rainfall	260 ml (about 2 hours of collection) of Cumulative Rainfall
Air-drying	4.9 cde	3.7 ef
Kiln drying (rapid)	3.9 de	3.6 ef
Kiln drying (slow)	3.2 e	2.9 f
1 hr Steaming	6.2 bcd	6.9 bcd
3 hr Steaming	10.4 ab	8.9 ab
6 hr Steaming	11.8 a	10.7 a
1 hr Hot water bath	6.1 bcde	5.7 cd
3 hr Hot water bath	5.9 bcde	5.0 de
1 hr Ammonia bath	8.1 abc	8.0 abc
3 hr Ammonia bath	8.0 abc	6.4 bcd
A values followed by the same letter(s) do not differ significantly from one another by a Least Significant Difference test at $\alpha=0.05$ with a Holm adjustment.		

Both air-drying and kiln drying were associated with significantly lower copper levels in the runoff from boards treated with the ACZA high retention (6.4 kg/m³) at both collection times (Table 2). Copper concentrations in runoff were less than 11 ug/ml in both air and kiln drying groups after 80 ml of rainfall exposure. There were no significant differences in copper concentrations between steaming, hot water or ammonia bathes in

the runoff after 80 ml of rainfall exposure. Mean copper concentrations in runoff from boards subjected to the other BMPs ranged from 22~35 ug/ml over the first 80 ml of rainfall exposure. Mean copper concentrations after 260 ml of rainfall exposure were highest in the 1 hour hot water bath group (30.9 ug/ml). Copper concentrations in runoff from boards subjected to a 3 hour hot water bath (20.9 ug/ml) were significantly lower than those subjected to a 1 hour hot water bath (30.9 ug/ml). Similarly, copper concentrations in runoff from boards subjected to a 3 hour ammonia bath (26.6 ug/ml) were significantly lower than those subjected to a 1 hour ammonia bath (16.6 ug/ml). Increasing the hot water or ammonia bath time from 1 to 3 hours tended to decrease copper losses, suggesting that prolonged hot water or ammonia exposure led to the formation of more insoluble complexes with copper or that mobile copper was removed by the bath. However, increasing steaming from 1 to 6 hours did not significantly influence copper concentrations in runoff.

Table 2 - Average copper concentrations in runoff from Douglas-fir lumber treated with ACZA to a target retention of 6.4 kg/m ³ and exposed to simulated rainfall until 80 ml or 260 ml of cumulative rainfall was collected.		
BMP Treatment	Average Copper Concentration in Runoff (ug/ml)	
	80 ml (45-60 min of collection) of Cumulative Rainfall	260 ml (about 2 hours of collection) of Cumulative Rainfall
Air-drying	8.4 b	6.0 d
Kiln drying (rapid)	10.7 b	8.3 d
Kiln drying (slow)	7.7 b	5.9 d
1 hr Steaming	22.2 a	20.5 bc
3 hr Steaming	25.1 a	19.2 bc
6 hr Steaming	25.6 a	22.8 abc
1 hr Hot water bath	32.6 a	30.9 a
3 hr Hot water bath	30.8 a	20.9 bc
1 hr Ammonia bath	34.7 a	26.6 ab
3 hr Ammonia bath	24.0 a	16.6 c
A values followed by the same letter(s) do not differ significantly from one another by a Least Significant Difference test at $\alpha=0.05$ with a Holm adjustment.		

Copper concentrations in runoff from the high ACZA retention (6.4 kg/m³) group were generally higher than those in runoff from samples treated to the low target retention (4.0 kg/m³) (Figure 12), suggesting the presence of large amounts of non-precipitated copper at higher retentions. This is consistent with previous findings that copper stabilization occurs faster at lower retentions and that higher losses of copper are associated with

higher retentions (Ung and Cooper, 2005; Pasek, 2003; Ruddick, 2003). Copper migration initially occurs at or near the wood surface with losses of unfixed copper. More mobile copper is then transported by diffusion from deeper in the wood to the surface as the wood wets and dries, providing a small but steady supply for continued copper migration (Gonzalez, 2007). A comparison of copper concentrations in runoff with actual board retention showed that copper levels increased exponentially with increased copper retention ($R^2=0.7365$) (Figure 12). These results illustrate the benefits of BMP practices that avoid overtreatment to help minimize metal losses.

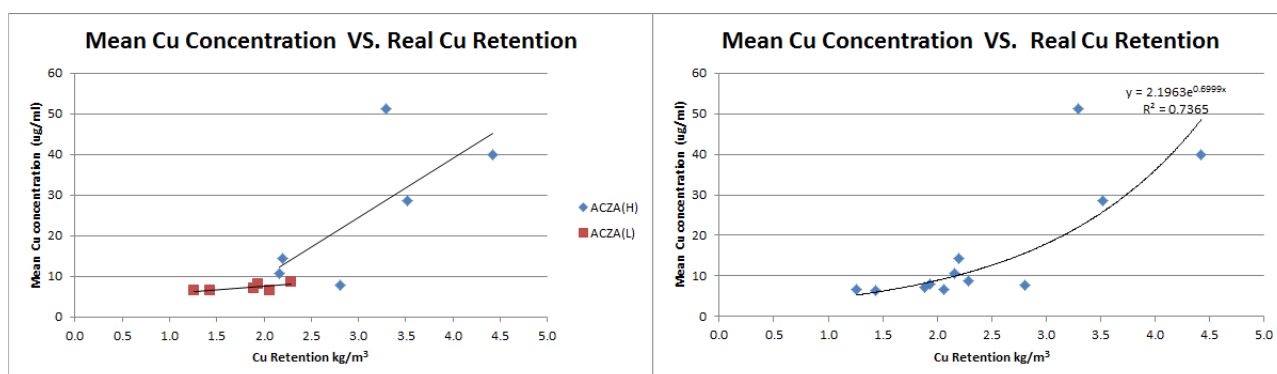


Figure 12 - Relationship between actual copper retention in a board and mean copper concentration in 260 ml of simulated rainfall runoff from Douglas-fir lumber treated with ACZA to target retentions of 4.0 kg/m³ or 6.4 kg/m³. Retentions only considered the copper levels in the system.

Immobilization of ACZA components in wood occurs primarily via evaporation of ammonia coupled with copper reactions with the wood. Ammonia evaporation is time and temperature dependent (Copper, 1991; Lebow, 1992) and the BMP treatments affect this process. Except for air drying, which is time dependent, all the other BMP treatments accelerate evaporation using some form of heating.

Both air drying and kiln drying had clear effects on copper fixation for both ACZA retentions. This is consistent with previous findings that copper immobilization was most rapid and complete with kiln drying (Kumar et al., 1996). Copper/wood interactions and losses in ammonia to the point where copper (and zinc) was immobilized can occur more completely using these approaches. The other BMP processes, especially steaming of low retention boards or a 1 hour hot water bath of high retention boards, resulted in more mobile copper. The reasons for the differences are unclear. Steaming or hot water bathes should help accelerate ammonia evaporation, but the high moisture environment appeared to slow metal immobilization. It is also possible that all of the reaction sites on the wood surface were occupied by copper or other metals and that steaming or hot water bathes moved the additional copper to the wood surface where it was more available for mobilization.

4.2 Effects of BMPs on fixation of copper in CA treated wood

BMP processes varied in their ability to limit metal losses from CA treated boards.

Copper concentrations tended to be highest in the first two or three water collections, and then declined with continued rainfall (Figure 13, 14, 15, 16). These results were similar to those found with ACZA. Copper concentrations tended to decrease with continued rainfall exposure and generally reached a steady state after boards were subjected to 120 ml of rainfall (Figure 13, 15). Copper concentrations in both CA retention groups were generally lowest in samples that were hot water or ammonia bath treated prior to rainfall exposure. Conversely, steaming or rapid kiln drying were associated with higher copper concentrations in runoff from both CA retention groups (Figure 17, 18, 19, 20). As expected, cumulative copper in the runoff increased with cumulative water and the BMP treatments varied in controlling the rate of copper release (Figure 21, 22).

Figure 13 - 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 BMP procedures. Each figure represents data from a given board.

