LEACHING OF COPPER FROM AMINE – COPPER TREATED SOFTWOOD DECKING

by

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Abstract

The leaching of copper from softwood lumber treated with three different copper-amine preservative systems (ACQ, CAz and CX™) was studied. The lumber samples were exposed to natural conditions in a field test, which was designed to simulate the use of treated wood as decking. A variety of species were analysed in the experiment. ACQ treated samples were composed of hem-fir (a commercial mixture of western hemlock (*Tsuga heterophylla* Raf.) and amabilis fir (*Abies amabilis* Forb.)) and spruce (*Picea* sp.). CAz treated samples were composed of jack pine (*Pinus banksiana* Lamb.), hem-fir, and lodgepole pine (*Pinus contorta* Dougl.), while CX™ treated samples were only hem-fir. Monthly observations of copper leachate were analysed. It was found that the leaching of copper from the treated wood in natural conditions can be divided in two periods. During the first period a rapid increase in copper leaching was observed, as unfixed copper from the surface of the board was leached out. The amount of leaching during this period was dependent on the amount of rainfall and lasted for 4 to 8 months, depending on the season when the boards were installed. A linear model was fit to the observations collected during this initial time period. During the second period a slow decrease in leaching was observed, though some increases occurred after a drying period prior to the beginning of the rainy season. Copper was found to be leached from the inner portion of the samples through a process of diffusion, which was affected by the wetting and drying of the sample. This period is dependent on the diffusion of copper and could be extended if the unfixed copper in the treated wood is not depleted. The observations from this period were fitted to a power or a logarithm model depending on the species and treatment type.

An accelerated laboratory leaching test was conducted on reference samples to determine the total amount of leachable copper. A comparison was made with the values obtained from the field leaching test. For hem-fir samples it was found that the amount of copper leached after 26 months of exposure was significantly lower than the total amount leached during the laboratory test due to the extreme conditions in latter one. For the pine and spruce samples, the amount leached during the laboratory test was significantly lower than the amount leached during the field test. This is possibly due to the lower penetration of preservative into these species, which made it difficult to calculate the total amount of leachable copper. To decrease copper loss due to leaching, two post-treatments were designed: a water pressure wash and a water repellent finish. While the water pressure wash designed to dissolve surface mobile copper and remove it,

did not provide any positive results, the application of water repellent was found to decrease the amount of copper leached. Finally, a study on the migration of copper into the checks (formed in the wood surface during exposure) was conducted. It was observed that unfixed copper relocated to the untreated surfaces of the checks during rainfall as leached copper from the surface of the board was deposited into these checks.

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List of Abbreviations

AAC	Alkyl ammonium compounds
ACA	Ammoniacal copper arsenate
ACQ	Alkaline Copper quaternary
ACZA	Ammoniacal copper zinc arsenate
BAC	Dialkyldimethyl ammonium chloride
CAz	Copper Azole
CA-B	Copper Azole type B
CBA-A	Copper Boron Azole type A
CCA	Chromated copper arsenate
CX™	Copper HDO
DDAC	Alkyl dimethyl benzyl ammonium chloride
EPA	Environmental protection agency
HDO	copper bis-(N-cyclohexyldiazeniumdioxy)
HHRA	Human health risk assessment
Quat	quaternary ammonium compounds
Teb	tebuconazole
WPT	Water pressure treatment
WRT	Water repellent treatment

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Chapter 1
Background

1.1 Introduction

The impregnation of timber with preservatives has several benefits, of which the main one is the extending of the product life thereby leading to a reduction in the use of a limited natural forest resource. Contrary to this positive contribution, wood preservatives have a negative image mainly because of the perceived alteration of the material and the interaction of the treated wood with the environment. Moreover, wood preservatives have gained increased media attention as a result of recent questioning of the permanence of arsenic in chromated copper arsenate CCA treated wood, when it is in service and possible losses into the environment (Preston, 2000).

The most important preservatives currently used are creosote, pentachlorophenol, and CCA. The first two have traditionally have been used for protection of industrial products, while CCA gained importance as the dominant preservative for residential timber. For the last 20 years, CCA has been used to preserve poles, fencepost, piles, decking, etc. Before the year 2004, it was the major preservative in North America, representing roughly 75% of the treated wood market in addition to representing over 97% of the market of waterborne preservatives (Solo-Gabriele *et al.*, 2000). During the last few years, the pressure to use preservatives other than CCA has increased due to the perceived negative environmental impact of the arsenic present in this preservative (Ruddick, 1999). In some countries e.g. Finland and Switzerland, arsenic preservatives are banned because they may introduce environmental pollution (Richardson, 1993). Recently, the North American industry voluntarily restricted the use of CCA treated wood for residential purposes by the year 2004 (Health Canada, 2003). These changes will result in a major decrease in the previous 70-80 % CCA-treated wood use (Lebow, 2004). For this reason, wood preservation research has been focused for the last 5 to 10 years on finding new preservatives capable of addressing the current and future environmental regulations.

The alternative biocides to CCA are arsenic and chromium-free and in the short term will be copper-based preservatives. All current alternative preservatives have copper as a primary biocide because it is an excellent fungicide, relatively inexpensive and has relatively low mammalian toxicity (Lebow, 2004). The alternative preservatives designated by researchers to replace CCA are the copper ammonia/amine based preservatives such as alkaline copper

quaternary (ACQ), Copper Azole (CAz) and copper bis-(N-cyclohexyldiazeniumdioxy) (Copper HDO or CX™). These preservatives have the potential to dominate the market of treated wood for residential purposes.

Much of the research for these alternatives preservatives has been focused on evaluating the fixation chemistry of amine/ammonia copper in wood under laboratory conditions. Leaching tests have been used to study the fixation mechanism of these preservatives. These tests were done using small wood samples (cubes or stakes) which were treated with preservative solution, the chemical allowed to fix, and then the samples leached by soaking them in distilled water, buffers or through soil contact. The information obtained gave an idea of the effect of the substrate on leaching and the leaching rate. Other studies tried to simulate rain conditions in the laboratory by spraying water over several periods of time (Lebow *et al.*, 2004). This procedure was believed to decrease the duration of testing, since this would normally be lengthy under natural weather conditions. However, this simulation does not address other factors that could have an effect in the chemical leachability because they are difficult to reproduce in the laboratory. Environmental factors such as temperature, hours of sunshine, time of exposure, etc., in conjunction with product size or exposure surface, may influence on the amount of chemical leached.

Little information is available on the leachability of copper from alkaline copper treated wood under natural exposure. Exposure to natural conditions varies according to whether the wood is in service below ground, above ground or in fresh water contact. Several above ground uses of treated wood such as decks, fencing, and shakes, are exposed as large areas to all weather conditions including rain.

Since the use of CCA treated wood for residential purposes is not longer permitted, it was a priority to have the alternative preservatives registered to replace CCA treated wood in the marketplace. To understand the environmental impact of these new preservatives is essential. An important part of the environmental impact is the information on the leachability of the product under residential exposure conditions. It will be important to relate leachability to the climatic conditions since different climates could make a difference in the amount of chemical leached. Because water is the medium that carries the chemicals out from the wood, it is believed that rainfall is the most important factor influencing leaching. One of the best places in

Canada to do research in leaching under natural conditions is Vancouver, BC, due to the relatively mild temperature and high seasonal rainfall.

1.2 Literature review

Creosote and pentachlorophenol, both oilborne preservatives, were the most common preservatives in the early 1970's, where they were used in industrial and agricultural applications. However, both preservatives became restricted-use preservatives for human contact in 1986 (Cassens *et al.* 1995). The oilborne preservatives are used only to treat products only for the industrial markets, such as railways ties, utility poles, posts, piling and heavy construction timbers. CCA has always dominated the residential market since its initial development in the early 1970's (Stephen, 1994).

CCA has been the most important waterborne preservative in North America because it is a very effective, can be very well fixed after treatment and leaves the surface of the treated wood free of chemical deposits (Jiang, 2000). The concern for the general public over CCA treated wood is the presence of arsenic and chromium which are considered hazardous to humans. However, the chemical forms present in treated wood are not the toxic forms Cr (VI) and As (III). In addition, there is concern when the treated wood is recycled due to the high levels of the metals that could go into the wood waste stream (Solo-Gabriele *et al.*, 2000). At some point treated wood products must be removed from service due to biological degradation, mechanical damage, or obsolescence (Stephens, 1995). The treated wood could end up being recycled as a fuel for energy cogeneration or mulch that produces ash with high levels of arsenic and chromium (Solo-Gabriele *et al.*, 2000). Arsenic and chromium are present in the environment in small quantities. Hexavalent chromium which is present in Canadian CCA wood preservation facilities has been reported to be carcinogenic (Connell *et al.*, 1990, Environment Canada, 2002 a-b).

With the recent restrictions on the use of CCA treated wood, the search for alternatives preservatives has begun. This encouraged the chemical suppliers to innovate and produce not only arsenic- and chromium-free copper based preservatives, but also efficient and inexpensive products that protect wood from biological deterioration without having a high mammalian toxicity (Evans, 2003).

In this context, the ammoniacal copper based systems have increased in importance due to their excellent performances against fungi and insects and because they are free of arsenic and chromium (Lucas, 2002).

1.2.1 Copper ammoniacal/amine based preservatives

Approximately 60 years ago ammoniacal copper preservatives were identified as excellent wood preservatives but due to poor appearance difficulties with the treatment and cost of use together with the rapid emergence of CCA as a preservative, the use of ammoniacal copper preservative was limited (Ruddick, 1996). However, with the CCA restrictions, the interest to know more about the fixation mechanism of the ammoniacal preservatives has increased.

The fixation of preservatives in wood is very important as it profoundly affects the performance and the environmental impact of the product (Ruddick, 1996). It is known that the efficiency of a preservative is determined by the degree of fixation of the components in wood. Copper is the most widely used biocide component in preservatives. Unlike in CCA, where the fixation in wood is driven by the chromium (VI) to form insoluble chromium complexes, in alkaline copper systems the fixation depends solely on the formation of insoluble copper complexes in/or with wood (Pizzi, 1982, 1990; Druz *et al.*, 2001).

Much research has been done on the fixation of ammoniacal copper based preservatives and the studies suggest that the ammoniacal copper wood preservatives fix by precipitation and complex formation reactions as the pH of the solution in the wood lowers (Ruddick, 1995 and 1996). During the fixation several reactions are taking place:

- reaction of ammonia from the solvent with wood substrate
- the formation of di(ammine) copper (II) complexes with the heartwood extractives
- the formation of di(ammine) copper (II) lignin complexes
- the precipitation of copper compounds in the wood
- possible copper complexes with cellulose or lignin

In ammoniacal or amine copper preservatives, the ammonia or amine is used to dissolve copper compounds in the treating solution. During the treatment, the solution reacts with wood and the ammonia/amine to copper ratio in the solution is reduced. This initiates the fixation reaction,

which is accelerated by the loss of ammonia or by neutralization of the amine by the wood to form complexes between the copper and the wood (Ruddick, 1992). Xie, (1995) and Ruddick *et al(* 2001), using vanillin, a lignin model compound, proposed that during the reaction between the ammoniacal copper solutions with wood a diamminocopper complex is formed, bound to the guaiacyl units of lignin in wood. This diamminocopper- lignin complex is stable and insoluble in water. The insolubility of the copper complex leads to good leaching resistance. Moreover, the addition of carbonates to the preservative solution significantly enhances the insolubility of the copper in treated wood (Ruddick, 1996), thus further improving the insolubilisation fixation of any remaining mobile copper.

It is possible that copper could also react with hemicelluloses and extractives in wood. It has been suggested (Jiang, 2000) that the reaction in wood involves the phenolic hydroxyl in lignin and the carboxylic groups in hemicelluloses.

A limited amount of research has been done on heartwood of pine. The phenolic extractives in certain heartwoods provide resistance to decay and insect attack. They also reduce the treatability of preservative solutions. The extractives can be oils, waxes and gums (Harju *et al.*, 2002; Haygreen, 1996). The presence of extractives in heartwoods could affect the fixation and leachability of copper. In Douglas-fir, heartwood turns black when it is treated with ammoniacal copper preservatives. Ruddick *et al.* (1994) found that taxifolin reacts with ammoniacal copper solutions producing a black complex. Jiang (2000) found that copper amine system shows reactions with both Scots pine and Douglas-fir extractives. Large amounts of green precipitate were produced when copper methanolamine was dissolved with ethanol extractive solution.

Ammoniacal based products have shown good fixation characteristics and results have indicated good performance against soft rot fungi due to good cell wall penetration (Ruddick 1996; Rhatigan, 2003). However, three main concerns exist with these products. The first is the problem with the evaporation of ammonia during drying that leaves undesirable water insoluble copper salts on the surface of the treated wood (Jiang, 2000). Also, using ammoniacal preservatives requires modification in the treatment process to allow for the control of vapours, and an increase safety standard in plants to avoid dangerous exposure of workers to ammonia gas (Connell *et al.*, 1990). An alternative solution to this problem is to dissolve the copper in amine solution. The amine solvents do not evaporate like ammonia, and maintain similar properties to

ammoniacal copper (Lucas, 2003). Considerable work has also been carried out on the use of alkaline systems in which the copper is dissolved in an aqueous solution of ammonia, a short chain water soluble amine, or ethanolamine for timber treatment (Connell *et al.*, 1990). Lucas (2002) studied the influence of two different amine solutions, monoethanolamine and ethylenediamine, in the fixation of copper and found that using monoethanolamine provides greater resistance to leaching than using ethylenediamine. This resistance to leaching could be enhanced with the addition of ammonia to produce mixed ammonia/ethanolamine copper systems.

The second concern is that a fixation time is required after treatment to complete the reactions with wood and to minimize the chemical leaching (Jiang, 2000; Kumar *et al.*, 1996; Lucas, 2003). Ruddick (1992 and 1995) found that increasing the amount of ammonia increases the copper fixation when treated wood blocks were wrapped in polyethylene and allowed to fix for one week at 20°C. However, the amount of ammonia in the treating solutions was much higher than would be used commercially. The fixation time can be reduced by keeping the treated wood wrapped and increasing the temperature. According to Kumar (1996) and Lucas (2003) who used the same methodology and increased the temperature, the degree of fixation improved after a post-treatment of one hour at a temperature above 60°C compared to a post-treatment of one week at 22°C.

The third concern is that the treated wood is susceptible to degradation by copper tolerant fungi unless a secondary active ingredient is included (Greaves and Nilssen, 1982; Connell *et al.*, 1990). Organic biocides have been added to the alkaline copper preservatives to enhance and broaden protection against copper tolerant fungi.

1.2.2 Organic Biocides

Organic biocides that were developed for the agricultural sector have also been made available for use as wood preservatives. Research has been done on the development of new preservative combinations of copper based preservatives, as a primary biocide dissolved in amine or ammoniacal complex with organic biocides, to provide protection against copper tolerant fungi and termites. Compounds like alkyl ammonium compounds (AAC) or triazoles are used by the industry to produce wood preservatives (Preston, 2000; Evans, 2003).

An increasing amount of work has gone into the development and utilization of the Alkyl ammonium compounds (AAC). The research has been carried out to analyze their properties and determine their potential for a variety of uses such as household disinfectants, eye drops, fabric softeners, hair conditioners, cosmetics, paint-film fungicides, anti-sapstain compounds and alternative waterborne fungicides (Connell *et al.*, 1990). AACs have also been registered in New Zealand, Japan and Scandinavia for above ground use as are waterborne organic preservative for wood (Ruddick, 1999).

The AAC's have low mammalian toxicity compared to the inorganic preservatives. They are, however, a severe eye and skin irritant at concentrate levels. Operators need to use rubber gloves to process freshly treated wet lumber, but after the treated wood is dried they can be handled without gloves. The treated wood with AAC shows no colour change after treatment and, in field exposures, there is no tendency to discolour light-coloured paints as can sometimes occur with other salt treatments. Other features of the AAC treated wood to consider are its low effect on fire properties and the fact that it can undergo complete combustion in a furnace without leaving a toxic residue for disposal (Nicholas and Preston, 1980).

AAC are adsorbed onto lignin with almost no interaction with cellulose. AAC's are known to fix to wood cell walls by an ion exchange mechanism. Experiment done by Doyle (1995) treating small blocks with AAC's found that retention of AAC's in earlywood tracheids drops by 50% than the outer 5 mm shell, while in the latewood the retention remained constant. The fixation process is rapid under alkaline conditions and sometimes is a problem since it leads to the stripping of ACC active ingredients from the treating solution and poor penetration in the wood. Also, they have low persistence in the environment. This can be considered good for the manufacturer from the ecological point of view; however this feature could be reduced for the long term protection of wood (Connell *et al.*, 1990).

The group of AAC that has received most attention is the quaternary ammonium compounds (quats). This group has been included in the formulation of the alkaline copper quaternary preservatives (ACQ) as a second biocide.