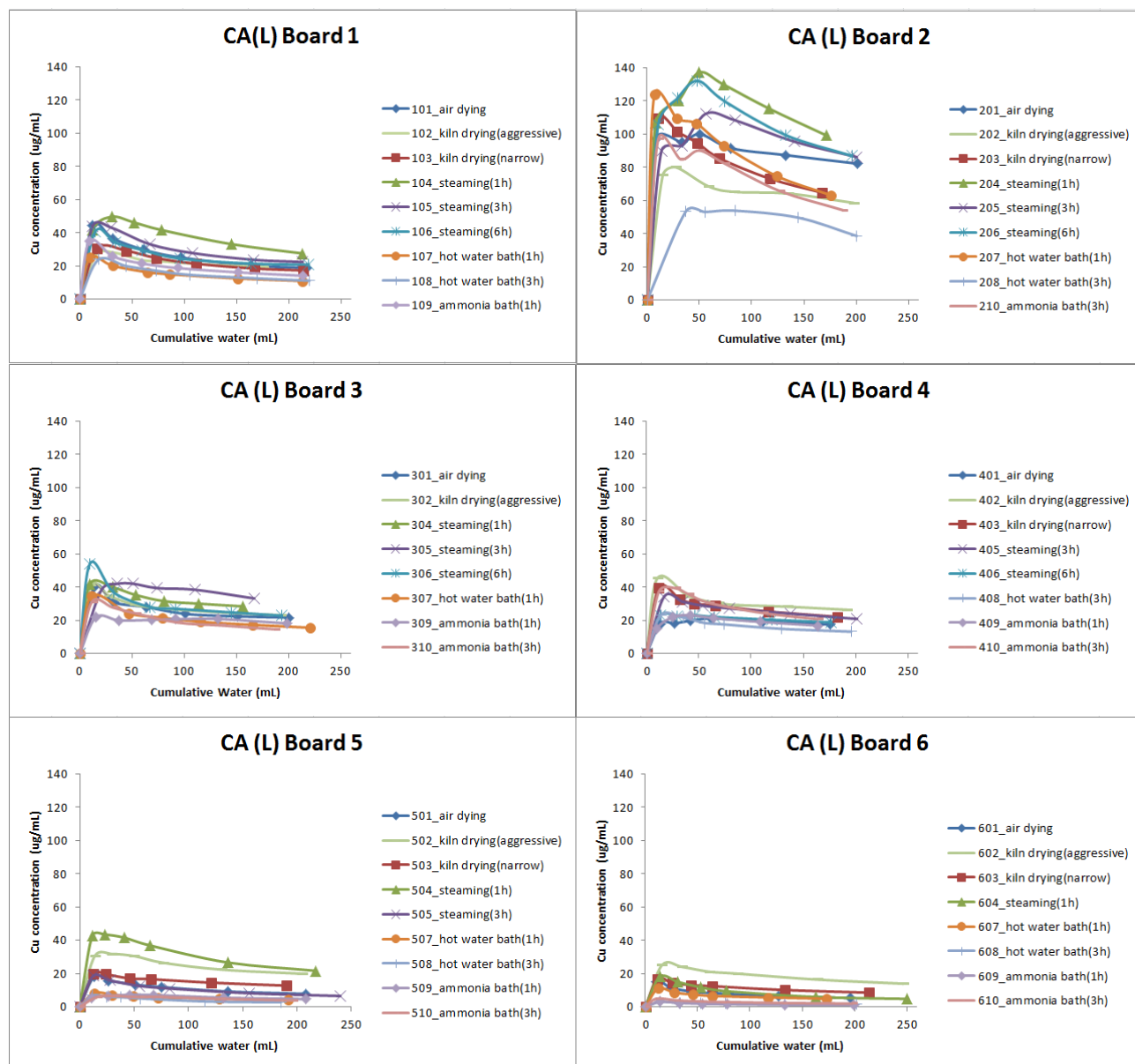


Figure 14 - Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with CA to a target retention of 0.96 kg/m^3 and subjected to one of the BMP procedures. Each figure represents data from all of the runs for a given BMP process.

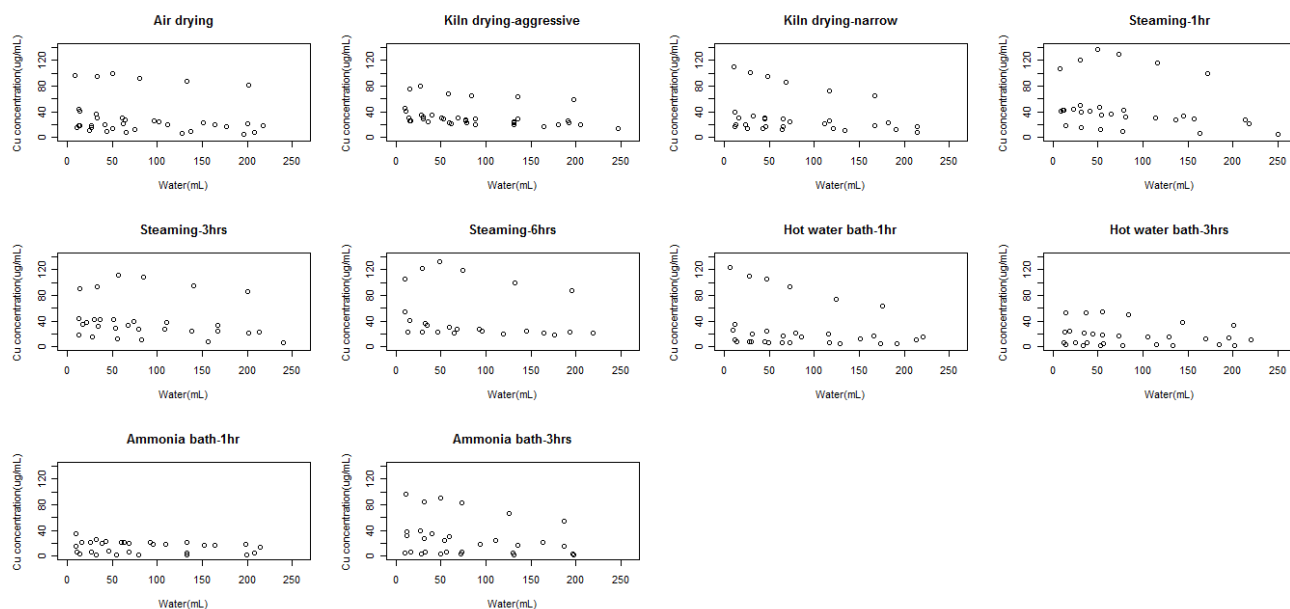


Figure 15 - Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with CA to a target retention of 2.4 kg/m³ and subjected to one of the BMP procedures. Each figure represents data from a given board.

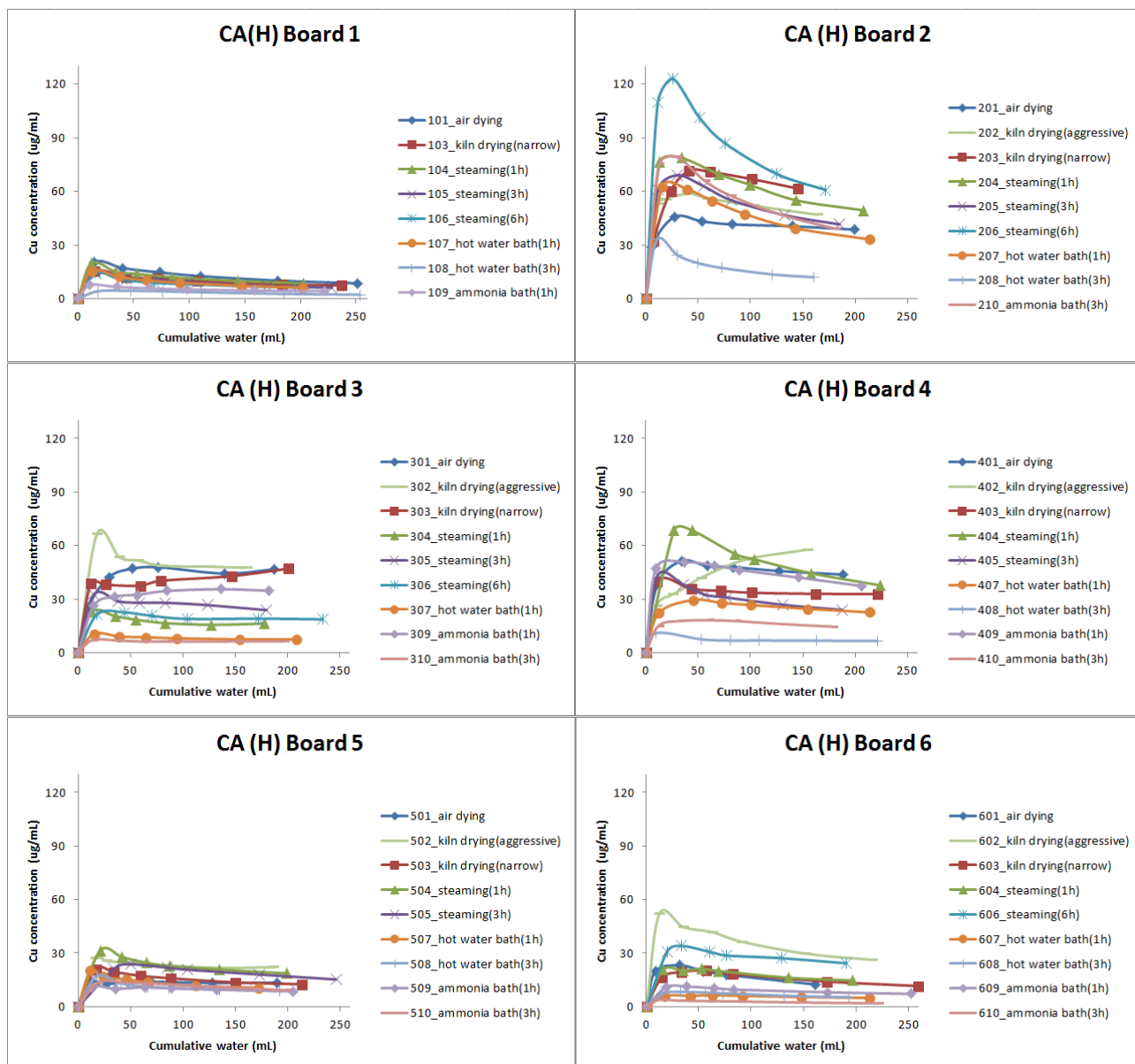


Figure 16 - Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with CA to a target retention of 2.4 kg/m^3 and subjected to one of the BMP procedures. Each figure represents data from all of the runs for a given BMP process.