Quats are surfactants, molecules that have hydrophobic alkyl chain and hydrophilic properties from the cation. Surfactants tend to accumulate at interfaces where the water contacts solids, air

or non-air aqueous liquids, thereby reducing the surface tension of water, producing emulsification, foaming, and dispersal of hydrophobic particles in a liquid medium (Dubois, 1999). Surfactants have been reported to improve the penetration of CCA (Kumar, 1992) and borates, because they decrease the surface tension and increase the wettability of wood (Morris, 1997). The alkyl chain is the toxic factor in the compound. Chains of C8-C10 were found the most effective to prevent decay. Moreover, quats with twin alkyl chains are more toxic to fungi (Butcher *et al.*, 1977).

Quats have shown good performance in laboratory tests. Two quats were identified to be suitable for the wood preservation: alkyl dimethyl benzyl ammonium chloride (DDAC) used in the ACQ type C and dialkyldimethyl ammonium chloride (BAC) types used in the ACQ types B, and D (Connell *et al.*, 1990).

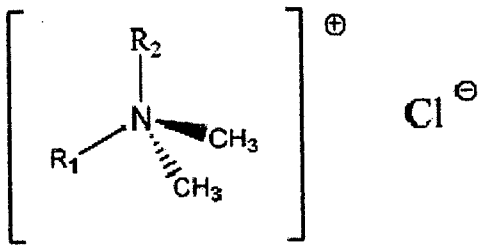

Figure 1-1 Chemical structure of DDAC (Nicholas and Preston, 1980)

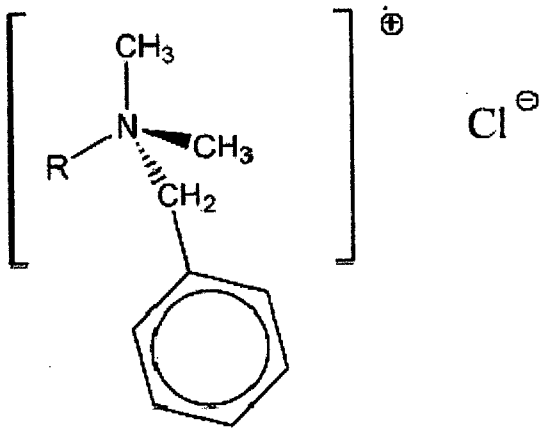

Figure 1-2 Chemical structure of BAC (Nicholas and Preston, 1980)

Several studies of the performance of AACs have been done, and all of them agree that most ACCs have good biological efficacy when tested under laboratory conditions, are cost effective and have some good properties regarding environmental safety (Butcher and Greaves, 1982). Research in the laboratory showed that DDAC treating solution is very effective at controlling brown- and white-rot fungi a 0.25 to 0.5 % (Preston and Chittenden, 1982; Preston and Nicholas, 1982). For alkyl dimethyl benzyl ammonium chloride (BAC), the same concentration range is enough to prevent brown-rot fungi attack, but a higher level in the treating solution (0.5 to 1 %) is necessary to control the white-rot fungi.

The quats do, however, have some disadvantages, of which the most critical is the failure to reproduce the excellent laboratory performance under field conditions due to increase leaching and the ability of fungi to remove them (Dubois, 1999). Particularly when used in ground contact, they can provide poor or non-uniform penetration in wood (Barth *et al.*, 1993). This is the reason why quaternary compounds are combined with copper to produce an effective preservative.

Another group of organic biocides are the azoles, of which the most common used is the tebuconazole (1H-1,2,4-Triazole-1-ethanol,α-[2-(4-chlorophenyl)ethyl]-α-(1,1-dimethylethyl)) that is used in the agriculture as a fungicide. Tebuconazole class C is used in wood preservation in the formulation of Copper-Azole preservative. This compound is categorized as non carcinogenic by the U.S. Environmental Protection Agency (EPA) (Kyzer, 2002).

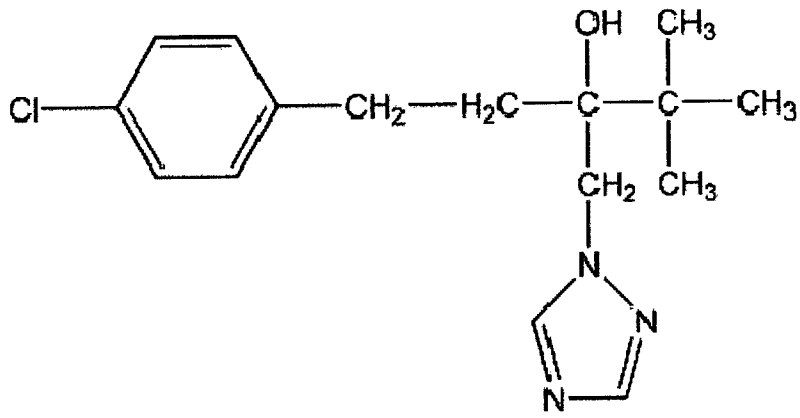

Figure 1-3 Chemical structure of tebuconazole

1.2.3 The alternative preservative formulations

The alternative preservatives which have reached commercialization are generally waterborne due to the low cost of such systems, although a few organic emulsions have also been developed. It is generally agreed that the amine-copper systems have replaced CCA for residential products as of January 2004. The most common in use are alkaline copper quaternary (ACQ) from Chemical Specialties Inc. and copper azole (CAz) from Arch Chemicals. Another preservative Copper HDO (CX™) from Dr. Wolman GmbH. is not registered yet in Canada or the USA. Such non-arsenical copper-based products have found good markets in Europe and Japan. To date only ACQ and CAz have been commercialized successfully in the United States (Preston, 2000). Copper azole is also available in the North American market. Both preservatives are listed by the American Wood Preservers' Association (AWPA) and Canadian Standard Association (CSA) standards. CX™ is in process of completing all the regulations to enter into the North America market.

One disadvantage of the use of alternative preservatives compared to CCA is corrosion. Fastener producers have observed corrosion on standard bolts and nails used with treated wood. This corrosion is produced by the high copper content of the preservative in conjunction with the changing moisture content of the wood when it is exposed outdoors (Dr. Wolman, 2003; Bartok, 2004). Generally, it is recommended to use hot-dipped galvanized or stainless steel fasteners. Although corrosion is a disadvantage of alternative preservatives, the lack of arsenic provides more benefits compared to the use of CCA treated wood (Solo-Gabriele, 2000; Lebow, 2004).

1.2.3.1 Alkaline Copper Quaternary (ACQ)

Alkaline copper quaternary (ACQ) is a mixture of ammonium hydroxide, copper and quaternary ammonium compound. It has been developed for ground contact, above ground and marine applications. It is widely used in USA, Japan and Europe. There are four types of ACQ: A, B, C and D. The ACQ type A was added to the AWPA standard in 1992 but deleted in 2000 without prejudice due to lack of use (AWPA, 2003). The other three formulations are listed in the AWPA standards. ACQ type B and ACQ type D use dialkyldimethyl ammonium chloride (DDAC) as the quaternary ammonium compound (quat). The difference between them is the carrier solvent used. In the case of type B, a solution of ammonium hydroxide (NH_4OH) is used,

while in the type D ethanolamine is used. In ACQ type C, the quaternary ammonium compound is alkyl benzyldimethylammonium chloride (BAC) and the solvent can be a combination of ammonia and ethanolamine (AWPA, 2003). In this solvent combination, the ammonia improves the penetration of the preservative in refractory species while the ethanolamine provides more uniform surface appearance (Lebow, 2004). In ACQ types B, C and D, the ratio of copper to quat is 2:1 (66.7% copper and 33.3% quat) (AWPA, 2003).

Unlike the DDAC alone, the ACQ colours wood green-brown. The colour depends on the species of the wood, heartwood and sapwood content, chemical retentions and treatment cycle. Heartwood turns brownish, while sapwood turns green. After weathering, the wood turns a grey brown tone (Solo-Gabriele *et al.*, 2000).

ACQ treated wood can be disposed via landfill and incineration followed by chemical extraction of copper from the ash produced. The gaseous products of the incineration will be similar to those for untreated wood (Archer, 2003).

1.2.3.2 Copper Azole (CAz)

CAz is another developed copper amine preservative formulation which is a mixture of at least two chemicals - copper and triazole. In the first formulation, boron was also included and it was known as Copper boron azole (CAz type A or CBA-A). The components of this preservative were 49% copper, 49% boric acid and 2% tebuconazole. This preservative was initially introduced in Europe, USA and Japan. However, when it was approved in Canada in 2003, the boron was removed, to avoid impacting the long term performance due to the rapid boron leaching. The new product was called Copper azole type B (CA-B). The components of CAz type B are 96.1% copper and 3.9% tebuconazole (AWPA, 2003; Kyzer, 2002; Lebow, 2004). Normally, CAz is listed as an amine formulation; however ammonia could be included when refractory species need to be treated (Lebow, 2004). The formulations are listed in the AWPA standards for treatment of a range of softwood species used above ground or in ground contact.

The tebuconazole (TEB) co-biocide is synergistic with the copper and provides protection against copper tolerant fungi and is effective at suppressing attack by R*eticulitermes flavipes* and *Coptotermes formosanus* termites (Hickson, 1998). TEB is an effective fungicide used to protect the integrity of wood used primarily for outdoor structures. CAz has low mammalian toxicity

and is non-mutagenic. The concentrate was found to be an irritant to the skin and, like other copper containing wood preservatives, it has a high toxicity to aquatic organisms (Solo-Gabriele *et al.*, 2000). According to Shipp *et al.* (2004) there is no appreciable risk of adverse health effects from exposures to TEB in CA-B treated wood based on the sufficiently large margin of exposure (MOE: The ratio of the no-observed adverse-effect-level to the estimated exposure dose), calculated for the exposure scenarios in human health risk assessment (HHRA).

Both CB-A and CA-B give a green color to the treated wood, which turns to brown after weathering. The treated wood has little or no odours. However, the inclusion of ammonia in some treating solutions could have some minor effects on the surface and initial odours of the treated wood (Lebow, 2004; Solo-Gabriele et al, 2000).

The recommended method for the disposal of CAz treated wood is by landfill or incineration in special recycling centres. The gaseous products of combustion are similar to those for untreated wood. As with the treated wood disposal, in wood stores or use as cooking fuel is strongly prohibited. Copper in treated wood or in ashes after incineration in recycling plants can be extracted with acid for recycling (Arch Wood Protection Inc., 2003; Hickson, 1998).

1.2.3.3 Copper HDO (CX™)

Copper HDO is an amine copper based preservative that has been used in Europe and recently standardized by the AWPA. It was introduced in 1989 by Dr. Wolman GmbH and the product is known commercially as Wolmanit® CX (Dr. Wolman GmbH, 2003). The active ingredients are copper oxide, boric acid and copper–HDO (Bis-(N-cyclohexyl-diazeniumdioxy copper)). The appearance and handling characteristics of wood treated with CX-A are similar to those of other copper-based-treatments. Extensive testing has found that CX-A is not carcinogenic, mutagenic, teratogenic, nor sensitising. CX-A formulations have been evaluated in a range of exposures, but at this time have only been standardized for uses above ground. It is anticipated that CX™ will be registered by the Environmental Protection Agency (EPA) during 2005 (Lebow, 2004).

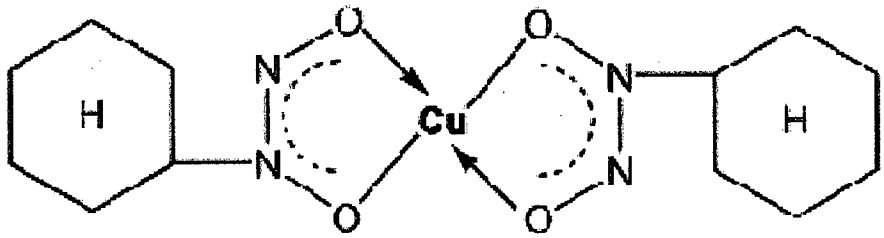

Figure 1-4 Molecular structure of Copper HDO

1.2.4 Leaching studies

Over the past few years, interest in chemical depletion or leaching has greatly increased in importance. This is because of concern from the general public over the loss of chemicals to the aquatic environment and to build up in drinking water or damage to fresh water habitat for fish. The assessment of the leachability of treated wood can give us information about the fixation rate of the preservative after the treatment. Much research has focused on the use of leaching to compare fixation of different preservatives under different treatment and post-treatment conditions. Another reason for the increase in interest is to predict long term performance of new preservatives in the shortest period possible (Jin *et al.*, 1992).

Leaching studies have been done with several methodologies in the laboratory. Generally, small wood samples have been used. They are generally treated with the preservative solution, allowed to dry and then leached. The leaching methods vary depending on the medium used to leach the chemicals. There are two conventional substrates used to leach the chemicals, soil and solutions. Soils substrate simulates the use of the treated wood in ground contact. The wood samples are deposited in a soil bed inside a greenhouse, where the temperature and relative humidity are controlled. Other substrates used for leaching are a solutions such as distilled water, a buffer solution, and acidic or basic solutions. The treated sample is usually placed in a beaker with the solution and leached in a magnetic stirrer, ultrasonic bath, or an undisturbed pool of water.

Although laboratory leaching tests are a fundamental component in assembly in possible improvements in preservative fixation, they are not representative of the results of leaching under service conditions. This is mainly due to the different factors (i. e. weather which includes

rainfall, temperature, sun hours, relative humidity, etc.) involved when the wood is in service, which is very difficult to reproduce in the laboratory. Also, preservative retention, penetration and dimension of the commercially treated wood are different from the treated wood used in research in the laboratory. Generally, small sapwood samples are treated and leached in the laboratory. However, they are not representative of either dimension lumber or the treatment process (Lebow, 2004). Surface area to volume ratio of small samples means the rate of leaching is always greater in laboratory than for the actual items in service. Lower surface area per volume in real life reduces leaching rate.

1.2.4.1 Factors affecting the leachability in field conditions

While it is an admirable goal to use accelerated leaching studies to predict the leaching behaviour of treated wood under natural conditions, there is a major risk in failing to understand how the leaching process of the treated wood occurs in service. Environmental factors play an important role in the leaching process. This section will identify the more important parameters which impact on loss of copper from alkaline copper treated wood.

The time of exposure of the treated wood determines the total amount of chemical that is going to be leached from wood. Generally, the leaching of the treated wood commences with a rapid leaching of the unfixed preservative components from the treated wood, followed by a decrease in the leaching until it reaches stabilization in the rate of loss (Lebow, 1996; Choi *et al.*, 2004). It is expected that longer periods of exposure would have higher amount of components leached.

The weather is the important factor in the leaching process, especially the precipitation and the temperature and sun hours. Rainfall is the key factor for leaching. Water is the carrier of the free chemicals that are not bonded to the wood. For treated wood exposed above ground, water comes into contact with wood through rainfall (Choi *et al.*, 2004). For exposures in ground and below ground, the water contacts the wood through the rainfall and the soil. It has been suggested that drizzling rain results in stronger leaching than does heavy rain (Evans, 1987).

Temperature has an effect on the drying and wetting of wood, on the solubility of the unfixed preservative components and diffusion rate of those components to the wood surface (Choi *et al.*, 2004; Waldron *et al.*, 2004). Higher temperatures can increase the solubility and the diffusion of the components, and therefore their mobility inside the wood. Sun hours can have an effect on

the surface of the wood, first, by increasing the temperature of the wood surface and second through the action of UV light that causes the degradation of the lignin (Choi *et al.*,2004).

The wood properties of the species are other factors to consider. Some species in Canada are refractory, i.e. very difficult to treat and have the minimum penetration required by the Canadian wood preservation standard, mainly due to the high content of heartwood (Choi *et al.*, 2004). Other species with less heartwood content are easier to treat and the penetration is deeper. Total copper is greater in many sapwood species, but that could be more available in heartwood than sapwood.

The size and orientation of the treated wood determines the exposed surface area. In decking, the boards are exposed horizontally: the top of the surface is directly exposed to the rain. Treated sides of the wood could also be a source of leaching but may be less important than the top surface.

The substrate is another factor by which the leaching is affected. Generally, the exposure above ground is less severe because the wood is not in contact with either soil or water, and the leaching is produced only by the rainfall. In ground contact, the moisture content of the soil determines the amount of water available for the leaching process. The leaching is also affected by the composition of the soil, pH, etc. Soils with high organic content have greater copper leachate than sand or clay soil. Also, soils with high content of humic acid solutions have shown to extract copper from copper metal and also to dissolve copper. Values of pH vary from acidic soils with a pH 4, which can be found in bogs to a pH close to 8, which is found in hard water lakes. Studies found that soils with pH values of 3 have about 6-25 % copper leached in CCA treated wood, and decrease to 1 % at pH values 4 (Lebow, 1996). The leaching of AAC compounds depends on the pH of the soil. Higher amounts of BAC were leached at pH 4 than at pH 10 in an accelerated leaching of BAC treated wood (Nicholas and Preston, 1980).

1.2.4.2 Field Leaching Testing

Little research on leachability of treated sawnwood has been reported from wood in service, and most studies were done with CCA treated wood. Leaching studies on alternative preservative treated wood were generally done comparing the amount the chemical leached with that of CCA

treated wood. Most of the investigations were trying to support the introduction and regulation of the new preservatives into the North American market after the restriction of the use of CCA treated wood for residential purposes.