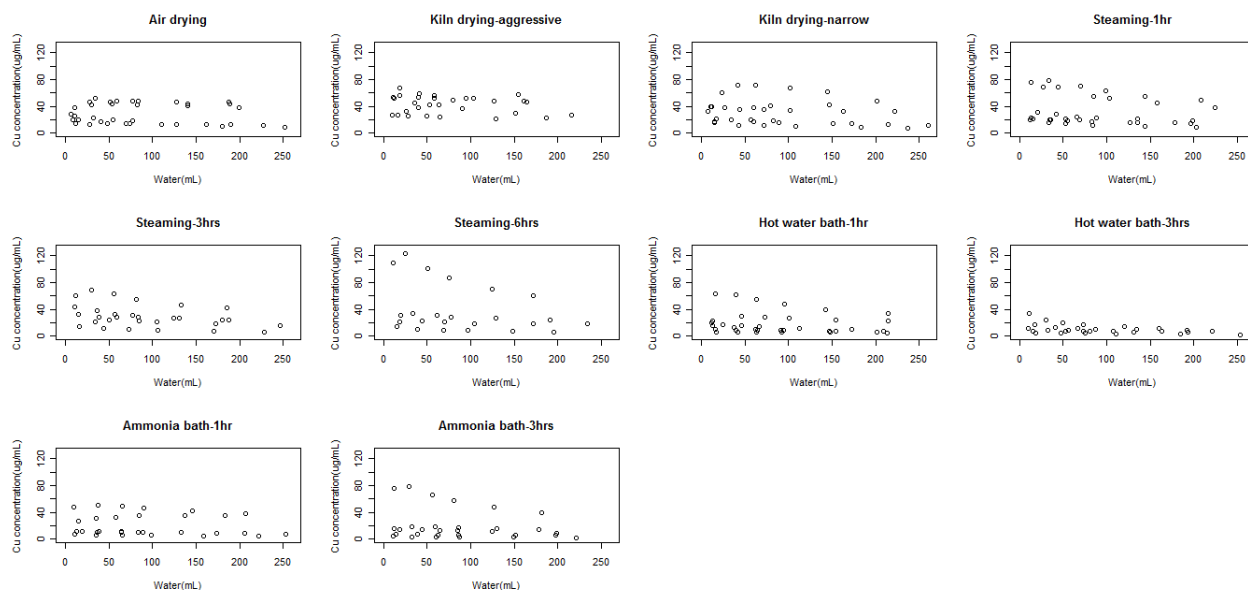


Figure 17 - Box and whisker plots showing copper concentrations in 80 ml of runoff from Douglas-fir lumber treated with CA to a target retention of 0.96 kg/m^3 and subjected to one of the BMP procedures.

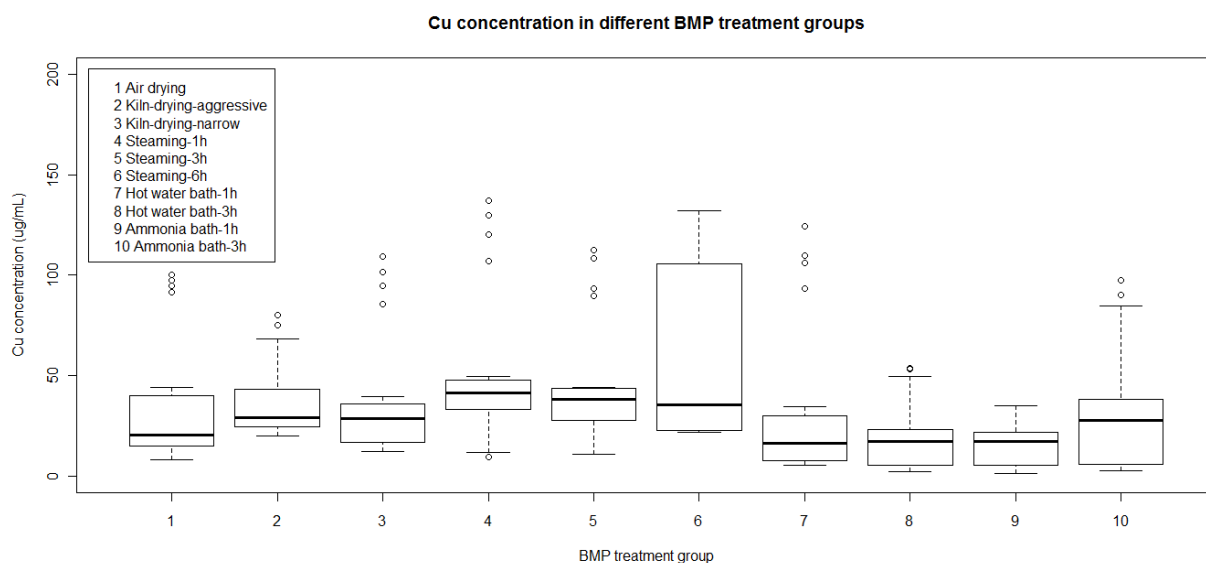


Figure 18 - Box and whisker plots showing copper concentrations in 260 ml of runoff from Douglas-fir lumber treated with CA to a target retention of 0.96 kg/m^3 and subjected to one of the BMP procedures.

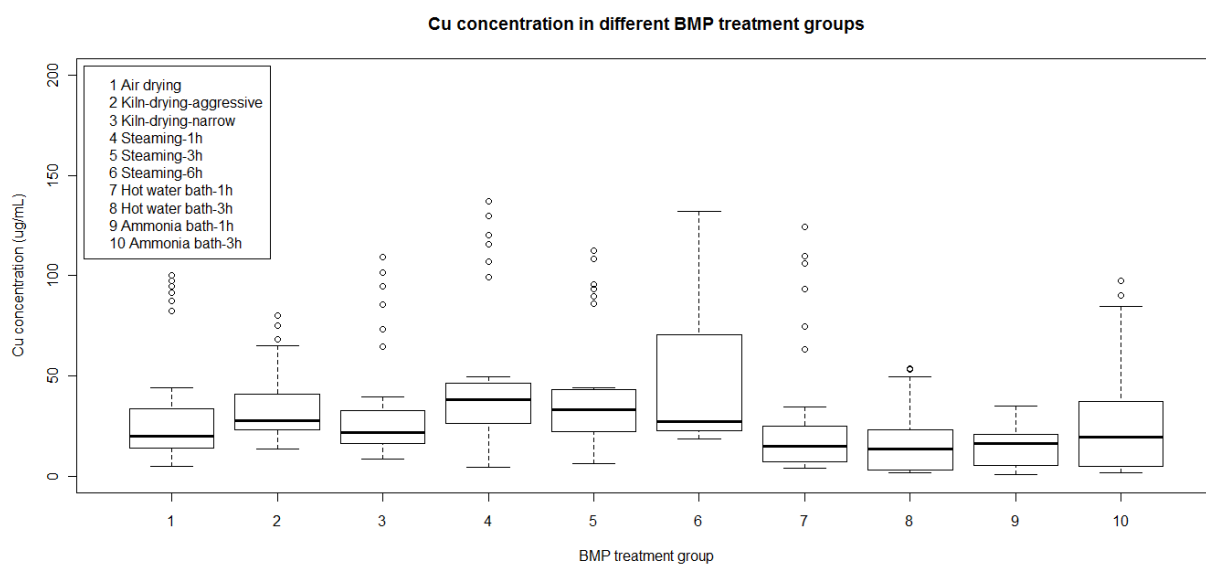


Figure 19 - Box and whisker plots showing copper concentrations in 80 ml of runoff from Douglas-fir lumber treated with CA to a target retention of 2.4 kg/m^3 and subjected to one of the BMP procedures.

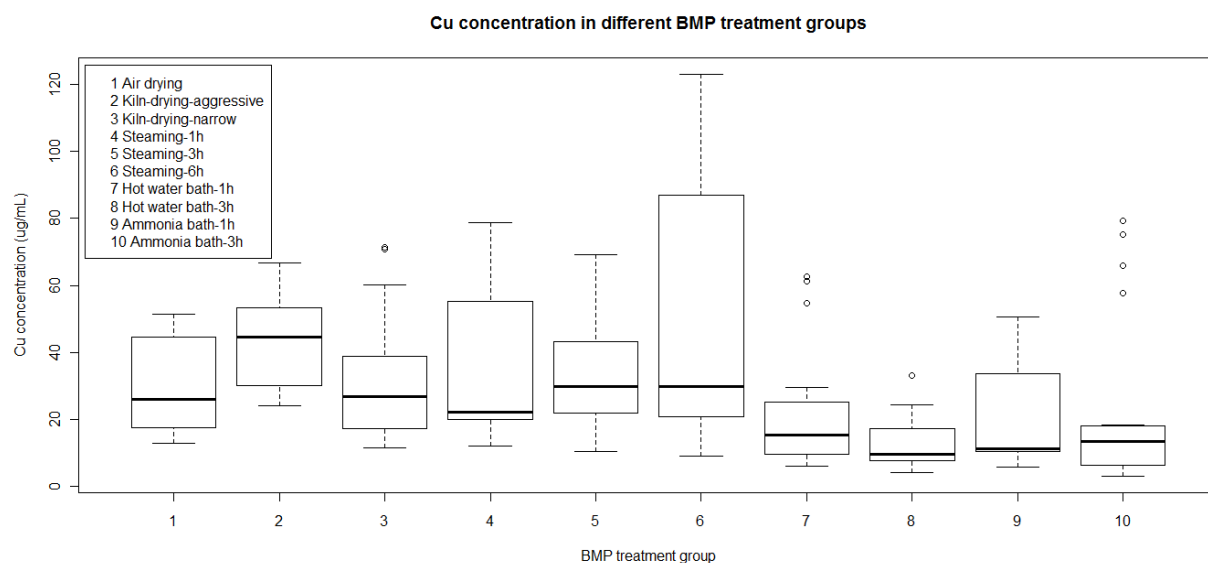


Figure 20 - Box and whisker plots showing copper concentrations in 260 ml of runoff from Douglas-fir lumber treated with CA to a target retention of 2.4 kg/m^3 and subjected to one of the BMP procedures.

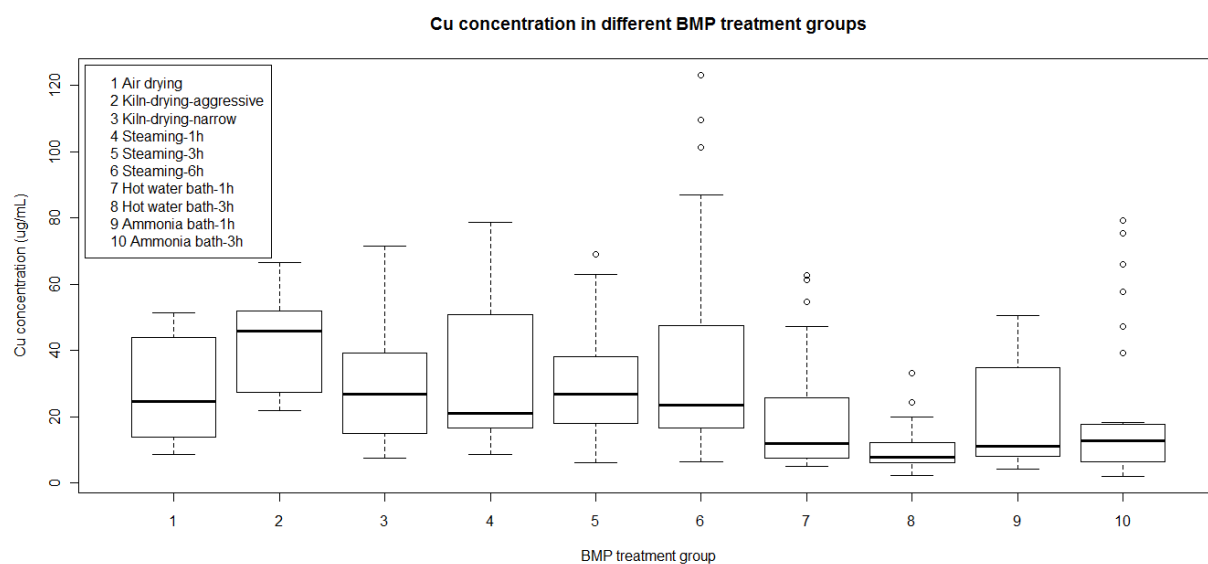


Figure 21 - Cumulative copper losses in runoff from Douglas-fir lumber treated with CA to a target retention of 0.96 kg/m^3 and subjected to one of the BMP procedures. Each figure represents data from a given board.

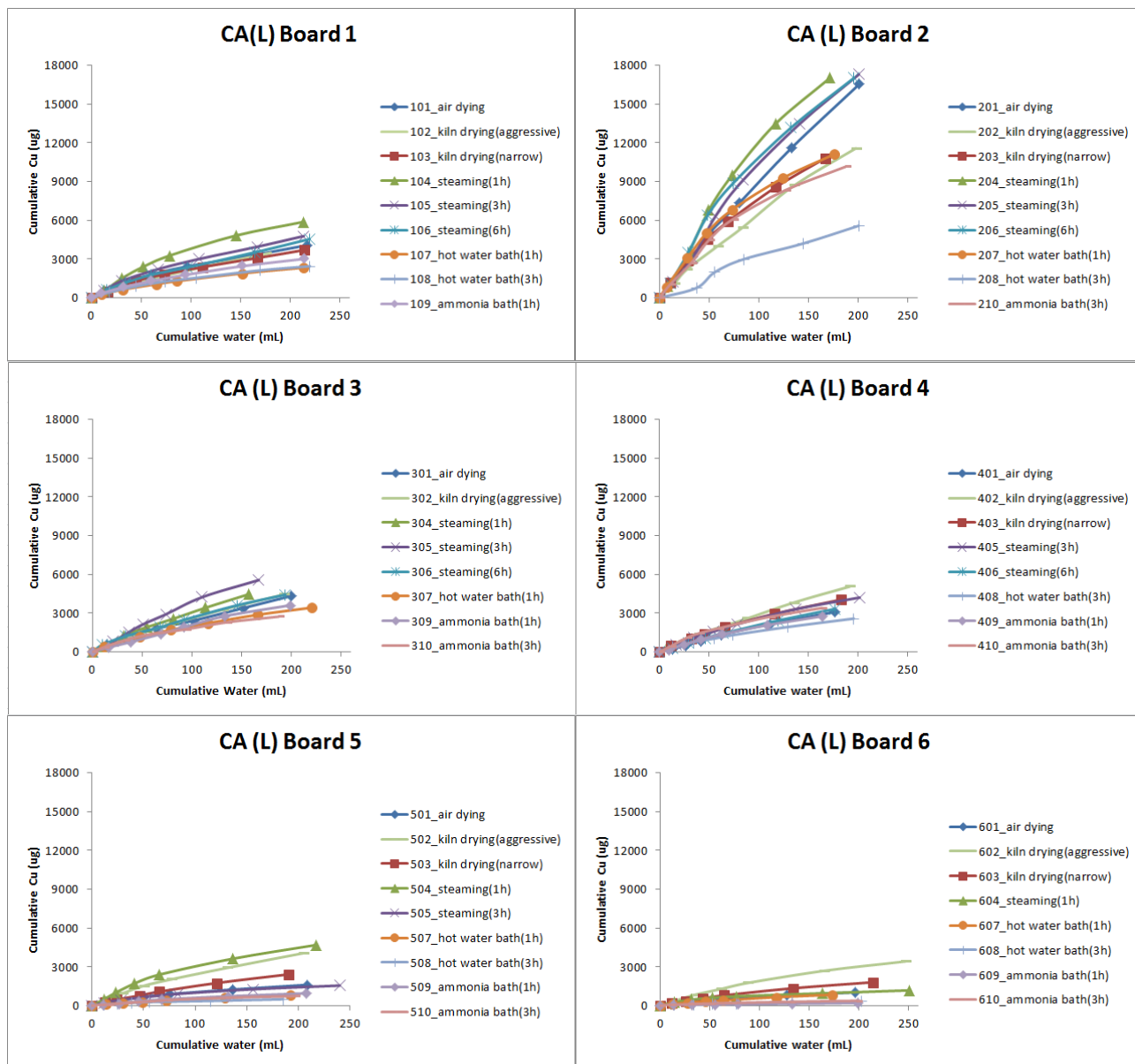
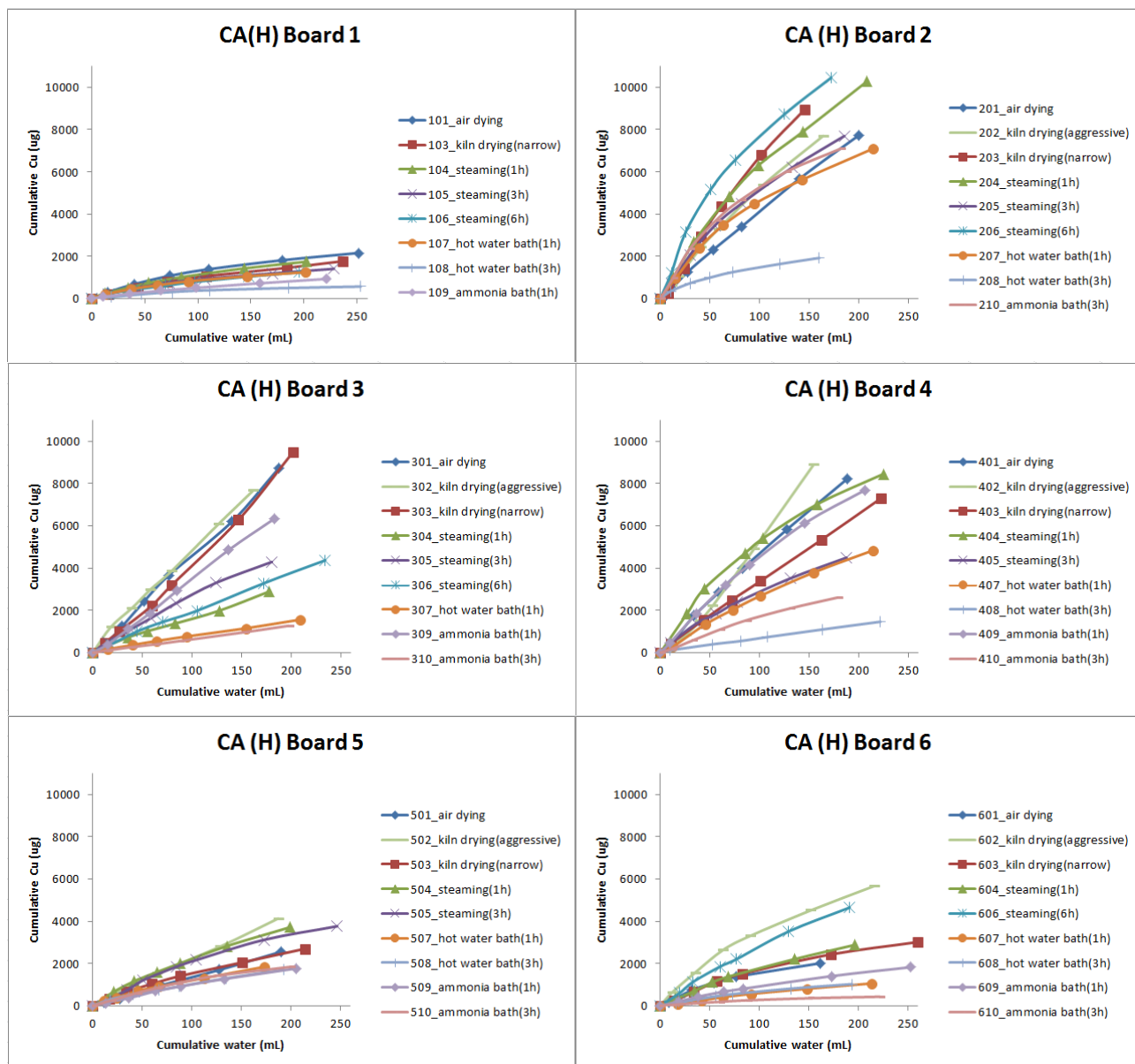