Research done by Archer (2003) on ACQ leaching, compared the ACQ type C, ACQ type D and CCA 2 x 6" treated boards exposed above ground after 18 months of exposure in Harrisburg, North Carolina (Table 1-1). The results showed that the amount of copper leached for a retention of 2 kg/m^3 was around 6% for ACQ type C and D and 11% for CCA type C. For retentions of 4 and 6.4 kg/m^3, the amount of copper leached was similar (around 3%) among the preservative treatments with one exception of ACQ type D at 6.4 kg/m^3 for which the amount of copper leached was 0.7%. The percentage of quat leached was higher for ACQ type C (33% for 2 kg/m^3, 15.4% for 4 kg/m^3 and 2.8% for 6.4 kg/m^3) than that shown for ACQ type D (7.2% for 2 kg/m^3, 3.6% for 4 kg/m^3 and 0.9% for 6.4 kg/m^3). The results suggested that DDAC (ACQ type D) has higher leaching resistance than BAC (ACQ type C). In another experiment, a comparison of leaching of ACQ and CCA treated southern yellow pine blocks (19 x 19 x 450 mm) at ground line exposed for 15 months in Hilo, Hawaii was done (Table 1-2). The results showed that ACQ types C and D have a similar amount of copper leached (around 23%); however this amount was a little higher than that of CCA treated wood (16%). The quantity of quat leached, from ACQ type D and type C (solvent amine) treated wood was similar (around 38%). For ACQ type C (solvent amine: ammonia 1:1) the quantity of quat leached was lower (28.8%). ACQ type B also has a low amount of quat leached (17.2%). Using only ammonia as a solvent in ACQ type C, the amount of quat leached decreased to 8.1%. Finally, a laboratory leaching was also conducted (Table 1-3) and the results showed that ACQ type B (3.7% for 2 kg/m^3, 6.8% for 4 kg/m^3 and 9.8% for 6.4 kg/m^3) had the lowest amount of chemicals leached. ACQ types C and D were found to have similar amounts of copper leached (8-9% for 2 kg/m^3, 13% for 4 kg/m^3 and 17-19% for 6.4 kg/m^3). These results suggest that using ammonia as a solvent reduces the amount of chemical leached, since ACQ type B uses only ammonia as a carrier solvent. This was confirmed by Lucas (2003), who when using two different ratios of ammonia/amine (2:4 and 4:4) decreased the amount of copper leached in wood compared to the amount of copper leached only using amine as a solvent in preservative solution. Finally, those values are higher than the amount of copper leached from CCA treated wood (around 5%).

Table 1-1 Amount of preservative losses from 2 x 6 boards exposed above ground after 18 months of exposure at Harrisburg, North Carolina (Archer, 2003)

Preservative	Preservative Retention (kg/m^3)	Percentage of losses from treated wood	
		CuO	Quat
ACQ Type C	2	6.6	33.1
	4	2.6	15.4
	6.4	3.4	2.8
ACQ Type D	2	6.3	7.2
	4	3.2	3.6
	6.4	0.7	0.9
CCA	2	11.5	
	4	3.0	
	6.4	3.7	

Table 1-2 Amount of preservative losses from southern yellow pine stakes exposed above ground after 15 months of exposure at Hilo, Hawaii (Archer, 2003)

Type of Preservative	Retention (kg/m^3)	Leaching at ground line (%)	
		CuO	Quat
ACQ type B	4.94	23.6	17.2
ACQ type D	4.58	23.7	39.1
ACQ type C (amine)	5.88	23.6	37.4
ACQ type C (ammonia)	5.22	20.5	8.1
ACQ type C (1:1 amine: ammonia)	5.53	23.5	28.8
CCA	6.74	16.3	

Table 1-3 Copper lost from radiata pine blocks during laboratory leaching test (Archer, 2003)

Preservative	Preservative Retention (kg/m^3)	Percentage of CuO losses from treated wood
ACQ Type B	2.17	3.7
	4.37	6.8
	6.97	9.8
ACQ Type C	2.16	9.6
	4.31	13.0
	6.87	19.2
ACQ Type D	2.03	8.9
	4.21	12.9
	6.52	17.5

Not much research on leachability with CuAz treated wood has been reported. Tests were generally done by Arch Wood Protection (2003a) as part of the supporting data to introduce the preservative in North America. A water leaching test in ground contact in the laboratory was done using southern pine blocks treated with CA-B and CBA-A. The result showed that both preservatives have similar amounts of chemicals leached, however these amounts were somewhat higher than ACZA, in the same test. Also, field tests in ground contact were done with southern pine CBA-A treated stakes exposed for 13 months in Conley, Georgia and Gainesville, Florida (Table 1-4). The results were similar for both places; approximately 2% of copper losses in above ground tests and 11% in below ground tests. The amount of tebuconazole leached was around 30%. Additional tests with longer exposure periods were carried out in Madison, Georgia and Gainesville. The results after 38 months of exposure were also similar for below ground tests; losses of copper were around 30% and losses of tebuconazole around 16%. For the above ground test the copper losses were 17.2% for Madison and 8% for Gainesville. No test above ground without ground contact has been reported; therefore the Canadian Standards Association Wood Preservative technical committee regulations specified that additional tests on leaching above ground are necessary.

Table 1-4 Amount of preservative losses from southern yellow pine stakes exposed at field (Arch Wood Protection, 2003a)

Location	Time of exposure	Type of exposure	Percentage of losses	
			Copper	Tebuconazole
Conley, Ga	13 months	Above ground	2.9	29.5
		Below ground	10.5	29.5
Madison, Ga	38 months	Above ground	17.2	23.4
		Below ground	28.9	15.9
Gainesville, Fl	13 months	Above ground	2.1	30.5
		Below ground	12.2	31.6
	34 months	Above ground	8.1	25.7
		Below ground	31	17.6

Research on the leachability of CuHDO treated wood is less than on either of the other alternative preservatives. In a preliminary study, Morsing and Lindegaard (2003) reported that the amount of copper after 500 ml of rainfall was around 2% from the original retention. More research on this preservative is in progress.

1.2.5 Mobility of copper in wood

When it is in service, wood is repeatedly wetted and dried by rain. In this process, the preservative chemicals in the wood are brought to the surface. Since copper salts are water soluble, they could be brought to the surface when the wet wood is drying (Connell *et al.*, 1990), as well as during extended rain by diffusion.

The performance of the CCA treated decking over long period service has been studied. In refractory species shell penetration is present. Shell penetration gives only external protection at the surface of the wood and the wood core remains untreated. In service, wood develops checks due to dimensional changes caused by the wetting and drying. When checks are produced on the wood surface, the untreated part of the wood is exposed. Although the untreated part inside the checks looks vulnerable to fungi, decay does not appear rapidly. An explanation for this phenomenon was given by Choi *et* al. (2004) when it was found that unfixed copper migrated after rainfall and became fixed inside the checks, thereby providing protection against fungi. No research has been done with alternative preservative treated wood.

1.2.6 Water Repellent Additives

Recently, interest in the application of water repellents to treated wood has grown. Water repellents were investigated in the early sixties, however the commercialization and expansion started in North America at the beginning of the 1980's. The use of water repellents can extend the protection to wood in service (Preston, 2000). Water repellents are designed to prevent changes of the dimensions of the wood caused by absorption of water, and prevent decay and checking, warping and other defects (Zahora, 1992, Williams and Feist, 1999). The water repellent not only provides the treated wood with protection against the direct effects of moisture, but also could decrease the leaching of the preservative components.

Some studies of the effect of the water repellent on the performance of treated wood in service have been reported. Zahora (1992) found that CCA - water repellent treated wood exposed outdoors for one year had a much narrower range of moisture content than the reference CCA controls. Lebow *et al.* (2004) reported that including water repellent in the CCA treatment of wood did not decrease the leaching of arsenic from the treated wood when it was exposed to

simulated rain. However, the copper leaching was reduced compared to the CCA treated wood without water repellent. Moreover, the application of water repellent after the CCA treatment in wood was found to be more effective against chemical leaching.

Research on leaching of ACQ with water repellent treated wood was done by Archer and Baker (2003). The ACQ type C and D were used for the experiment. The results from accelerated leaching and field exposure above ground after 18 months suggested that the water repellent did not decrease the amount of copper lost compared to the treatments with ACQ alone. In another study with ACQ treated stakes exposed above ground and to the soil bed, Jin *et al.* (1992) found that while the water repellent decreased the losses of the co-biocide DDAC, it did not have an effect on decreasing copper losses.

1.2.7 Modelling leaching

Few researchers have tried to model the amount of chemical leached as a function of the factors involved in the leaching. Waldron *et* al. (2004) have tried to establish a relationship between the results of chemical lost from treated wood in the laboratory and field leaching, to predict the amount lost during the determined period of time. Using accelerated leaching of sawdust from CCA, ACQ and CAz treated blocks, Waldron *et al.* (2004) developed a model in which the inorganic compounds of the preservative leached was dependent on three factors. These factors were: the total leachable preservative component (based on intensive leaching of fine ground material), the amount of dissolved or dissociates of the preservative components in water saturated wood, and diffusion coefficients for movement of the preservative components out of wood. However, this model was based on the assumption that wood is totally saturated with water and did not involve the wetting and drying during natural exposure or the effect of the other environmental variables.

Another approach with data recorded from treated wood in service was done by Choi *et al.* (2004). After exposing CCA treated wood to simulate its use as a decking for two years, it was proposed that the amount of arsenic leached from CCA treated decking in service depended on the volume of the leachate, temperature and sun hours. No relationship was found for copper, since losses were minimal after the first ten months.

1.3 Objectives

The main objective of the current research was to evaluate the leaching of copper in copper – amine treated wood. This objective was supported by the following sub-objectives:

- Measure the leaching from ACQ, CA-B and CuHDO (CX™) treated wood exposed above ground.
- Measure the leaching of copper in ACQ, CA-B and CuHDO from sawdust and compare to the field leaching.
- Verify the effect of the post-treatments in the leaching of ACQ treated wood exposed above ground.
- Verify the redistribution of copper in ACQ treated decking

Chapter 2
Materials and Methods

2.1 Introduction

In this study the amount of chemical leached from treated wood simulating the use as a decking was evaluated. The leaching evaluation was conducted using both field leaching and laboratory leaching. During the field leaching, treated wood was exposed to natural environmental conditions, collecting the leachate that was produced by the rainfall. The laboratory leaching was an accelerated method using ground sawdust that was placed in water and either stirred with a magnetic stirrer or placed in an ultrasonic bath to leach all the free chemicals from wood. Comparisons between the field leaching and laboratory leaching were made and the influence of the different parameters such as retention of the preservative, wood species, dimensions of the treated wood, post-treatment applications and environmental conditions of the exposure were examined.

2.2 Materials

ACQ, CAz and CX™ treated boards were used in the study. Treated boards for the initial ACQ field leaching were provided by Chemicals Specialties Inc. (CSI), CAz treated boards were provided by Arch Wood Protection Inc. and CX™ treated boards were provided by Dr. Wolman GmbH. For the analysis of the effect of post-treatments on treated boards, additional ACQ boards were purchased from a local supplier (The Home Depot). The dimensions, retentions and penetrations of the boards were different depending on the supplier.

2.2.1 ACQ treated boards

Twelve hem-fir (commercial mixture of western hemlock *Tsuga heterophylla* Raf. and amabilis fir *Abies amabilis* Forb.) ACQ type C treated boards[1] (37.5 mm thick x 87.5 mm wide x 580 mm long, commercially labeled '2 x 4') were provided by CSI. The details of the treatment are

[1] After identification, all the boards were amabilis fir

presented in Table 2-1. According to the information provided, the twelve boards originated from three larger boards, which were cut into four individual boards before the preservative treatment.

Table 2-1 Information of the treated boards provided by Chemical Specialties Inc (CSI)

Board*	Weight uptake (kg)			ACQ solution	Treatment
	Initial weight	Final after treatment weight	Percentage		
1-1	0.83	1.36	64	Concentration: 1%	Initial pressure: 20 min at 91 kPa vacuum
1-2	0.85	1.41	66	• CuO 0.674%	
1-3	0.85	1.48	74	• BAC 0.336%	
1-4	0.83	1.45	75		Pressure: 90 min. at 1049 kPa of vacuum
2-1	0.84	1.69	101		
2-2	0.83	1.59	92		
2-3	0.86	1.61	87		
2-4	0.87	1.59	83		Final 15 min. vacuum
3-1	0.74	1.59	115		
3-2	0.79	1.73	119		
3-3	0.85	1.80	112		
3-4	0.83	1.66	100		

*** The first number represents the original board. The second number represents section of the original board**

2.2.2 CAz treated boards

Arch Wood Protection Inc. provided 30 CAz type B treated boards (38 mm thick x 140 mm wide x 1.22 m long, commercially named '2 x 6'). Three different species were included: ten boards each of jack pine (*Pinus banksiana* Lamb.), lodgepole pine (*Pinus contorta* Dougl.) and hem-fir (4 hemlock and 6 amabilis fir).

2.2.3 CX™ treated boards

Dr. Wolman GmbH provided fifteen hem-fir boards treated with CX™. Nine of the boards had dimensions of 37.5 mm thick x 87.5 mm wide x 1.29 m long, commercially labeled '2 x 4'; and the other six were 38 mm thick x 140 mm wide x 1.29 m long, commercially labeled '2 x 6'. The boards were treated in three different charges. None of the cross cut of the boards were sealed.

The details of the treatment are presented in Table 2-2. Two retentions are shown in the table, the retention of the charge by measured by assay of the core of the boards (AWPA, 2003) and the retention calculated via uptake of the solution and solution concentration.

Table 2-2 Information of the treated boards provided by Dr. Wolman GmbH

Charge	Retention (kg/m^3) *	Board	Dimensions (mm) (1.29 m long)			Gauge retention board** (kg/m^3)
			thickness	width	label	
Charge 1 Treatment: Full Cell	4.32	A 3	37.5	87.5	2 x 4	4.30
		A 10	37.5	87.5	2 x 4	5.91
		A 11	37.5	87.5	2 x 4	2.87
		A 56	37.5	140	2 x 6	5.38
		A 58	37.5	140	2 x 6	4.84
Charge 2 Treatment: Modified Full Cell A	3.81	2 B	37.5	87.5	2 x 4	3.87
		6 B	37.5	87.5	2 x 4	2.58
		14 B	37.5	87.5	2 x 4	4.30
		51 B	37.5	140	2 x 6	4.79
		53 B	37.5	140	2 x 6	4.11
Charge 3 Treatment: Modified Full Cell B	2.86	15 A	37.5	87.5	2 x 4	4.15
		18 A	37.5	87.5	2 x 4	5.46
		19 A	37.5	87.5	2 x 4	3.68
		59 A	37.5	140	2 x 6	4.11
		63 A	37.5	140	2 x 6	5.57

2.2.4 ACQ treated boards for post treatment test (ACQ-t)

To investigate the influence of the post-treatments on the leachability of copper, four spruce (*Picea* spp) ACQ treated wood (37.5 mm x 90 mm x 3.05 m, commercially labeled 2 x 6) were purchased from a local provider (The Home Depot).

2.3 Methods

2.3.1 Field Leaching

2.3.1.1 Initial Measurements

The dimensions of the samples were measured using a steel ruler to the nearest ± 0.1 mm and its mass was measured using an analytical balance. Since the copper penetration was not the same along the board, an average was calculated from three measurements on the side with the deepest penetration.

2.3.1.2 Sample Preparation

The boards were cut in small samples that were either 280 or 270 mm in length. The length was determined by the size of the board placed over a plastic container of approximately 10 L capacity. The boards were supported by untreated wooden sticks, simulating the use as a decking (Figure 2-1).

For the initial ACQ study, the twelve boards were cut into small samples 280 mm long. This provided two samples per board. The twenty-four samples obtained were distributed into three groups according to the original board from which they came. To simulate the use as a decking, three samples from the three original boards were chosen and placed together over an empty basin supported by untreated wooden sticks (Figure 2-1). Eight basins were set up for the exposure test (Table 2-3). By distributing the various sections from each parent board in different basins it was hoped to maintain a similar retention among the basins and decrease variability between basins for an easier analysis of copper losses. The remaining pieces of the board were kept as a reference material and were used to determine total mobile copper using an accelerated laboratory leaching.

Figure 2-1 ACQ treated boards over a basin

Table 2-3 Distribution of the ACQ treated boards in basins to be exposed

Basin	Sample	Basin	Sample
	2-1 A		1-1 B
1	1-1 A	5	2-1 B
	3-1 A		3-1 B
	1-3 A		1-3 B
2	2-3 A	6	2-3 B
	3-3 A		3-3 B
	1-4 A		1-4 B
3	2-4 A	7	2-4 B
	3-4 A		3-4 A
	1-2 A		1-2 B
4	2-2 A	8	2-2 B
	3-2 A		3-2 B

In preparing the CAz treated boards for exposure, ten 2 x 6 boards of each species were cut into four samples 290 mm long: A, B, C, D. The sections A and D had one treated end, while sections B and C had two freshly cut ends. Since the boards were wider than the ACQ treated boards, only two sections of each board were placed over a basin to be exposed to environmental conditions (Figure 2-2). For each species, ten basins were set up for the field leaching with five basins composed of samples A and D and five with samples B and C. In total, thirty basins of CAz treated wood were prepared to be tested in the field leaching (Table 2-4). The sections not used for the exposure test were kept as reference samples for the laboratory leaching test.

Figure 2-2 Jack pine CAz treated boards over a basin

Table 2-4 Distribution of the CAz treated boards in basins to be exposed

Species	Basin	Sample	Species	Basin	Sample	Species	Basin	Sample
Jack pine	1	JP 1 A JP 1 D	Hem-fir	6	HF 1 A HF 1 D	Lodgepole Pine	11	LP 1 A LP 1 D
	2	JP 2 A JP 2 D		7	HF 2 A HF 4 A		12	LP 2 A LP 2 D
	3	JP 3 A JP 3 D		8	HF 4 D HF 4 D		13	LP 3 A LP 3 D
	4	JP 4 A JP 4 D		9	HF 5 A HF 5 D		14	LP 4 A LP 4 D
	5	JP 5 A JP 5 D		10	HF 6 A HF 6 D		15	LP 5 A LP 5 D
	26	JP 14 B JP 14 C		21	HF 8 B HF 8 C		16	LP 8 B LP 8 C
	27	JP 12 B JP 12 C		22	HF 11 B HF 11 C		17	LP 6 B LP 6 C
	28	JP 8 B JP 8 C		23	HF 18 B HF 18 C		18	LP 11 B LP 11 C
	29	JP 10 B JP 10 C		24	HF 21 B HF 21 C		19	LP 17 B LP 17 C
	30	JP 7 B JP 7 C		25	HF 24 B HF 24 C		20	LP 20 B LP 20 C

For the CX™ leaching study, each 2 x 6 and 2 x 4 board was cut into 270 mm long sections. Depending on the board width, two or three samples were chosen, to be placed together over a basin. In total, fifteen basins were considered to be exposed to environmental conditions (Table 2-5). Figures 2-3 and 2-4 illustrate the configuration of the simulated decks based on sample-bond width. The remaining boards were kept for the laboratory leaching test.

Table 2-5 Distribution of the CX™ treated boards to be exposed

Charge	Basin	Sample	Dimensions (mm)	
			thickness	width
1	1	A3-1	37.5	87.5
		A3-2	37.5	87.5
		A3-3	37.5	87.5
	2	A10-1	37.5	87.5
		A10-2	37.5	87.5
		A10-3	37.5	87.5
	3	A11-1	37.5	87.5
		A11-2	37.5	87.5
		A11-3	37.5	87.5
	4	A56-1	37.5	140
		A56-2	37.5	140
	5	A58-1	37.5	140
		A58-2	37.5	140
2	6	2B-1	37.5	87.5
		2B-2	37.5	87.5
		2B-3	37.5	87.5
	7	6B-1	37.5	87.5
		6B-2	37.5	87.5
		6B-3	37.5	87.5
	8	14B-1	37.5	87.5
		14B-2	37.5	87.5
		14B-3	37.5	87.5
	9	51B-1	37.5	140
		51B-2	37.5	140
	10	53B-1	37.5	140
		53B-2	37.5	140
3	11	15A-1	37.5	87.5
		15A-2	37.5	87.5
		15A-3	37.5	87.5
	12	18A-1	37.5	87.5
		18A-2	37.5	87.5
		18A-3	37.5	87.5
	13	19A-1	37.5	87.5
		19A-2	37.5	87.5
		19A-3	37.5	87.5
	14	59A-1	37.5	140
		59A-2	37.5	140
	15	63A-1	37.5	140
		63A-2	37.5	140

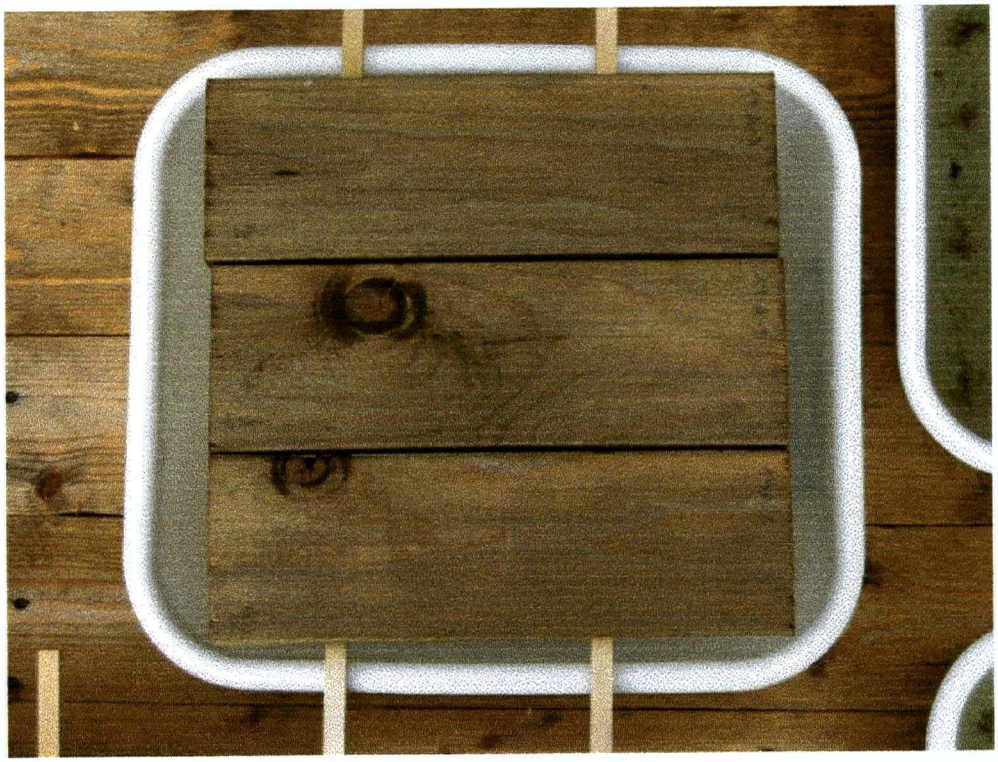

Figure 2-3 CX™ treated wood (37.5 mm x 87.5 mm) over a basin

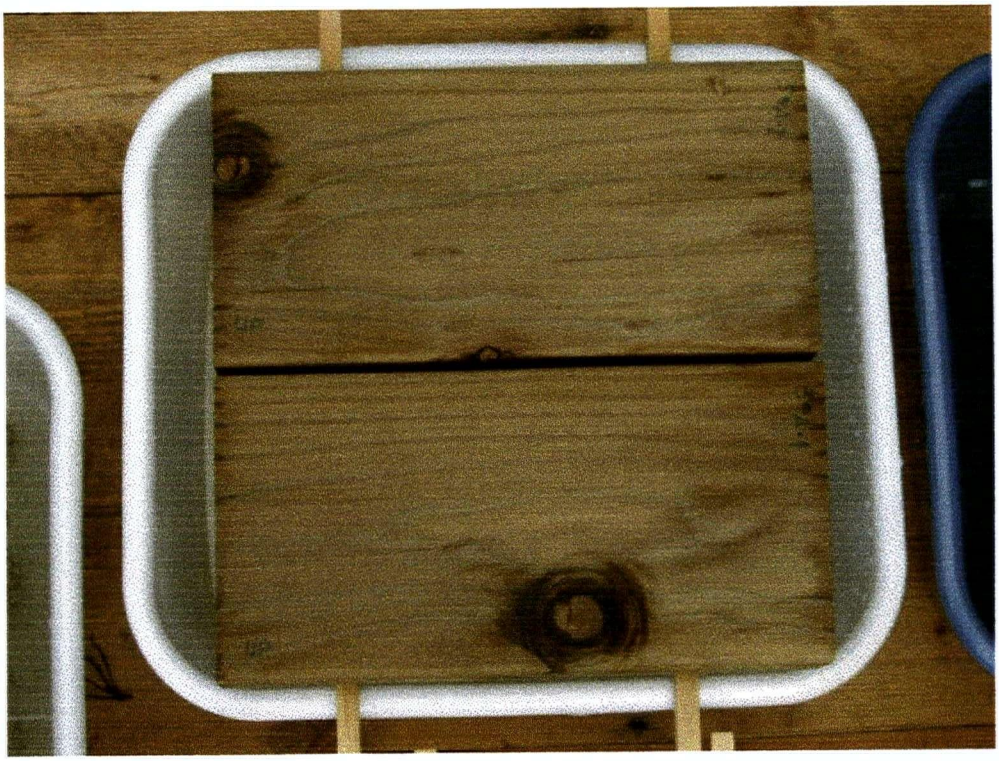

Figure 2-4 CX™ treated wood (37.5 mm x 140 mm) over a basin

2.3.1.3 Post-treatments Application

Each ACQ treated '2 x 4' board purchased at The Home Depot was cut into sections of 270 mm long. Ten samples were recovered from each original board. This allowed for the sample size to be increased to 40. Before the exposure, two post-treatments were applied to representative sections: a water repellent application and a water pressure treatment. Three sections from each original board were coated with a water repellent, while a second group of three sections were subjected to water pressure treatment. Three sections were included as control samples, and the last section was retained as a reference sample. Three sections of each post treatment and the control were placed over basins for exposure tests (Figures 2-5, 2-6 and 2-7). Each basin had boards with one variable: water repellent, pressure wash or no treatment. This part of the study therefore involved four replicates per post-treatment and per control from different boards (Table 2-6).

For the water repellent post-treatment, a commercial water repellent, Thompson's Ultra Waterseal brand was purchased from a local Home Depot™. This silicon based water repellent is waterborne and can be used with several materials that are to be used in outdoor structures. According to the manufacturer, the water repellent can remain active on the surface of the board for about 4 years. The treatment was conducted according to the specifications of the product:

- The surface to be coated was brushed to clean the surface of the board
- The water repellent was applied to all the sides of the small section boards with a brush.
- One coat of the water repellent was applied, according to manufacturer instructions.
- After 15 minutes the excess was removed from the surface.
- The surfaces coated were allowed to dry before being placed over a basin for exposure.

The water pressure post-treatment was conducted using a pressure vessel at Forintek Canada Corp., Vancouver, Canada. The three small sections from the same original board were placed inside the pressure unit and the door closed. An initial vacuum was applied for 15 minutes to remove the air from the wood and the unit. The vacuum was then used to drain water into the vessel until it was full. A pressure of 1035 kPa was then applied for 15 minutes. The water (leachate) was run off from the unit and a sample was collected for analysis. The methodology was repeated three more times without changing the water and taking a sample in every time that

the water was run off. The remaining three replicates from each of the other three original boards were also post-treated using this procedure.

Table 2-6 Distribution of the ACQ treated boards with post-treatments to be exposed

Control		Water Repellent		Water Pressure	
Basin	Board	Basin	Board	Basin	Board
	1-1		1-2		1-3
1	1-6	5	1-7	9	1-4
	1-9		1-10		1-8
	2-1		2-2		2-3
2	2-5	6	2-7	10	2-4
	2-9		2-10		2-8
	3-1		3-2		3-3
3	3-5	7	3-7	11	3-4
	3-9		3-10		3-8
	4-1		4-2		4-3
4	4-5	8	4-7	12	4-4
	4-9		4-10		4-8

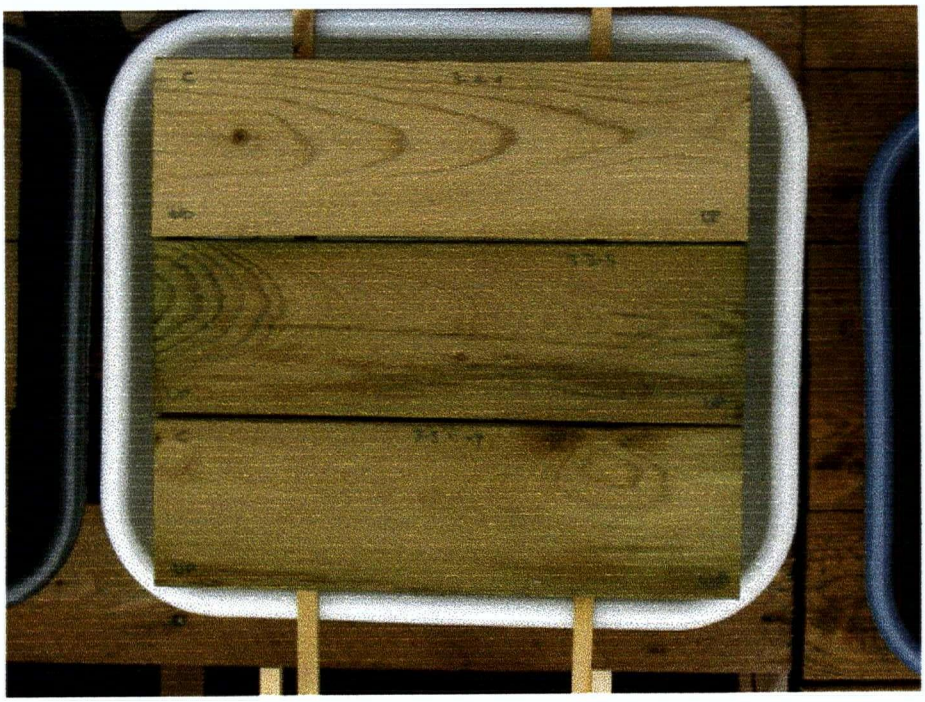

Figure 2-5 Control ACQ treated boards over a basin

Figure 2-6 ACQ treated boards with water repellent post-treatment over a basin

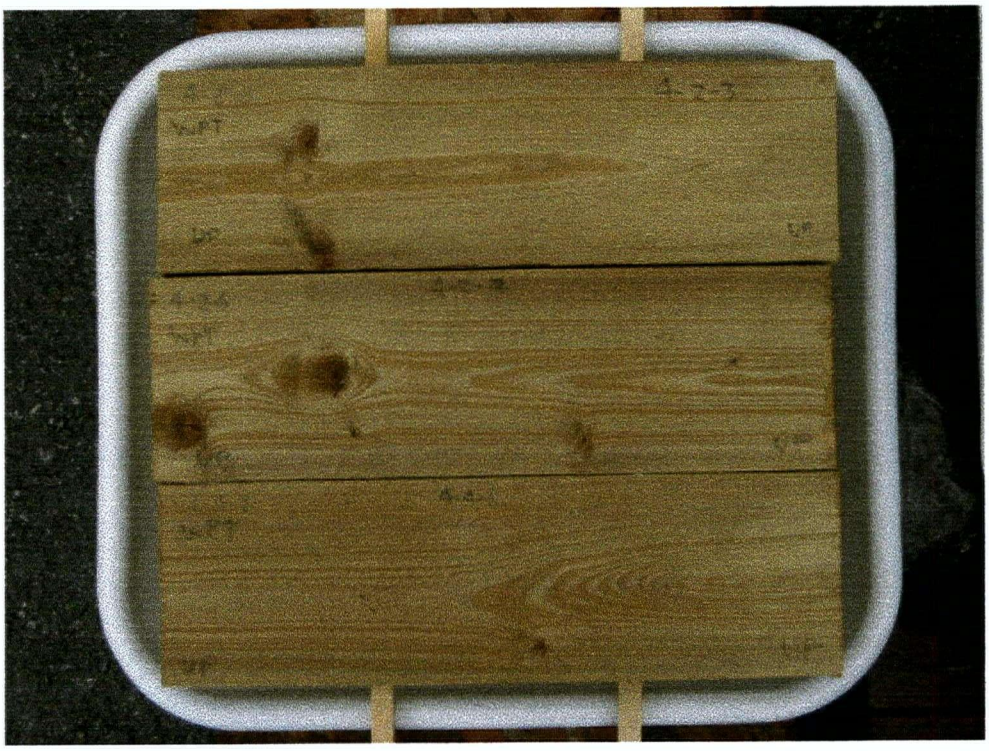

Figure 2-7 ACQ treated boards with a water pressure post-treatment over a basin

2.3.1.4 Exposure

The basins with the boards were exposed to the environmental conditions at the University of British Columbia, in Vancouver, Canada (Figures 2-8 and 2-9). The basins were placed in a location which maximized the amount of sun hours (east-west) and the direction of the rain (west-south).