Figure 22 - Cumulative copper losses in runoff from Douglas-fir lumber treated with CA to a target retention of 2.4 kg/m^3 and subjected to one of the BMP procedures. Each figure represents data from a given board.



Multiple comparison tests to investigate the effects of BMPs on copper losses from boards treated with CA after 80 ml or 260 ml of rainfall exposure were performed using a Least Significant Difference (LSD) test (Table 3). Pairwise comparisons for the low CA retention showed that 6 hours of steaming was associated with the highest copper losses with a mean copper concentration of 44.5 ug/ml after 80 ml of rainfall exposure and 37.6 ug/ml after 260 ml of rainfall exposure. However, reducing steaming time from 6 hours to 1 hour had no significant influence on copper concentrations in runoff. It appeared that instead of accelerating copper precipitation, steaming moved copper to the wood surface where it was more available for leaching. Copper levels in the runoff from a 3 hour hot water bath or a 1 hour ammonia bath were associated with significantly lower copper levels in both collection periods for the low CA retention (0.96 kg/m^3) group (Table 3). Increased hot water bath time from 1 to 3 hours significantly reduced the copper concentrations in runoff in both collection periods. This was consistent with the previous studies showing that copper stabilized much faster during hot water exposure and the process was highly dependent on temperature and duration (Yu et al., 2009). Conversely, increasing ammonia bath time from 1 to 3 hours was associated with significantly increased copper concentrations in runoff in both collection periods. It appeared that a high pH environment tended to help precipitate copper more quickly. However, prolonged ammonia bathes tended to have a negative effect on copper fixation, possibly because the ammonia enhanced copper movement to the wood surface where it was more available for leaching. Air drying or kiln drying produced the next lowest copper

immobilization, followed by steaming (Table 3). There were no significant differences in copper concentrations between the two kiln drying cycles over both collection periods.

Table 3 - Average copper concentrations in runoff from Douglas-fir lumber treated with CA to a target retention of 0.96 kg/m ³ and exposed to simulated rainfall until 80 ml or 260 ml of cumulative rainfall was collected.		
BMP Treatment	Average Copper Concentration in Runoff (ug/ml)	
	80 ml (45-60 min of collection) of Cumulative Rainfall	260 ml (about 2 hours of collection) of Cumulative Rainfall
Air-drying	24.3 cd	22.7 c
Kiln drying (rapid)	33.2 abc	31.1 ab
Kiln drying (slow)	29.7 bc	26.0 bc
1 hr Steaming	41.0 ab	34.9 a
3 hr Steaming	37.1 ab	32.5 ab
6 hr Steaming	44.5 a	37.6 a
1 hr Hot water bath	19.6 d	16.7 d
3 hr Hot water bath	11.2 e	10.5 e
1 hr Ammonia bath	10.0 e	9.6 e
3 hr Ammonia bath	17.6 d	15.2 d
A values followed by the same letter(s) do not differ significantly from one another by a Least Significant Difference test at $\alpha=0.05$ with a Holm adjustment.		

The 3 hour hot water treatment was associated with the lowest copper losses in the high CA retention (2.4 kg/m^3) group with a mean copper concentration of 10.3 ug/ml after 80 ml of rainfall exposure and 8.3 ug/ml after 260 ml of rainfall exposure. Boards subjected to a 3 hour ammonia bath, a 1 hour hot water bath or a 1 hour ammonia bath also had lower copper levels than the other BMP treatments at both collection times (Table 4). Copper losses from boards subjected to rapid kiln drying were significantly higher than those from boards air-seasoned prior to rainfall exposure after 80 ml or 260 ml of rainfall exposure. Reduced the rate of kiln drying was associated with significantly reduced copper concentrations after 260 ml of rainfall exposure. Increasing steaming time from 1 to 3 or 6 hours had no significant effect on copper concentrations at either collection period. Increasing the hot water bath from 1 to 3 hours was associated with significant lower copper concentrations after 260 ml of rainfall exposure, suggesting that added hot water exposure led to more complete copper complexes. This effect was similar to that found with the CA low retention (0.96 kg/m^3) group. However, increasing ammonia bath time from 1 to 3 hours had no significant effect on copper concentrations in runoff at either collection period.

Table 4 - Average copper concentrations in runoff from Douglas-fir lumber treated with CA to a target retention of 2.4 kg/m ³ and exposed to simulated rainfall until 80 ml or 260 ml of cumulative rainfall was collected.		
BMP Treatment	Average Copper Concentration in Runoff (ug/ml)	
	80 ml (45-60 min of collection) of Cumulative Rainfall	260 ml (about 2 hours of collection) of Cumulative Rainfall
Air-drying	25.6 bc	24.7 b
Kiln drying (rapid)	41.2 a	39.9 a
Kiln drying (slow)	28.3 ab	24.8 b
1 hr Steaming	29.4 ab	26.6 b
3 hr Steaming	29.2 ab	24.6 b
6 hr Steaming	32.5 ab	26.1 b
1 hr Hot water bath	16.3 cd	14.3 c
3 hr Hot water bath	10.3 d	8.3 d
1 hr Ammonia bath	16.2 cd	15.0 c
3 hr Ammonia bath	13.1 d	11.7 c
A values followed by the same letter(s) do not differ significantly from one another by a Least Significant Difference test at $\alpha=0.05$ with a Holm adjustment.		

A comparison between copper concentrations in the runoff and actual board retentions showed no clear relationship with retention ($R^2 = 0.2057$) (Figure 23). Copper in the runoff from one board (Board 2) in the CA low retention (0.96 kg/m³) group was abnormally higher (91.1 ug/ml) than those from the other boards. The retentions every 2 mm from the surface were tested on three boards including the board associated with higher copper level to determine if elevated surface retentions could explain this variation

(Table 5). However, there were no significant differences in retention in the outer 2 mm of the boards examined. The density of the board associated with higher copper losses was lower (412 kg/m^3) than the other 5 boards treated with CA to the low target retention (Table 6) and this may have reduced copper bonding sites, leading to more copper available for migration. The highest copper losses (55.3 ug/ml) in the CA high retention group (2.4 kg/m^3) occurred in a board with the lowest density (432 kg/m^3) which was consistent with the previous statement (Figure 18; Table 6).

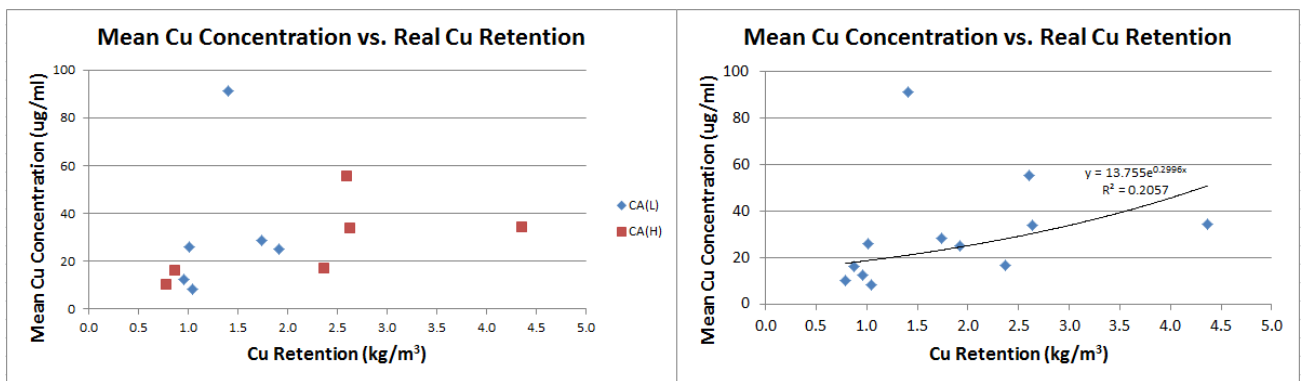


Figure 23 - Relationship between actual copper retention in a board and mean copper concentration in 260 ml of simulated rainfall runoff from Douglas-fir lumber treated with CA to target retentions of 0.96 kg/m^3 or 2.4 kg/m^3 . Retentions only considered the copper levels in the system.

Table 5 - Copper retentions at 2 mm increments from the surface of boards treated with CA to a target retention of 0.96 kg/m³.

Depth(mm)	Board #	Copper (%)	Density(kg/m ³)	Cu retention (kg/m ³)
2	2	1.558	412	6.42
2	4	1.154	451	5.20
2	5	1.330	596	7.921
4	2	0.833	412	3.432
4	4	0.533	451	2.402
4	5	0.521	596	3.101
6	2	0.355	412	1.465
6	4	0.293	451	1.322
6	5	0.198	596	1.179

Table 6 - Densities of boards treated with ACZA, CA or ACQ to target retentions (at approximate 19% moisture content).

Board #	Density (kg/m ³)				
	ACZA(4.0 kg/m ³)	ACZA(6.4kg/m ³)	CA (0.96 kg/m ³)	CA (2.4 kg/m ³)	ACQ(6.4 kg/m ³)
1	526	558	544	498	555
2	459	532	412	432	494
3	531	655	527	442	496
4	558	589	451	602	410
5	474	673	596	447	
6	473	586	499	516	

Copper stabilization is generally slower in wood treated with copper-amine systems than in acidic systems. The relatively high proportion of copper in CA and the limited reaction sites in wood generally results in higher copper leaching (Dickey, 2003). Copper stabilization occurs primarily via copper reactions with acid groups in wood by neutralization of the amine, followed the precipitation of the remaining copper (Jiang, 2000). The reaction is highly time and temperature dependent (Yu et al., 2009). Copper fixation on boards that were air seasoned, steamed or kiln dried prior to simulated rainfall exposure appeared to be less complete than on those that were soaked in hot water or ammonia. The high pH of the ammonia bath appeared to promote reactions with copper, possibly by enhancing the exchangeability of phenolic protons in wood (Jiang, 2000). However, soaking wood in hot water or ammonia water might have also increased copper losses from the wood surface into the water, resulting in low copper levels.

4.3 Effects of BMPs on fixation of copper in ACQ (6.4 kg/m^3) treated wood

BMP processes varied in their ability to limit metal losses from wood treated with ACQ to a target retention of 6.4 kg/m^3 (Figure 24, 25). Copper concentrations tended to be highest in the first two or three water collections. Copper concentrations tended to decrease with continued rainfall and generally became steady after boards were subjected to 220 ml of rainfall (Figure 24). These results were similar to those found with ACZA or CA. Copper concentrations tended to be higher in samples that were steamed for 6 hours prior to simulated rainfall exposure and the variation of the copper concentrations was large for samples that were steamed for 3 hours (Figure 25, 26). The amount of copper in runoff tended to increase steadily with cumulative water regardless of the BMP treatment employed, but there were differences between treatments (Figure 27).

Figure 24 - 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 BMP procedures. Each figure represents data from a given board.

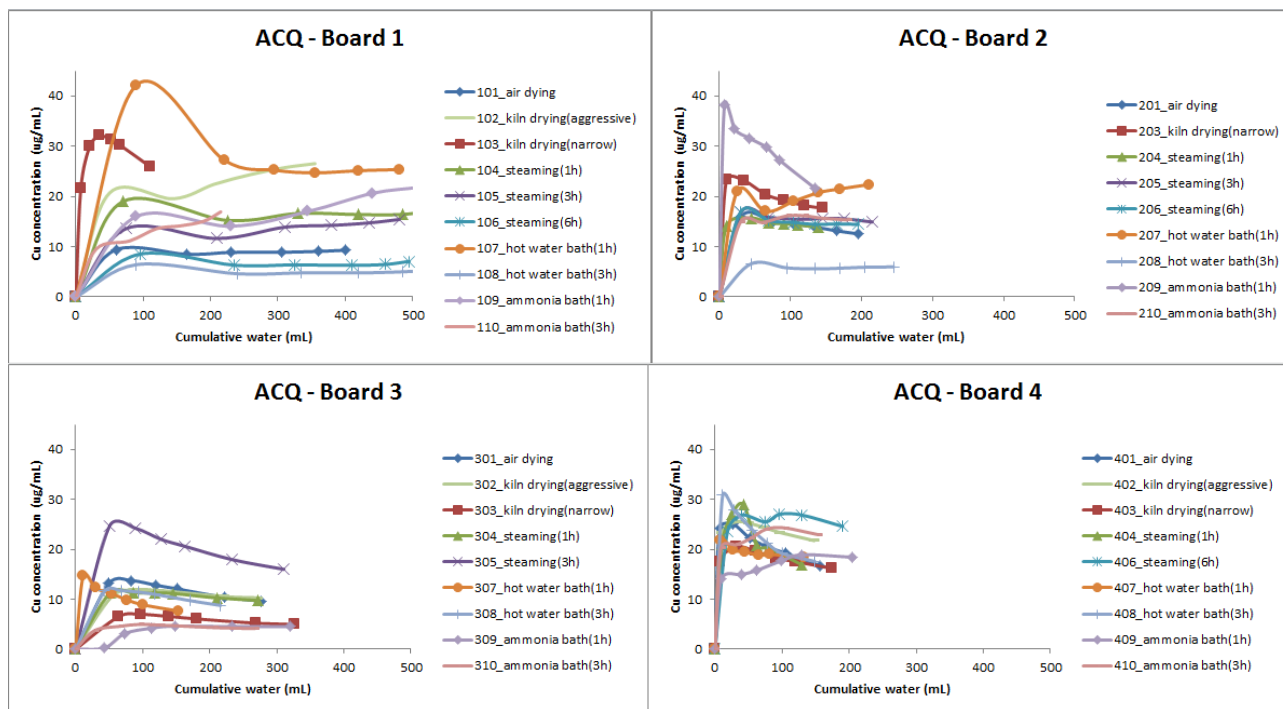


Figure 25 - Copper concentrations in simulated rainfall runoff from Douglas-fir lumber treated with ACQ to a target retention of 6.4 kg/m^3 and subjected to one of the BMP procedures. Each figure represents data from all of the runs for a given BMP process.

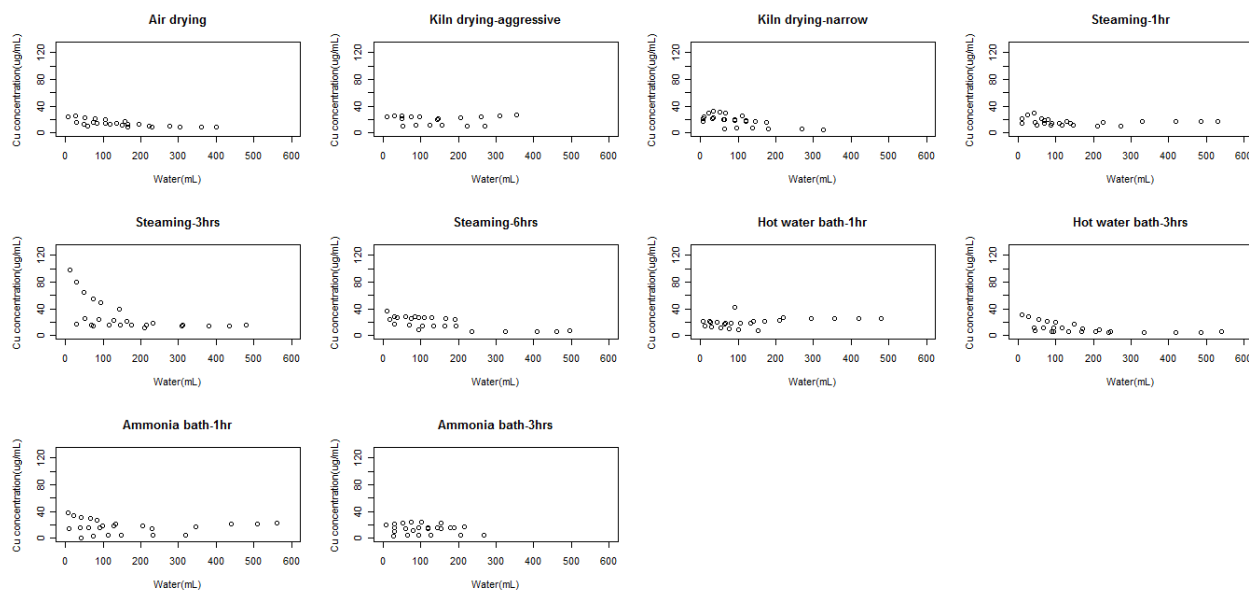


Figure 26 - Box and whisker plots showing copper concentrations in 80 ml of runoff from Douglas-fir lumber treated with ACQ to a target retention of 6.4 kg/m^3 and subjected to one of the BMP procedures.