The exposure test of the treated boards was initiated at different times. The original experiment with the ACQ treated boards began in August 2002, while that for the CAz treated boards began in June 2003. The CX™ treated boards were installed in test in February 2004, and finally, the ACQ-t (with supplemental treatment) exposure test began in March 2004. The different starting dates reflected the receipt of the test boards. Each month (or more frequently during heavy rain) a sample of leachate, produced by the rainfall, was collected from each basin and analyzed. The total leachate volume was also recorded together with measurements of weight, and surface moisture content of the samples. After the leachate was collected and the volume of leachate recorded, the basins were washed with distilled water and placed back in test with the boards to continue the exposure. In the reported study here, the times of exposure were 26 months for ACQ treated wood, 16 months for CAz treated wood, 7 months for CX™ treated wood and 6 months for ACQ-t boards. Records of the weather conditions during the time of the exposure were collected from Environment Canada web site.

Figure 2-8 Distribution of the basins for exposure (left view)

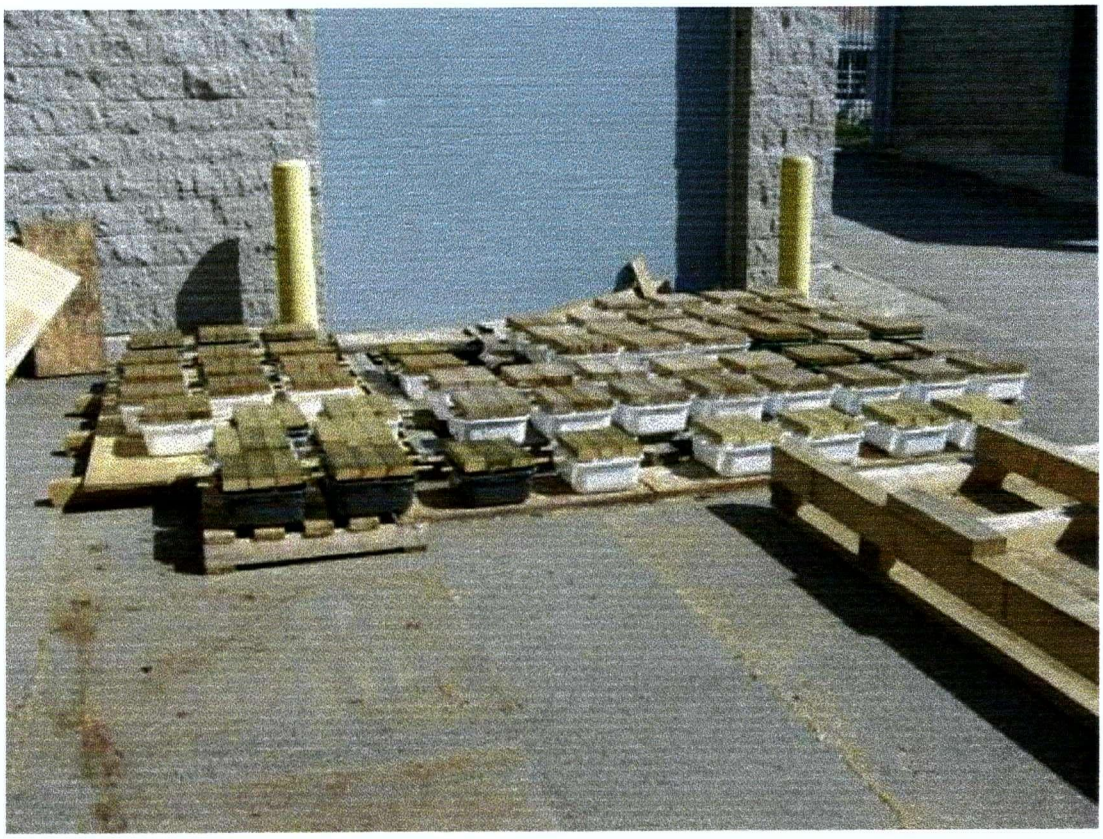

Figure 2-9 Distribution of the basins for exposure (front view)

2.3.1.5 Analysis of the leachate

The leachate samples collected every month from the basins and from the water pressure post treatment were analyzed for copper by Atomic Absorption Spectrometry (Varian Spectra 10/20) according to the AWPA A11-93-2003 standard. For calibration, standard copper solutions of 0.5 ppm, 1 ppm, 2 ppm, 4 ppm, 6 ppm, 8 ppm and 10 ppm were prepared using a commercial 1000 ppm standard copper concentration (BDH®). When the leachates produced higher copper concentrations, the samples were diluted with distilled water to ensure a maximum copper concentration of less than 10 ppm.

The amount of secondary biocide quaternary compound (quat) in the leachates from the ACQ boards was analyzed using a standard titration according to AWPA A17-03 and AWPA A18-03 (AWPA, 2003). Prior to every titration, the glassware used to do the analysis was washed with 0.1% sulfuric acid and distilled water. In addition, samples were sent to CSI to be analyzed for the amount of quat in the leachate by a High Performance Liquid Chromatography (HPLC) according to AWPA standard A16-93 (AWPA, 2003). To analyze the amount of tebuconazole in the leachates from the CAz treated boards, samples of leachate were sent to Arch Wood Protection Inc. to be analyzed by HPLC (AWPA A28-01, AWPA 2003).

2.3.1.6 Analysis of Copper mobility

The analysis of copper mobility into checks was conducted using the methodology reported by Choi *et al.* (2004). Only hem-fir treated boards, which developed the deepest checks compared to other wood species, were analyzed. Two hem-fir ACQ treated boards and three CAz treated boards were chosen for the analysis. The boards were selected based on the depth of the check that extended into the untreated part of the wood. To verify that the check reached the untreated part, the boards were visually compared to the reference sample. Three boards were selected for ACQ treated boards and the same number was selected for the CAz treated boards. A small sample that included a check was taken from each board (approximately 30 mm long, the width and depth depending on the size of the check-Figure 2-10). From each check sampling location, three sections were identified: surface check, inside check and treated part (Figure 2-11). A small thin section of each part was removed and then, measured, weighed and digested separately in nitric acid and analyzed by atomic absorption for copper, according to standards

AWPA A7-93 and AWPA A11-93 (AWPA, 2003). In addition, from the reference material, untreated and treated parts were also analyzed as a control.

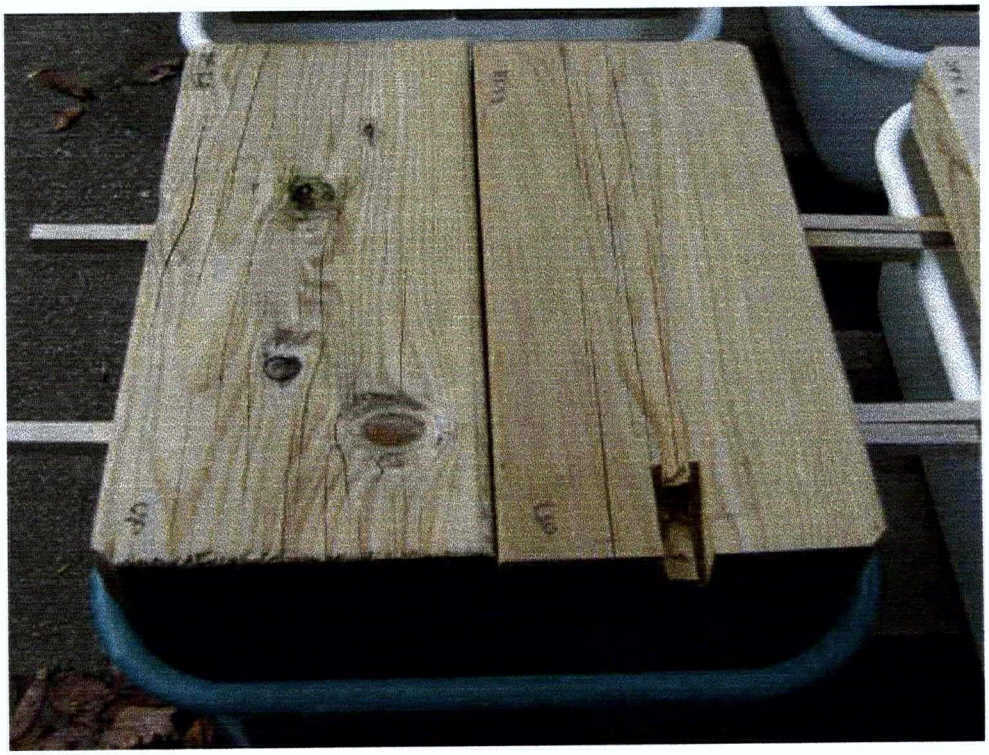

Figure 2-10 Check sample taken from the board exposed for analysis of copper mobility

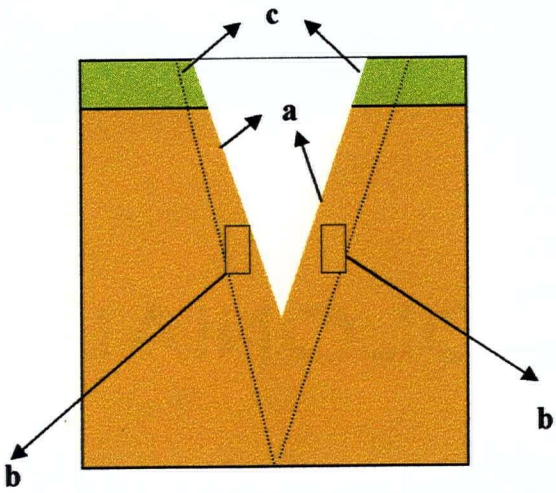

Figure 2-11 Diagram of the check for analysis: (a) check surface, (b) inside check, (c) treated part, and (d) outside untreated part

2.3.2 Laboratory Leaching

Accelerated laboratory leaching was conducted using sawdust generated from the upper surface of each reference sample corresponding to the upper surface of each board exposed in the field leaching. The purpose of this part of the study was to determine the maximum amount of copper that could be removed from the treated wood under the extreme laboratory leaching conditions. Since the sawdust has a very high surface area compare to solid wood, the recovery of the mobile copper should approach the total amount of mobile copper.

2.3.2.1 Sample Preparation

To verify the copper content of the samples prior to leaching, the upper sections of the reference samples were removed, ground to sawdust and analyzed using an Asoma™ X-ray Fluorescence Analyzer according to the AWPA A9-01 standard (AWPA 2003). The copper retention in the X-ray analyzer was expressed as a measure of copper oxide (CuO). The density used was the standard density recommended by AWPA A12-03 (AWPA 2003).

Two methods were used to produce sawdust from the references samples. In the case of ACQ treated boards, because the reference samples were small, the upper treated section (2-6 mm penetration) was removed and ground into 40-60 mesh sawdust using a Wiley mill. For the CAz treated wood, CX™ treated boards and ACQ-t treated boards, a router was used to produce the sawdust at several depths of the surface of the reference sample board (Figure 2-12). The sawdust produced by the router was collected in a 60 mesh filter attached to a vacuum machine (Figure 2-13). For the CAz and ACQ-t treated boards, sawdust was collected from the router at 1.5 mm depth from the surface of the boards since a shell treatment was observed in most of the boards (Figure 2-14). For the CX™ treated boards, sawdust was collected over the zone 0 to 5.0 mm from the surface because this was the typical penetration depth reached in those treatments. Before leaching, the sawdust was first screened from 40 to 60 mesh to maintain equal size of sawdust particles and the screened sawdust was then analyzed by the X-ray.

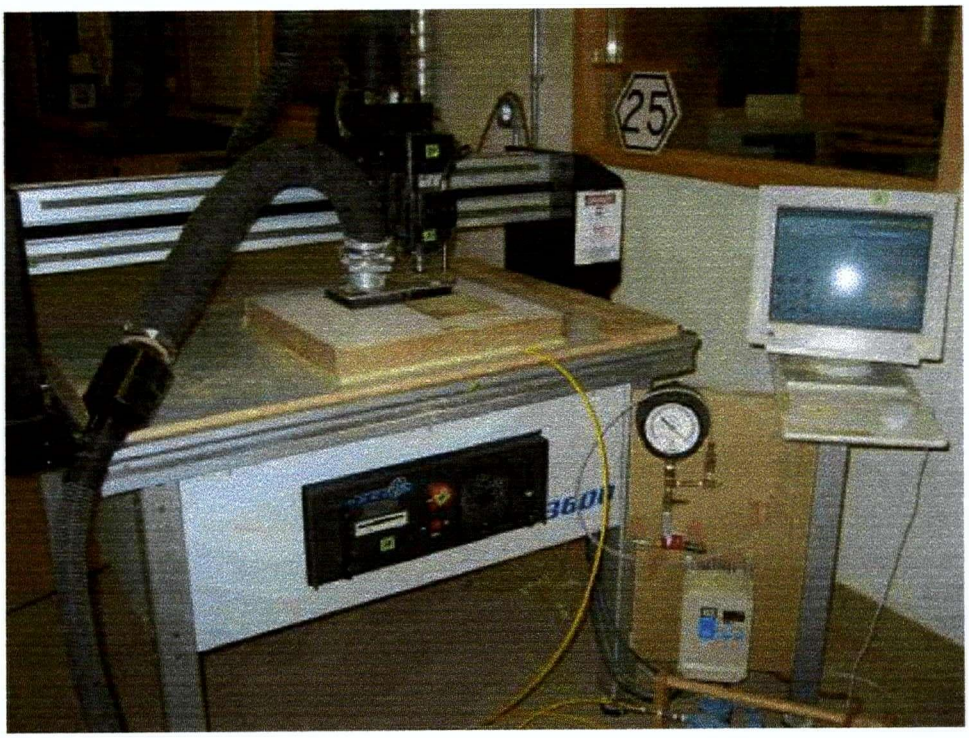

Figure 2-12 Router used to produce sawdust

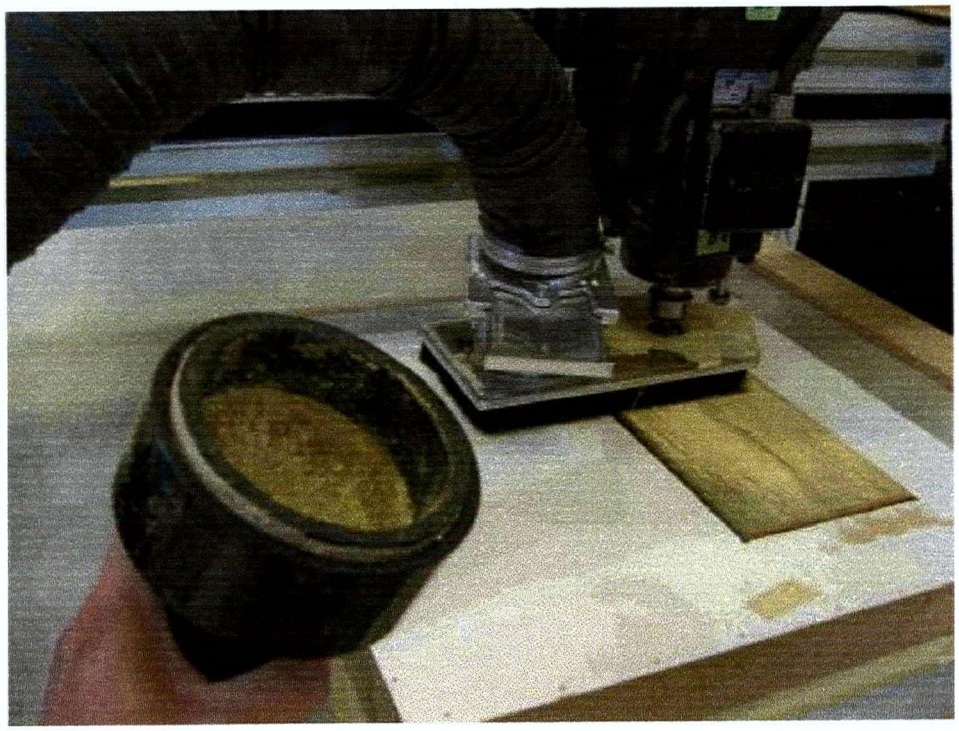

Figure 2-13 Filter used to collect the sawdust

Figure 2-14 Comparison of the Jack Pine board before and after being sawn by the router

2.3.2.2 Leaching

The laboratory leaching was done in two different ways. The first method was designed for the original ACQ treated boards, in which the reference samples were smaller. The second approach was designed for all the other boards. In the first method, approximately 2 g. of sawdust produced from the reference samples of each ACQ treated board were placed in a beaker with 100 ml of distilled water. Plastic film and parafilm were used to cover the beaker to avoid vapour losses during leaching. To perform the leaching process, the beakers were placed in an ultrasonic bath for 24 hours and then allowed to stand on the bench for 48 hours of static leaching. The sawdust was then removed by filtering with Whatman N°1 filter paper. The leachate was collected for analysis. The sawdust was returned to the beaker with a fresh 100 ml of distilled water and covered with plastic and parafilm and then subjected to the leaching process again. This procedure was repeated one more time so that each sample was subjected to a total of three leaching phases. After being leached three times, the sawdust was dried and analyzed by the X-ray analyzer to determine the amount of copper remaining in the sawdust after leaching.