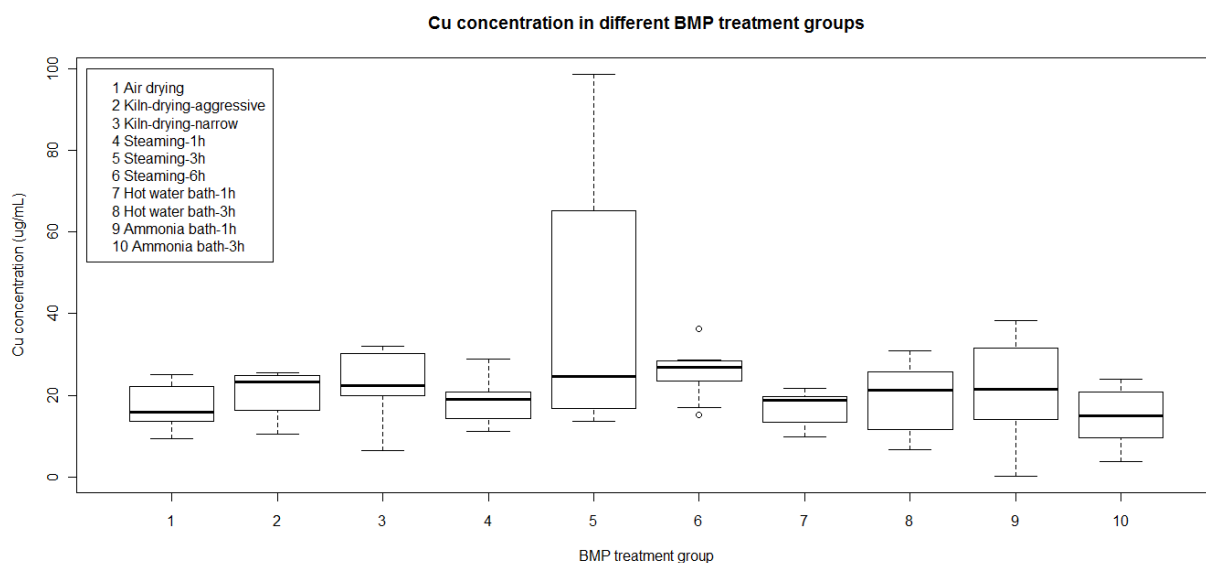


Figure 27 - Box and whisker plots showing copper concentrations in 260 ml of runoff from Douglas-fir lumber treated with ACQ to a target retention of 6.4 kg/m^3 and subjected to one of the BMP procedures.

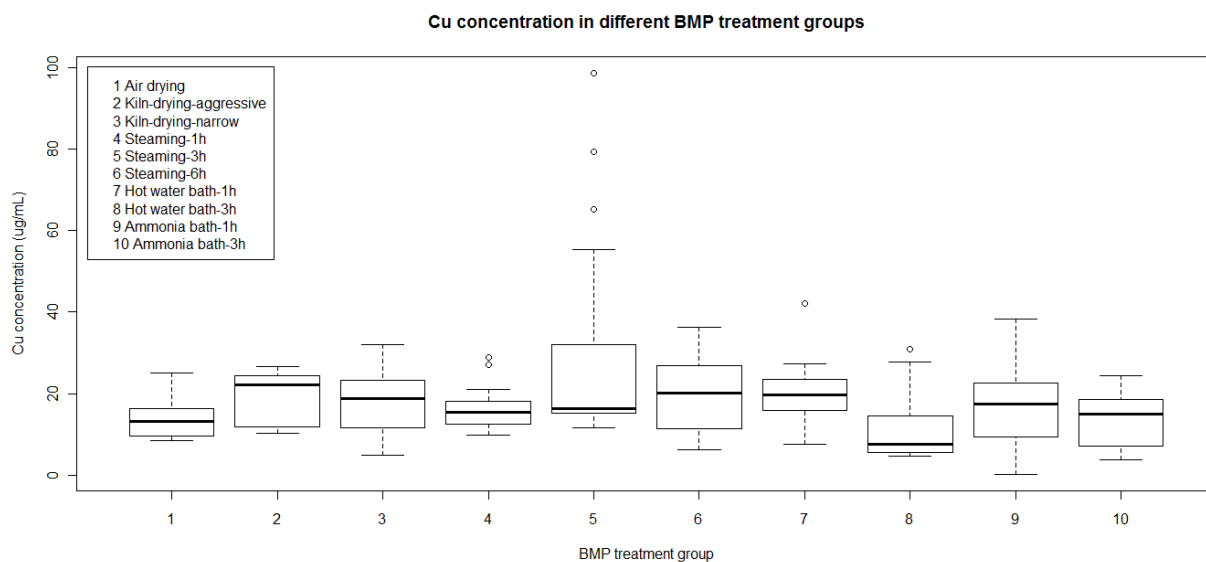
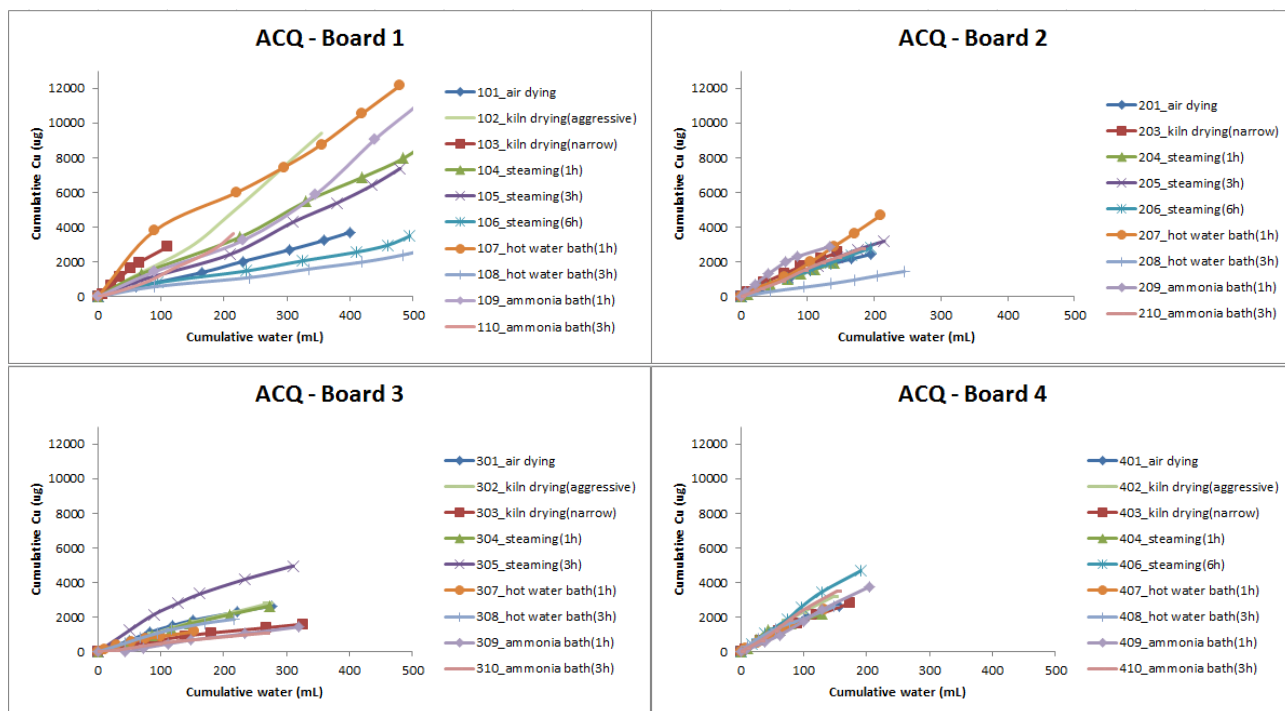


Figure 28 - Cumulative copper losses in runoff from Douglas-fir lumber treated with ACQ to a target retention of 6.4 kg/m³ and subjected to one of the BMP procedures. Each figure represents data from a given board.



Multiple comparison tests investigated the effects of BMPs on copper losses from boards treated with ACQ to a target retention of 6.4 kg/m^3 after 80 ml or 260 ml of rainfall exposure were performed using a Least Significant Difference (LSD) test (Table 7). Pairwise comparisons showed that steaming for 3 hours was associated with the highest copper losses with a mean copper concentration of 35.5 ug/ml in runoff after 80 ml of rainfall exposure and 22.9 ug/ml after 260 ml of rainfall exposure. Copper levels in runoff from boards subjected to 1 or 3 hours ammonia bathes (11.1 ug/ml and 12.6 ug/ml) were significantly lower than those from boards steamed for 3 hours prior to rainfall exposure, suggesting that the ammonia bath may have immobilized more copper in the wood than 3 hour steaming. Increasing ammonia bath time from 1 to 3 hours had no significant effect on copper concentrations. There were no significant differences in copper concentrations after 80 ml of rainfall exposure among boards that were air seasoned, kiln dried, bathed in hot water or steamed regardless of the duration of treatment.

Table 7- Average copper concentrations in runoff from Douglas-fir lumber treated with ACQ to a target retention of 6.4 kg/m ³ and exposed to simulated rainfall until 80 ml or 260 ml of cumulative rainfall was collected.		
BMP Treatment	Average Copper Concentration in Runoff (ug/ml)	
	80 ml (45-60 min of collection) of Cumulative Rainfall	260 ml (about 2 hours of collection) of Cumulative Rainfall
Air-drying	17.4 ab	13.4 bcd
Kiln drying (rapid)	20.7 ab	18.3 abc
Kiln drying (slow)	21.5 ab	15.8 abc
1 hr Steaming	18.4 ab	17.7 abc
3 hr Steaming	35.5 a	22.9 a
6 hr Steaming	24.3 ab	16.6 abc
1 hr Hot water bath	16.0 ab	18.4 ab
3 hr Hot water bath	16.9 ab	9.3 d
1 hr Ammonia bath	11.1 b	9.1 d
3 hr Ammonia bath	12.6 b	11.9 cd
A values followed by the same letter(s) do not differ significantly from one another by a Least Significant Difference test at $\alpha=0.05$ with a Holm adjustment.		

After 260 ml of rainfall exposure, boards that were steamed for 3 hours were still associated with the highest copper losses, with a mean copper concentration of 22.9 ug/ml (Table 7). Runoff from boards subjected to a 3 hour hot water bath or a 1 hour ammonia bath were associated with significantly lower mean copper concentrations than most of the other treatments except a 3 hour ammonia bath, although increasing ammonia

bath time had no significant effect on copper levels. Increasing steaming time or changing kiln drying cycle had no significant effect on mean copper concentrations in the runoff. Increasing the hot water bath time from 1 to 3 hours was associated with significantly lower mean copper concentrations from 18.4 ug/ml to 9.3 ug/ml in the runoff after 260 ml of rainfall exposure. This was similar to the results from previous studies on ACQ showing that hot water post-treatment helped stabilize copper and prolonged hot water exposure accelerated this process (Yu et al., 2009).

ACQ contains 67% copper oxide while ACZA contains 50% copper oxide. As a result, copper losses should be higher from ACQ treated wood. Similarly, CA contains more copper than ACQ. ACQ and CA systems used for these trials contained both ammonia and ethanolamine and copper stabilization and migration patterns should be similar. As expected, hot water and ammonia bathes seemed to have similar effects on copper in these systems. Copper-amine fixation mostly relies on the reaction between amine-copper and acid groups in wood (Jiang, 2000). It is possible that the hot water or the high pH environment helped move the amine solubilized copper deeper into the wood where there were more sites for reaction. However, steaming had a negative effect on copper that was similar to that found in the CA low retention group.

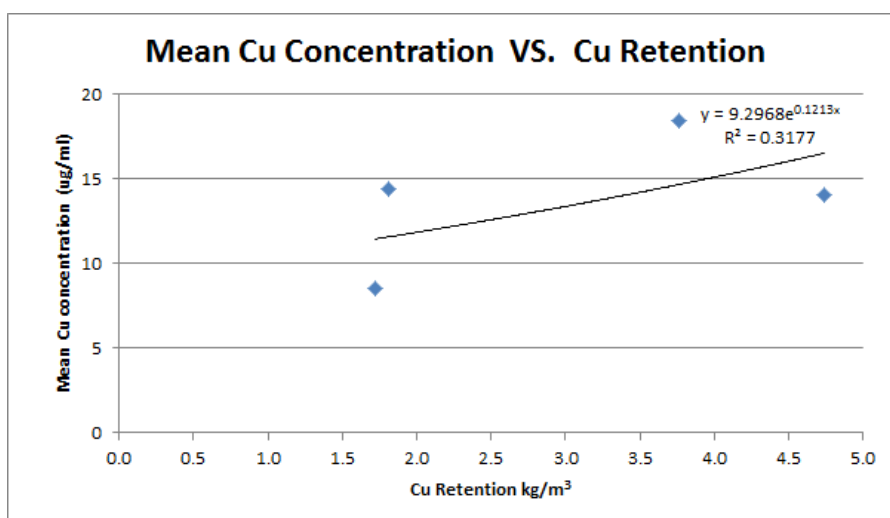


Figure 29 - Relationship between actual copper retention in a board and mean copper concentration in 260 ml of simulated rainfall runoff from Douglas-fir lumber treated with ACQ to target retentions of 6.4 kg/m³. Retentions only considered the copper levels in the system.

An examination of copper concentrations in the runoff with actual board retentions showed no clear relationships with retention ($R^2 = 0.3177$) (Figure 29), however, the sample size was small.

CHAPTER 5 – CONCLUSIONS

The method of BMP processing had varying effects on the rate of copper losses from boards treated with ACZA, CA or ACQ when subjected to overhead simulated rainfall. Copper concentrations in runoff tended to be highest during the initial rainfall exposure and then decreased to a steady state. Cumulative copper in the runoff increased over time.

Copper losses tended to be lower from boards treated with ACZA than those found with CA or ACQ. ACZA contains less copper oxide than CA or ACQ. ACZA also uses only ammonia to solubilize copper oxide which leads to the different fixation processes than those for CA or ACQ which use both amine and ammonia. Fixation reactions in ACZA are initiated by the rapid loss of ammonia present in the solution coupled with the reaction between solubilized copper and acid groups in wood. However, CA or ACQ, which are mostly solubilized by amine rather than ammonia, have a different fixation process which starts with the neutralization of amine by active anionic groups in wood along with a much slower amine evaporation. These differences appeared to result in varying effects of BMPs on ACZA, CA or ACQ.

A comparison between average actual copper retentions and target copper retentions of boards showed that the boards were unlikely treated to the retentions that were exactly same to the target retentions (Table 8). The average copper retentions of ACZA or CA low retention boards were higher than the target retentions, while those found in CA high retention or ACQ boards were lower than the target retentions.

Table 8 - A comparison between average actual copper retentions and target copper retentions of boards treated with ACZA, CA or ACQ.

Preservative	Copper Retention (kg/m ³)	
	Target	Actual
ACZA (4.0 kg/m ³)	1.6	2.5
ACZA (6.4 kg/m ³)	2.6	3.1
CA (0.96 kg/m ³)	0.92	1.3
CA (2.5 kg/m ³)	2.4	2.3
ACQ (6.4 kg/m ³)	3.4	3.0

Rainfall exposure of boards treated with ACZA to target retentions showed that air seasoning and kiln drying reduced the rate of copper migration for both retentions. The results suggest that both ammonia evaporation and copper/wood interactions were more complete using these approaches. However, 6 hours of steaming of the ACZA low retention boards or a 1 hour hot water bath of the ACZA high retention boards resulted in more mobile copper. Steaming or hot water may have slowed metal immobilization or moved copper to the wood surface where it was more available for leaching. Increasing hot water bath time from 1 to 3 hours or decreasing ammonia bath time from 3 hours to 1 hour were associated with significantly lower copper losses from boards treated with ACZA to the high retention. Increased copper retention was associated with exponentially increased copper losses ($R^2 = 0.7365$). This result suggests that larger

amounts of mobile copper are present at the higher retention, and illustrates the benefits of BMPs that avoid overtreatment to help minimize metal losses.

BMPs exhibited different effects on copper losses from wood treated with CA or ACQ to target retentions. The lowest copper losses were generally from boards subjected to hot water or ammonia bathes prior to rainfall exposure for CA or ACQ. Increasing the hot water bath time from 1 to 3 hours was associated with lower copper losses from CA or ACQ treated boards subjected to a hot water bath. This result was similar with that found in ACZA, suggesting that prolonged hot water exposure helped promote reactions between copper and wood. Increasing the ammonia bath time from 1 to 3 hours was associated with higher copper losses in boards at the low CA retention. The results indicate that the pH of the ammonia bath accelerated copper reactions with wood; however, prolonged ammonia bath exposure resulted in more mobile copper on the wood surface. Boards treated with CA and subjected to 6 hours of steaming or rapid kiln drying were associated with higher copper losses, suggesting less complete copper immobilization. Lower density boards appeared to experience higher copper losses from boards treated with CA. A comparison between copper concentrations in the runoff and actual board retentions of CA or ACQ showed no clear relationships with retention.

The effects of each BMP on copper losses compared to air drying were assessed (Table 8). Air seasoning is the simplest method for producing cleaner wood. Air seasoning is low-cost and uses less energy than other BMPs. However, it takes the longest time (about a month) for processing and usually requires large areas of space.

Table 9 - Effects of each BMP on copper losses as compared to air drying for boards treated with ACZA, CA or ACQ and subjected to 260 ml of rainfall.

Preservative	Target Retention	Kiln drying		Steaming			Hot water bath		Ammonia bath	
		Rapid	Slow	1 hr	3 hrs	6 hrs	1 hr	3 hrs	1 hr	3 hrs
ACZA	4 kg/m ³	Similar	Similar	Higher*	Higher	Higher	Higher	Similar	Higher	Higher
	6.4 kg/m ³	Similar	Similar	Higher	Higher	Higher	Higher	Higher	Higher	Higher
CA	0.96 kg/m ³	Higher	Similar	Higher	Higher	Higher	Lower	Lower	Lower	Lower
	2.4 kg/m ³	Higher	Similar	Similar	Similar	Similar	Lower	Lower	Lower	Lower
ACQ	6.4 kg/m ³	Similar	Similar	Higher	Similar	Similar	Similar	Similar	Similar	Similar
* Indicate that differences between air seasoning and this BMP were significantly different ($\alpha = 0.05$).										

Copper losses from kiln drying were similar to those from air drying on ACZA treated boards (Table 8). Steaming, hot water or ammonia bathes, except the 1 hour hot water bath on ACZA low retention boards, were associated with higher copper losses. These results indicate that air drying or kiln drying would be the best BMPs for ACZA treated wood.

Rapid kiln drying was associated with higher copper losses effects than air drying on CA treated boards although slow drying had fixation effects that were similar to air drying. Conversely, hot water or ammonia bathes were associated with much lower copper losses than those from air drying on boards treated with CA. Steaming was associated with higher copper losses than air drying on boards treated to the CA low retention but had similar effects on boards treated to the high CA retention. These results indicate that hot water or ammonia bathes may be more appropriate BMPs for CA treated wood.

Although a 3 hour hot water bath or a 1 hour ammonia bath were associated with lower copper losses than air drying from ACQ treated boards, the losses were not significantly different. The BMPs for ACQ treated boards had similar effects on copper immobilization except for the 1 hour steaming which was associated with higher copper losses than air drying. However, the sample size was small.

Although this study provided some useful information about the performance of BMPs on reducing copper losses from ACZA, CA or ACQ treated wood, how each BMP affect copper immobilization remain unknown. Furthermore, it would be useful to expand this study to field trials to better assess the effect of BMPs on copper immobilization.

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