A second method was designed for the CAz, CX™ and ACQ-t treated wood to estimate the loss of copper at determined time intervals during the leaching process. A 3 g. of sample sawdust from each original board was placed in a beaker and 50 ml of distilled water was added. Three replicates from each board were used in the leaching study. A magnetic stirrer was placed in each beaker and the solution stirred at room temperature. At intervals of 1, 3, 6, 24, 48 and 72 hours, 10 ml samples of leachate were removed by pipette for analysis by atomic absorption spectroscopy (AWPA A11-93, AWPA 2003). Each time a sample was removed 10 ml of distilled water was added to maintain the volume of the leachate. After taking the last sample at the 72 hour interval, the sawdust was filtered out using Whatman N°1 filter paper, then dried and analyzed by X-ray analyzer to determine the amount of copper remaining after leaching.

2.3.2.3 Analysis of leachate

The analysis of leachate was done using the same methodology described in the section 2.3.1.5, Field leaching.

2.3.2.4 Analysis of copper leached

The amount of copper leached during the field experiment is expressed in two different ways. The first is the amount of copper leached per upper surface area exposed in the basins (mg/m^2) and as the percentage of the amount of total copper contained in the four treated sides of the boards. The analysis of the copper loss in the laboratory leaching is expressed as a percentage of the total initial copper content measured by the X-ray analyzer from the unleached sawdust.

2.3.3 Statistical Analysis

Statistical analysis of the results was conducted using the software JMP IN version 4.0.3. (SAS Institute Inc.) and Microsoft Excel 2003. For the analysis of the field leaching, analysis of variance was used per each group of treated boards to determine differences among the variables of the leaching. Also, a mathematical model of the copper losses during the period of exposure was suggested for the three groups of treated boards. For the laboratory leaching, analysis of variance was used per group of treated boards, as well. The type of the analysis depended on the

group of treated board. A Tukey-Kramer's test was conducted after the analysis of variance to determine the differences among the means. In addition, with the information obtained in the laboratory leaching and with the mathematical model suggested for copper losses, a prediction of the time remaining to deplete the total amount of free copper was calculated. For all the statistical analysis the level of confidence was 95% (α=0.05).

2.3.3.1 CAz treated boards

For the CAz field leaching, a block design analysis of variance was considered per species, being the blocks the basins containing boards with or without treated ends section. For the laboratory leaching, a one way analysis of variance was also considered. The analysis allowed determination of the differences in copper leaching from the ten boards (retention), using three replicates per board.

2.3.3.2 CX™ treated boards

In the case of CX™ treated boards, the field leaching experiment was analyzed with an analysis of variance with factorial 3 x 2 (Table 2-7). The first factor was the treatment charge. According to the information from Dr. Wolman GmbH, the boards were treated in three different treatment charges: full cell, modified full cell A and modified full cell B. The second factor was the dimension of the boards. Two different dimensions of the sizes were exposed to the field leaching: 35.7 x 87.5 mm. and 37.5 x 140 mm. Three replicates were taken for the dimension 35.7 x 87.5 mm. and two replicates for the dimensions 37.5 x 140 mm. For the laboratory leaching, a one way analysis of variance was also considered.

Table 2-7 Design of experiment for the CX™ treated boards

Factor A: Treatment Charge	Full Cell: 4.32 kg/m^3		Modified Full Cell A: 3.81 kg/m^3		Modified Full Cell B: 2.86 kg/m^3	
Factor B: Dimension	2 x 4	2 x 6	2 x 4	2 x 6	2 x 4	2 x 6
Replicates	3	2	3	2	3	2

2.3.3.3 ACQ-t treated boards

For the ACQ-t, the analysis of variance used was a complete randomized design one way analysis of variance. The treatments were the two post-treatments and control and the replicates were the twelve basins. The design could determine the effect of the post-treatment in the amount of copper leached. The laboratory leaching was analyzed by a complete randomized design.

Chapter 3

Leaching of Copper in ACQ treated wood

3.1 Introduction

ACQ is one of the new preservatives that has replaced CCA for the treatment of wood for use in residential construction. Currently, ACQ treated wood has become commercially successful in Europe, Japan and the USA. Although four types of ACQ have been standardized in North America, the type C is the formulation most widely used. No studies have been reported on leachability of copper from hem-fir decking treated with this preservative. Information on the leaching resistance of the ACQ-treated wood is required to support ongoing registration in Canada.

The objective of this part of the research was to determine the rate of copper loss during the initial 26 months of exposure, from boards simulating the use as a decking. This loss was compared with the results of a laboratory-accelerated leaching study. The data obtained were used to fit an equation that can predict the cumulative amount of copper leached after a 20 year-period of exposure. The amount of "quat" compound leached was also determined. An additional analysis was conducted to confirm the redistribution of the copper onto the untreated surface of checks which developed in the upper surface of ACQ treated wood when it is in service. Finally, the impact of two post-treatments of the ACQ-treated boards on copper leaching was analyzed. It was hypothesized that a water pressure post-treatment would remove much of the unfixed copper thus decreasing the initial amount leached when the treated wood is first placed in service. Since water repellents protect wood against the effect of rain, by lowering water penetration into wood. This should reduce copper losses. In addition, the water repellent will reduce the dimensional changes and diffusion of copper from the interior to the surface of the wood.

3.2 Results and Discussion

3.2.1 Initial Measurements

The weight uptake data of the preservative in the boards provided by CSI is shown in Table 3-1. The average weight uptake was 0.75 kg of 1% ACQ solution, with a composition of 67.4% of copper (as CuO) and 33.6% of quat BAC. The average copper retention was 5.05 g/board, while the average quat retained was 2.52 g/board. Also, the copper penetration was measured from four surfaces of the boards, taking the average from three measurements of the side. The side chosen for the upper face exposed directly to the sunlight was the wide face with the lower penetration. The average of copper penetration was 3 mm for the top surface and 5-6 mm for the other three faces. By combining the amount of copper retained in the treated wood with the volume of treated wood, the total available copper for each test sample could be determined. This was used in determining the percentage loss of copper during exposure.

Table 3-1 Initial Measurements of the ACQ treated wood

Board	Weight before treatment (kg)	Weight after treatment (kg)	Weight uptake (kg)	Amount of copper (CuO) in wood (g)	Amount of quat in wood (g)	Penetration (mm)			
						Top	Bot.	Side 1	Side 2
1-1	0.83	1.36	0.53	3.57	1.78	2	3	2	3
1-2	0.85	1.41	0.56	3.77	1.88	2	4	6	2
1-3	0.85	1.48	0.63	4.25	2.12	2	5	7	1
1-4	0.83	1.45	0.62	4.18	2.08	2	2	4	1
2-1	0.84	1.69	0.85	5.73	2.86	4	3	9	6
2-2	0.83	1.59	0.76	5.12	2.55	3	5	10	4
2-3	0.86	1.61	0.75	5.06	2.52	3	4	4	7
2-4	0.87	1.59	0.72	4.85	2.42	4	3	5	3
3-1	0.74	1.59	0.85	5.73	2.86	3	7	7	6
3-2	0.79	1.73	0.94	6.34	3.16	4	7	13	4
3-3	0.85	1.8	0.95	6.40	3.19	6	6	3	12
3-4	0.83	1.66	0.83	5.59	2.79	3	6	4	10
Average	0.83	1.58	0.75	5.05	2.52	3	5	6	5
St. dv.*	0.04	0.13	0.14	0.95	0.47	1.2	1.7	3.1	3.1

*** Standard deviation**

3.2.2 Analysis of copper leaching

The exposure conditions for the test samples are listed in Appendix 1 and the amount of copper (expressed as CuO mg/basin) measured on a monthly basis are shown in the Table 3-2; together with the volume and pH of the leachate. The results of the study suggest that the volume of leachate is correlated with the amount of monthly precipitation. It is obvious to think that the rainfall causes the copper leaching and that the higher amount of rainfall, the higher amount of volume leachate. In extended periods of hot weather, the high temperature may cause some evaporation of the leachate slightly decreasing the volume collected. However, when evaporation occurs, the copper remains in solution in the basin, and the copper concentration is increased slightly. In the first months of exposure, the pH of the leachate was approximately 7, which is slightly higher than the pH of the rain (5-6, see Table 3-2). This is interpreted as being caused by a small amount of amine being leached (0.01M Monoethanolamine has approximately pH 11). After about 10 months, the pH began to decrease becoming similar to the pH of the rain. The variation of pH in the leachate could be influenced by the amount of copper leached. The relationship between the amount of copper leached and pH was reported previously by Ruddick (1992). During accelerated leaching of ammoniacal copper arsenate treated blocks the pH of the leachate decreased with decreased copper leaching

Higher amounts of leachable copper were found in the first four months of exposure (August to November). During this period, it was clear that the first amount of rain, even though small, could leach high amounts of copper (54-27 mg of copper expressed as CuO). During the following months, the amount of copper that leached tended to decrease, reaching less than 1 mg of CuO (August, 2003; April, June, July 2004). These low values were determined even though the amount of rainfall was, in some cases, similar to that occurring during the first four months. In the month of June, 2003, no leachate was collected due to a combination of absorption by the dry wood and evaporation. The amount of copper leached in July, 2003 represents the cumulative effects of rain for both June and July, 2003. A small increase in the amount of copper leached was observed, after the summer seasons (June-August), and when the first rainfall started (September-October, 2003 and August, 2004). These small increases, after the summer season, were lower in the second year of the experiment presumably due to the decreasing amount of free mobile copper in the wood. The average cumulative amount of copper (expressed as CuO) leached after 26 months of exposure was 360.41 mg per basin.

Table 3-2 Monthly measurements of leachate volume and pH of rainfall and copper present in leachate from ACQ treated wood*

Month	Volume of leachate (L)	pH	pH of the rainfall	Amount of copper (CuO) leached (mg)	Cumulative amount of copper (CuO) leached (mg)
Aug-02	0.95 (0.23)**	7.14 (0.25)	n.a.	54.60 (15.29)	54.60
Sep-02	0.43 (0.11)	7.09 (0.42)	n.a.	27.25 (7.28)	81.85
Oct-02	4.75 (0.68)	7.67 (0.45)	n.a.	46.89 (14.08)	128.74
Nov-02	11.72 (1.11)	7.10 (0.33)	n.a.	52.16 (8.49)	180.90
Dec-02	6.40 (0.89)	7.06 (0.29)	n.a.	17.38 (6.24)	198.28
Jan-03	6.85 (0.93)	7.16 (0.12)	5.90	11.14 (3.44)	209.42
Feb-03	0.95 (0.18)	7.37 (0.18)	n.a.	3.21 (0.92)	212.63
Mar-03	6.59 (1.12)	7.25 (0.07)	6.69	7.47 (2.78)	220.10
Apr-03	5.60 (1.27)	6.85 (0.12)	6.62	7.19 (3.19)	227.29
May-03	0.48 (0.22)	6.72 (0.16)	n.a.	5.34 (1.84)	232.63
Jun/Jul-03	3.77 (1.16)	6.41 (0.12)	n.a.	12.82 (1.83)	245.45
Aug-03	0.04 (0.01)	6.93 (0.04)	n.a.	0.95 (0.16)	246.40
Sep-03	0.37 (0.18)	6.40 (0.06)	6.72	10.75 (2.89)	257.14
Oct-03	17.12 (0.98)	6.34 (0.76)	5.69	23.36 (3.76)	280.51
Nov-03	15.08 (0.65)	6.40 (0.07)	n.a.	10.19 (2.66)	290.70
Dec-03	10.22 (0.47)	6.51 (0.07)	5.60	11.05 (1.44)	301.75
Jan-04	13.62 (1.30)	6.60 (0.05)	5.43	14.65 (3.96)	316.39
Feb-04	6.02 (0.36)	6.74 (0.06)	5.99	6.36 (1.67)	322.75
Mar-04	6.03 (0.54)	6.75 (0.03)	6.49	5.11 (1.05)	327.87
Apr-04	0.25 (0.00)	6.50 (0.14)	5.99	1.03 (0.16)	328.90
May-04	3.09 (0.19)	6.46 (0.05)	6.50	7.53 (0.77)	336.43
Jun-04	0.41 (0.07)	6.34 (0.06)	5.99	1.78 (0.29)	338.21
Jul-04	0.53 (0.04)	5.56 (0.06)	6.03	1.85 (0.31)	340.06
Aug-04	3.64 (0.14)	6.28 (0.08)	6.12	13.75 (1.09)	353.33
Sep-04	6.91 (0.54)	6.12 (0.12)	4.84	7.08 (1.63)	360.41

***Average of the evaluations**

**** Values within parenthesis represent the standard deviation of the measurements**

n.a. not available

The relative loss of copper is presented in four ways (Table 3-3 and 3-4 and Figures 3-1 to 3-4). First, the copper leached was related to the total copper content in each group of boards based upon the weight uptake data provided by CSI. When measured this way the cumulative percentage copper leached after 26 months of exposure was 4.89%. The second approach was to determine the copper leached in terms of copper content based on the measured retention and the volume of treated wood in the test samples. This cumulative amount of copper leached was approximately 6.15%. Errors in this calculation arise due to the varying penetration of copper along the surface of the wood. Also, end penetration was ignored which will exaggerate the calculated copper loss slightly. The third approach was used to determine the loss of copper in relation to the deck upper surface area (top surface area). This approach is useful in expressing loss for a projected deck surface area, commonly of interest for calculating environmental load due to leaching, for the present study the area the simulated area of the deck in the basins was 0.0735 m^2. Based on this measure, the cumulative loss of copper after 26 months of exposure was 3917 mg/m^2. Finally, the fourth approach was used to determine the amount of copper leached in relation of the surface area, likely impacted by direct contact with the rainwater namely the top surface and the sides.. The ends in most cases were untreated and they tend to reduce copper loss by removing copper (ion exchange) from any leachate that passed over the end grain. For this study the exposed area of the boards in the basins was 0.137 m^2. Using this approach, the cumulative amount of copper leached after 26 months of exposure was 2640 mg/m^2.

The trend of copper losses shown in Figure 3-3 is based on the amount of copper leached monthly, expressed in mg/m^2 of the top surface only. In addition, the amount of leachate collected is shown. As mentioned, the first four months of exposure August-November, 2002, resulted in the highest amounts of copper leached. After the first four months, the general amount of copper leaching decreased to a low value of 10 mg/m^2 in August, 2003. A significant increase in copper leaching was observed when the dried wood was wetted by the first rain in the fall of 2003 (September-October). This process appears to be cyclical because a small increase was again observed at the start of the rainy season in August, 2004.

Table 3-3 Average of amount of copper leached per month referred in percentage from ACQ treated boards

Month	reference weight uptake		reference treated volume	
	Amount of copper (CuO) leached per month (%)	Amount of copper (CuO) leached per month (%) cumulative	Amount of copper (CuO) leached per month (%)	Amount of copper (CuO) leached per month (%) cumulative
Aug-02	0.74 (0.21)	0.74	0.92 (0.22)	0.92
Sep-02	0.37 (0.11)	1.11	0.47 (0.14)	1.39
Oct-02	0.64 (0.21)	1.75	0.80 (0.28)	2.19
Nov-02	0.71 (0.11)	2.46	0.42 (0.08)	3.07
Dec-02	0.24 (0.08)	2.69	0.30 (0.11)	3.37
Jan-03	0.15 (0.05)	2.84	0.19 (0.07)	3.57
Feb-03	0.04 (0.01)	2.89	0.06 (0.02)	3.62
Mar-03	0.10 (0.04)	2.99	0.13 (0.05)	3.75
Apr-03	0.10 (0.05)	3.09	0.12 (0.06)	3.87
May-03	0.07 (0.02)	3.16	0.09 (0.03)	3.96
Jun/Jul-03	0.17 (0.02)	3.33	0.22 (0.04)	4.18
Aug-03	0.01 (0.00)	3.35	0.02 (0.00)	4.20
Sep-03	0.15 (0.04)	3.49	0.18 (0.05)	4.38
Oct-03	0.32 (0.05)	3.81	0.40 (0.08)	4.78
Nov-03	0.14 (0.04)	3.95	0.17 (0.04)	4.96
Dec-03	0.15 (0.02)	4.10	0.19 (0.03)	5.15
Jan-04	0.20 (0.05)	4.30	0.25 (0.25)	5.40
Feb-04	0.09 (0.02)	4.38	0.11 (0.03)	5.50
Mar-04	0.07 (0.02)	4.45	0.09 (0.02)	5.59
Apr-04	0.01 (0.00)	4.47	0.02 (0.00)	5.61
May-04	0.10 (0.01)	4.57	0.13 (0.02)	5.74
Jun-04	0.02 (0.00)	4.59	0.03 (0.00)	5.77
Jul-04	0.03 (0.00)	4.62	0.03 (0.01)	5.80
Aug-04	0.18 (0.02)	4.80	0.23 (0.03)	6.03
Sep-04	0.10 (0.02)	4.89	0.12 (0.03)	6.15

** Values within parenthesis represent the standard deviation of the measurements

Table 3-4 Average of amount of copper (as CuO) leached per month referred in mg/m^2 from ACQ treated wood

Month	Reference deck area*		Reference exposed area**	
	Amount of copper (CuO) leached (mg/m^2)	Cumulative amount of copper (CuO) leached (mg/m^2)	Amount of copper (CuO) leached (mg/m^2)	Cumulative amount of copper (CuO) leached (mg/m^2)
Aug-02	593	593	400	400
Sep-02	296	889	200	600
Oct-02	510	1399	344	943
Nov-02	541	1966	382	1325
Dec-02	189	2155	127	1453
Jan-03	121	2276	82	1534
Feb-03	35	2311	24	1558
Mar-03	81	2392	55	1613
Apr-03	78	2470	53	1665
May-03	58	2528	39	1704
Jun/Jul-03	139	2667	94	1798
Aug-03	10	2678	7	1805
Sep-03	117	2794	79	1884
Oct-03	254	3048	171	2055
Nov-03	111	3159	75	2130
Dec-03	120	3279	81	2211
Jan-04	159	3438	107	2318
Feb-04	69	3507	47	2365
Mar-04	56	3563	38	2402
Apr-04	11	3574	8	2410
May-04	82	3656	55	2465
Jun-04	19	3675	13	2478
Jul-04	20	3696	14	2491
Aug-04	144	3840	97	2589
Sep-04	77	3917	52	2640

* upper surface board only

** Upper and two side surfaces per board

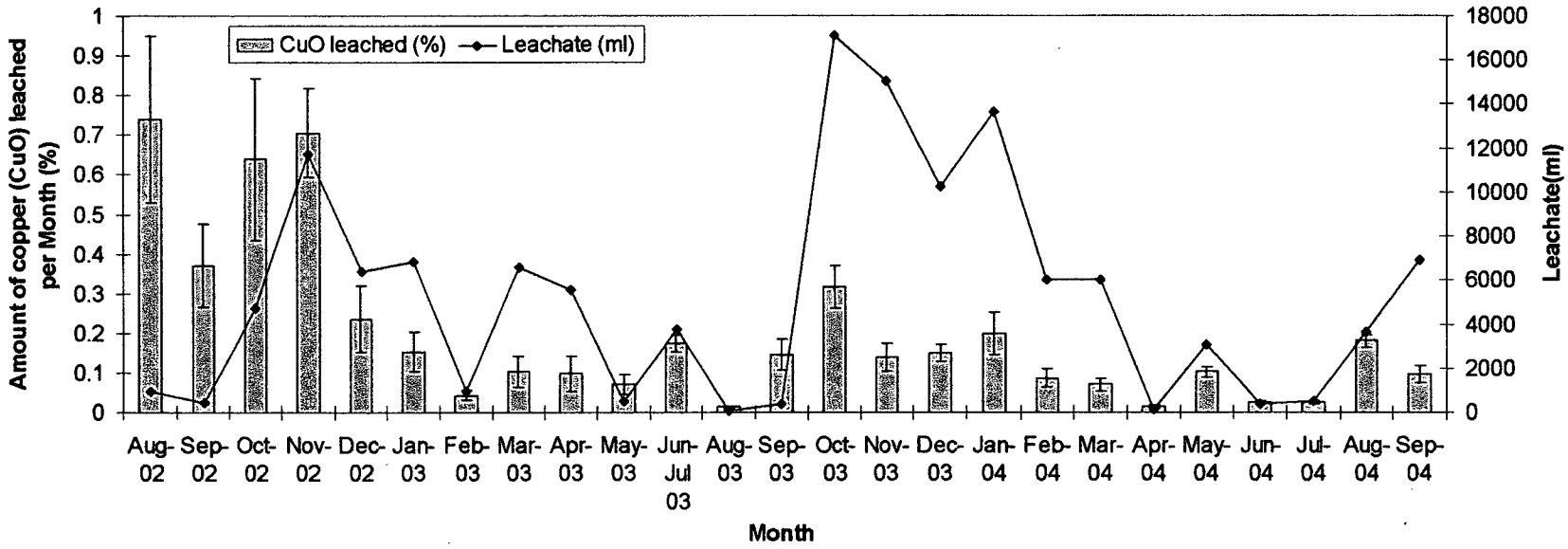

Figure 3-1 Amount of copper (as CuO) leached (% of the weight uptake) per month from ACQ treated wood exposed above ground

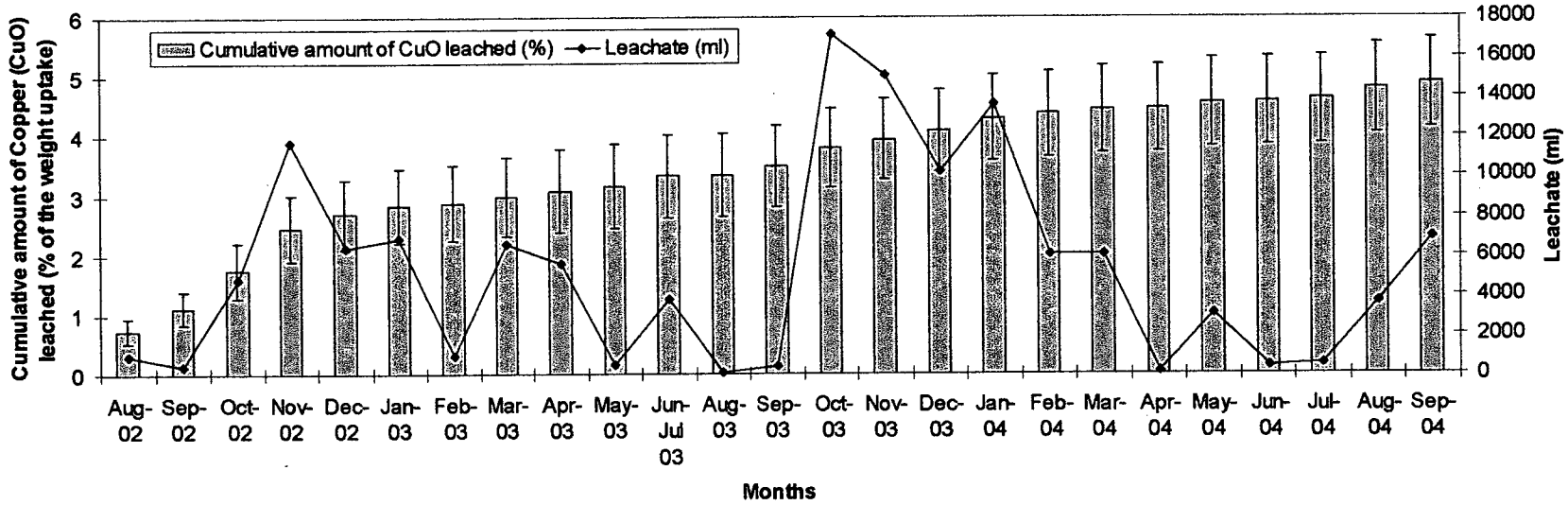

Figure 3-2 Cumulative amount of copper (as CuO) leached (% of the weight uptake) per month from ACQ treated wood exposed above ground

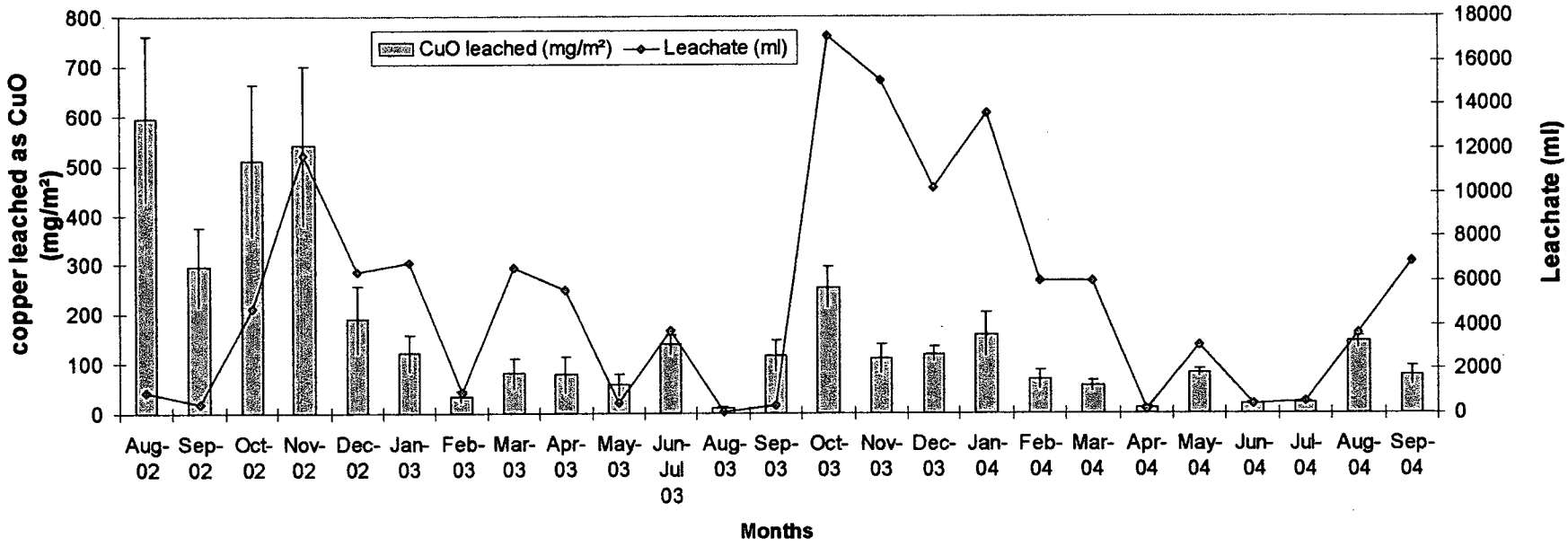

Figure 3-3 Amount of copper (as CuO) leached (mg/m^2) per month from ACQ treated wood exposed above ground based on upper surface area only

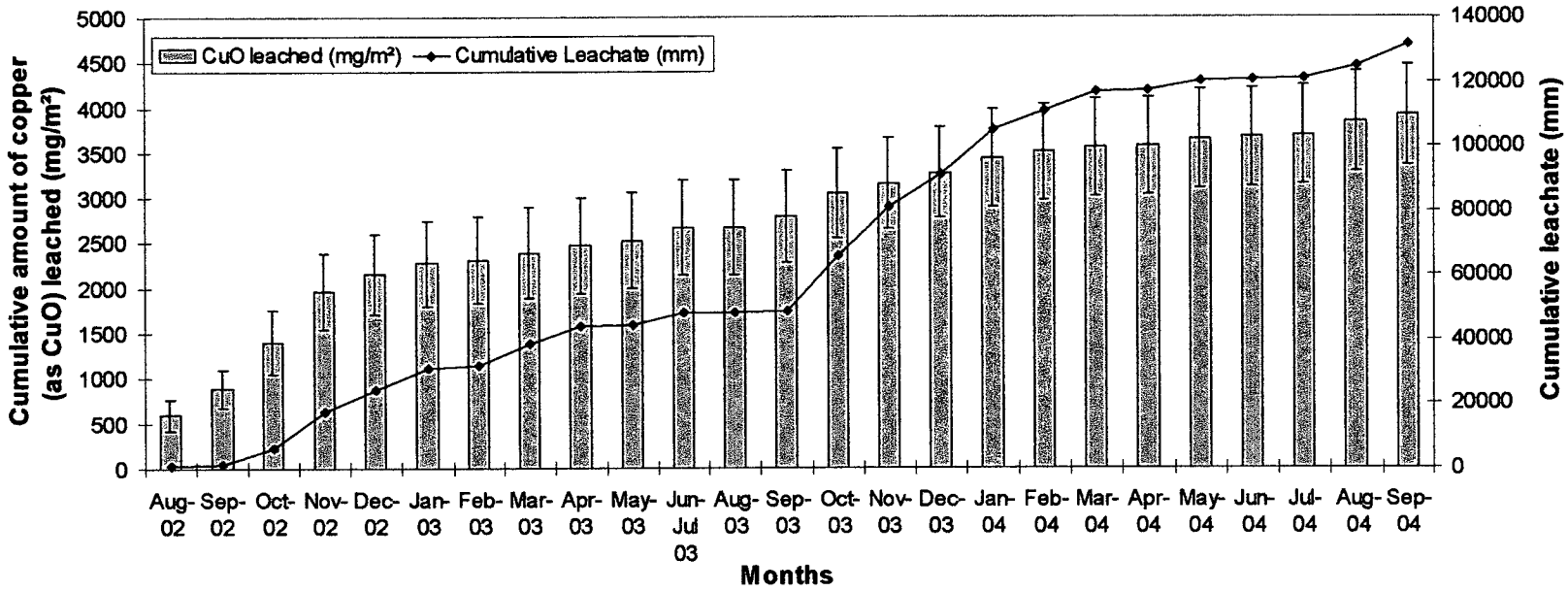

Figure 3-4 Cumulative amount of copper (as CuO) leached (mg/m^2) per month from ACQ treated wood exposed above ground based on upper surface area only

It is proposed that three different processes are involved in the copper leaching from decking. These include the rapid initial loss of unfixed copper from the surface of the wood; diffusion of copper from the inner treated zone when the wood is wet; and copper transportation by water movement during the evaporation of water from the wood surface during drying. These mechanisms combined to account for the first years of copper leaching during exposure and are illustrated in Figure 3-5. This figure shows the early loss of mobile copper located at or very close to the surface of the test boards during the first months. In this case, a small amount of rain can easily remove the unfixed copper (Figure 3-5a). This process can have a significant impact due to the high surface loading of preservative in pressure treated wood. Once this unfixed copper has been removed from the surface, even large rainfalls can not remove much copper (Figure 3-5b). Mobile unfixed copper more distant from the surface is more difficult to remove since it must first be transported to the surface. This occurs when differences in copper concentration between the surface (lower concentration) and the inner treated zone (higher concentration) produce diffusion of copper to the surface. This diffusion process is quite slow. The third process occurs when the summer season begins and the wood starts to dry. This brings moisture from the inner part of the wood to the surface; transporting the free copper (Figure 3-5c). When the rainy season starts again, the diffused mobile copper is available to be leached (Figure 3-5d). Though an increase in amount of copper was observed, the amount of copper leached was lower than that measured at the beginning of the exposure.

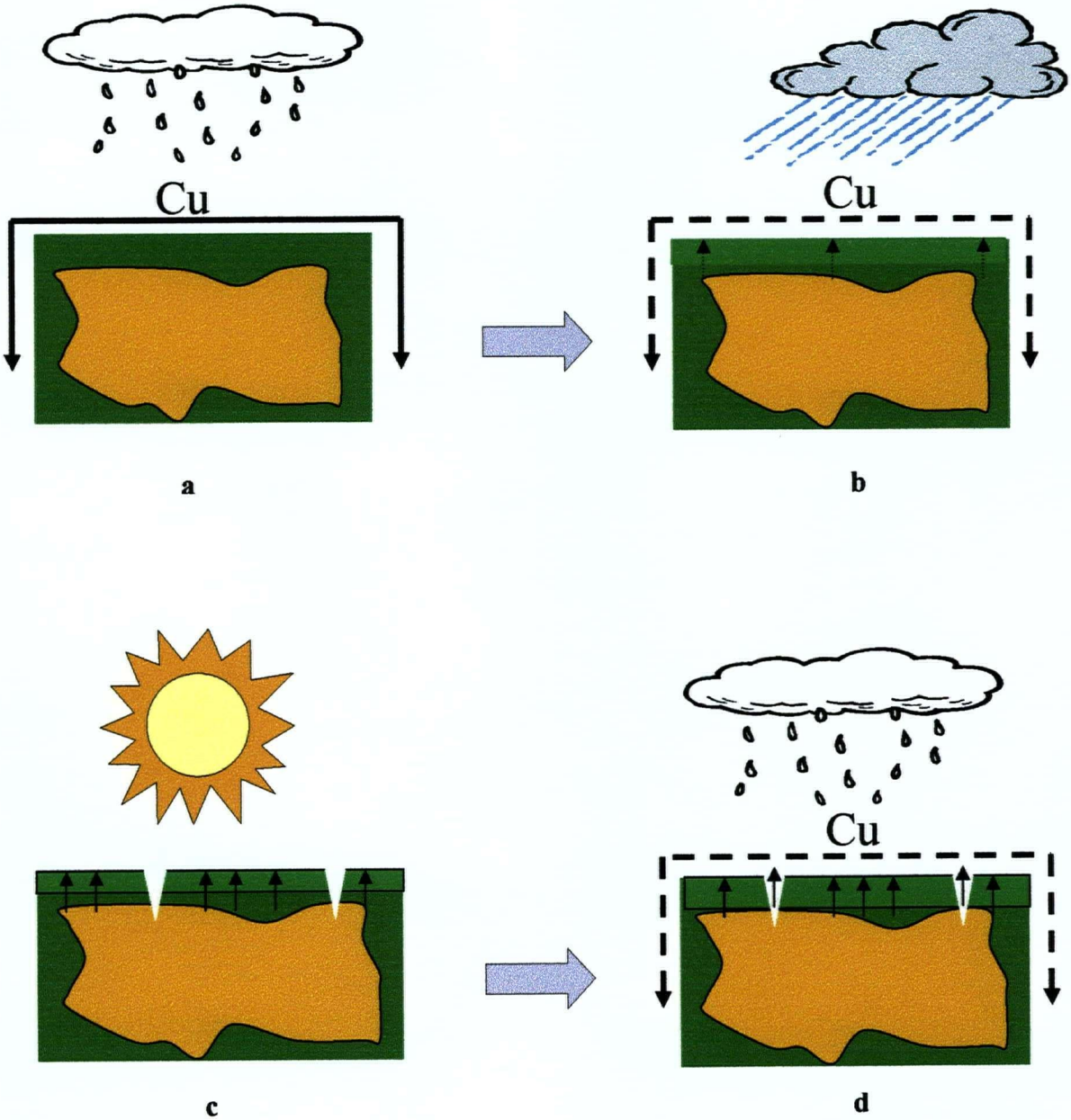

Figure 3-5 Mechanism of leaching of copper during the field exposure (a) at the beginning of the exposure (rapid copper losses), (b) during the raining season (decreasing copper losses), (c) during the summer season (migration of copper), (d) during the new raining season (small increases of copper losses)

3.2.3 Comparison of copper leaching between field and laboratory leaching

In order to assess the total amount of mobile copper present in the ACQ treated boards, small samples of each treated board were ground into sawdust and subjected to accelerated leaching. The results of the leaching are shown in Table 3-5 and Table 3-6. Table 3-5 shows the amount of copper leached per leaching phase in mg of copper (expressed as CuO) per g of sawdust. The leached copper values for board # 2 are shown in two groups due to different values being obtained. The first leaching phase removed the major portion of copper, with significantly less copper being removed during the second and third leaching phases. Similar trends were reported by Jiang and Ruddick (2004), when leaching copper amine-treated blocks. They used two different solutions and five leaching steps (two ultrasonic and three static leaching phases), and found the first ultrasonic phase removed the highest amount of copper.

Table 3-6 shows the copper content of the decking boards, before and after leaching, together with copper leached, expressed as a percentage of total copper in wood. As before, the values of the board # 2 were grouped into two: 2-a corresponds to the reference sections 2-1 and 2-4; and 2-b corresponds to the reference sections 2-2 and 2-3. The average values of these groups were different. Since, no difference in preservative retention was observed; the explanation for the difference in leached copper must be in the varying penetration of the reference samples. Figure 3-6 shows the ACQ reference samples used for the laboratory leaching test. The upper side of each reference sample was used for the experiment. The penetration varied among the samples with clear penetration along the latewood. The samples 2-2 and 2-3, which showed the highest amount of copper leached, had lower upper surface penetration than the other two samples 2-1 and 2-4. Although, four samples (2-1 to 2-4) were from the same board; samples 2-2 and 2-3 had more radial side in the top part than the other two samples and were placed with the radial surface uppermost while samples 2-1 and 2-4 were oriented with the tangential surface exposed. The latter would be less permeable and this may have influenced the latewood penetration.

The average total copper leached was 16.85% of the copper present in the treated wood. This is about three to four times that measured during the field exposure. However, it would be expected that leaching of sawdust will be much more effective in removing mobile copper than the leaching of large decking boards, thus field losses should be much smaller. The most

important information gained from the laboratory leaching is the total mobile copper present in the treated wood. This can provide a measure of the amount of mobile copper remaining in the field samples. Mobile copper provides an important protective role during service, by migrating onto check surfaces where it is bound by ion exchange. In this way check surfaces can prevent spores of wood decay fungi from germinating (Choi, Ruddick and Morris, 2001).

Table 3-5 Average of the amount of copper (as CuO) leached per leaching phase using sawdust from ACQ treated boards

Board	Amount of copper (CuO) leached mg / g sawdust			
	1st leaching	2nd leaching	3rd leaching	Total
1	1.35	0.20	0.07	1.63
2-a	1.51	0.25	0.10	1.86
2-b	2.89	0.41	0.11	3.41
3	1.89	0.27	0.10	2.26
Average	1.91	0.27	0.09	2.29

Table 3-6 Average of the results of the accelerated leaching using sawdust from ACQ treated boards

Board	Amount of copper (CuO) before leaching (kg/m^3)	Amount of copper (CuO) after leaching (kg/m^3)	Amount of copper leached (%)
1	4.67 (1.33)	3.96 (1.10)	15.08 (2.04)
2-a	5.50 (0.87)	4.79 (0.73)	12.90 (0.47)
2-b	4.97 (0.26)	3.83 (0.18)	22.92 (0.43)
3	4.67 (0.69)	3.79 (0.61)	16.50 (1.15)
Average	4.95	4.12	16.85

* Values within parenthesis represent the standard deviation of the samples

Comparing the copper leaching observed here with that from previous research, it was higher than those found by Jiang (2000) and Lucas (2003). However, both used ACQ treated blocks rather than sawdust, so higher values here would be expected. Lucas (2003) found the amount of copper leached (CuO) from monoethanolamine copper treated blocks (retention 3.92 kg/m^3 of CuO) was 8.64%. Jiang (2000) reported the amount of copper leached from similar blocks with retention of 11.19 kg/m^3 of CuO to be 13.64%. The almost doubling of retention in Jiang's study would certainly lead to greater leaching losses as Lucas confirmed greater losses of copper

occurred with increasing retention. This is due to the fact that high copper retentions will exceed the capacity of the wood to fix the copper, rendering the excess copper mobile. In the current study the greater surface of the sawdust is the key factor ensuring maximum leaching of the mobile copper.

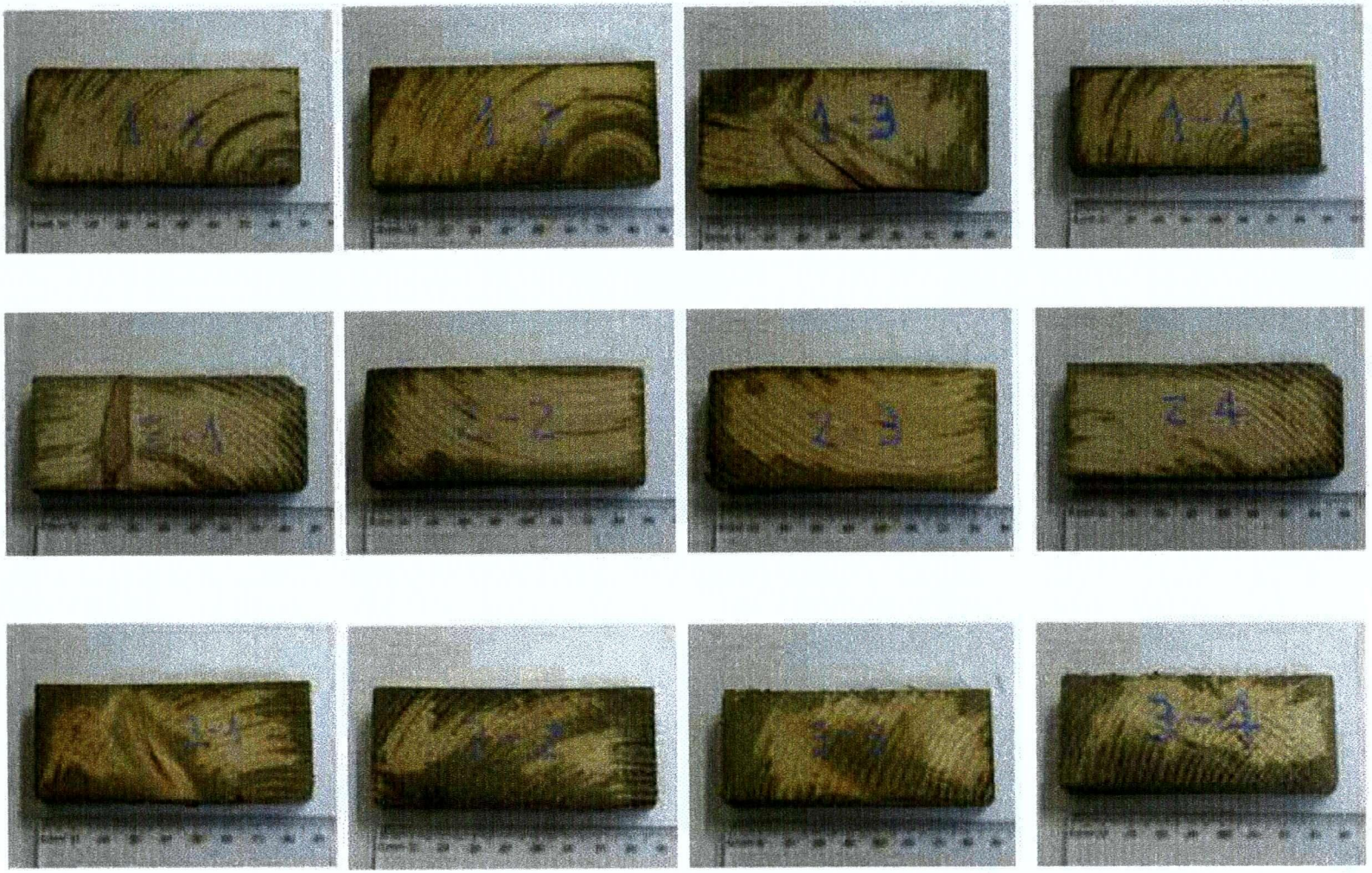

Figure 3-6 ACQ references samples used for the laboratory leaching test

3.2.4 Prediction of copper leaching

Studies of the service life of decks have confirmed that most are replaced within a 20 year life span because of their poor appearance due to excessive surface deterioration. Weathering of the treated wood in service causes checking or splitting, and surface discolouration. Recent research (Choi, Ruddick and Morris, 2004) has also shown that mobile chemicals in shell treated wood are able to migrate and to fix to the exposed surface in checks thereby protecting the untreated wood from decay and fungal spores. An important consideration therefore in shell treated decking is the need for mobile copper which can fix to the check surface and cross cut end grain throughout the service life. Excessive and rapid loss of copper is deleterious both to the environment, as well as the long term performance of the decking. It is therefore important to observe the rate of copper loss as a measure of the mobile copper presenting wood. By comparing this copper depletion with the known total amount of copper, it will be possible to model the anticipated copper leached during a 20 year service life. Such studies will identify the environmental impact and confirm the long term availability of mobile copper to protect check surfaces.

The amount of copper leached monthly per basin expressed as a percentage of the total amount of copper in the wood, was plotted against the time of exposure. Figures 3-7 to 3-11 show the trend of the cumulative losses after 8, 12, 17, 22, and 26 months of exposure, respectively. From the plots, it is clear that the depletion shows two distinct trends. The initially copper leaching is more rapid and shows a linear relationship with time (r^2=0.73). After approximately 4 months (122 days), the rate of loss of copper greatly decreases. This can be explained by the rapid loss of mobile copper on the wood surface. Once this copper has been depleted, further leaching is limited at which this surface copper content is replenished by the movement of mobile copper to the surface. This diffusion will be quite slow, so that the rate of depletion is reduced. After the 8th (243 days) and 12th months (365 days) of exposure (Figure 3-7 and Figure 3-8), the graph of leached copper versus time may be fitted by a power regression. Figure 3-9 shows a slight increase in the copper leaching following a period with almost no loss. This slight increase in the rate of copper leaching correspond for the 17th month (426 days) of exposure with the start of the rainy season and extends until December, 2003 (518 days). It is hypothesized that this loss is the depletion of migrated copper from the surface. Gradually, this copper content is again

depleted, and so the rate of copper loss again is reduced (Figure 3-10) at 22 months. Finally, Figure 3-11 shows the trend of the copper losses after 26 months of exposure (792 days). A new small increase in the copper leached was observed in August, 2004 (762 days) at the end of the summer season and the beginning of the rainy season. During the summer, a small amount of free unfixed copper had migrated to the surface and became available for leaching. Due to the slow and continuing movement of free unfixed copper to the surface of treated boards, the 26 month trends could also be modeled best with a power equation (r^2=0.51). The small increases in the copper leaching in the autumn are not big enough to change the trend. The small increases of copper leaching can be observed in Figure 3-12 in which the average of the cumulative amount of copper during the period of exposure is presented. In addition, with the 26 months data a one fit equation was considered (Figure 3-13) in which the trend have a coefficient of correlation of r^2=0.79.

A regression of the curve of leached copper with time was done using the 26 months of exposure data to find the best fit. The best equation was the power fit (Table 3-7, Appendix 2). Using the regression equations shown in Figure 3-7 to 3-13, the values of cumulative copper losses were calculated for a 20 years life. The results are presented in Table 3-8. The values calculate from the 8-month and 12-month equation predicted approximately 6% copper loss. For the 17-month equation, the prediction increased to 9% copper loss. And finally for the 22-month and 26-month equation, the predictions were approximately 11% copper loss. Not much difference was found between the predicted cumulative copper losses from the 26-month regression fit and average fit. Also, a cumulative copper loss over the 20 years based one fit equation was calculated (16.63%). This value was similar to total mobile copper determined in the laboratory sawdust leaching study (16.85%). These results would suggest that after 20 years of exposure in the field, all the mobile copper would be leached.

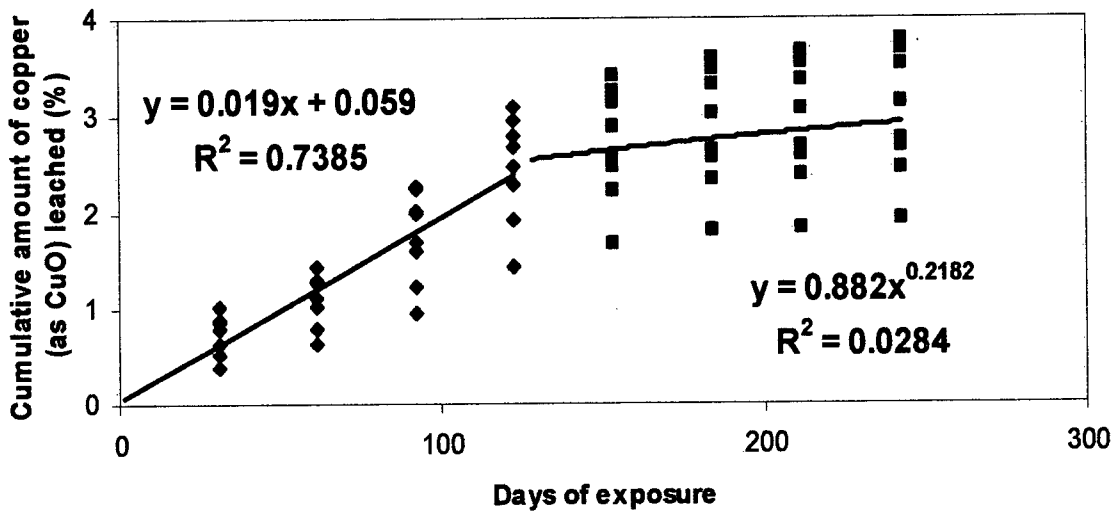

Figure 3-7 Cumulative amount of copper (as CuO) leached (%) from ACQ treated boards during days of exposure (after 8 months)

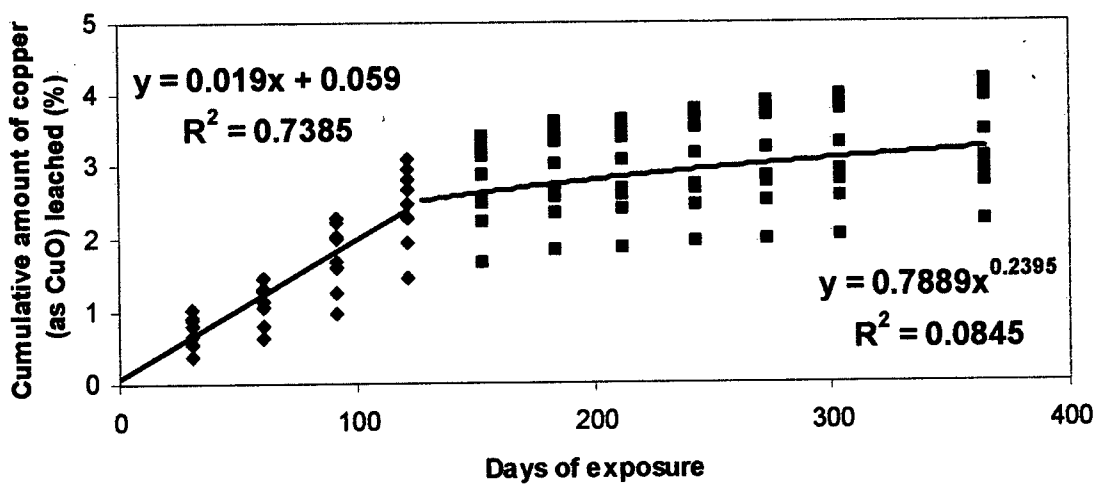

Figure 3-8 Cumulative amount of copper (as CuO) leached (%) from ACQ treated boards during days of exposure (after 12 months)

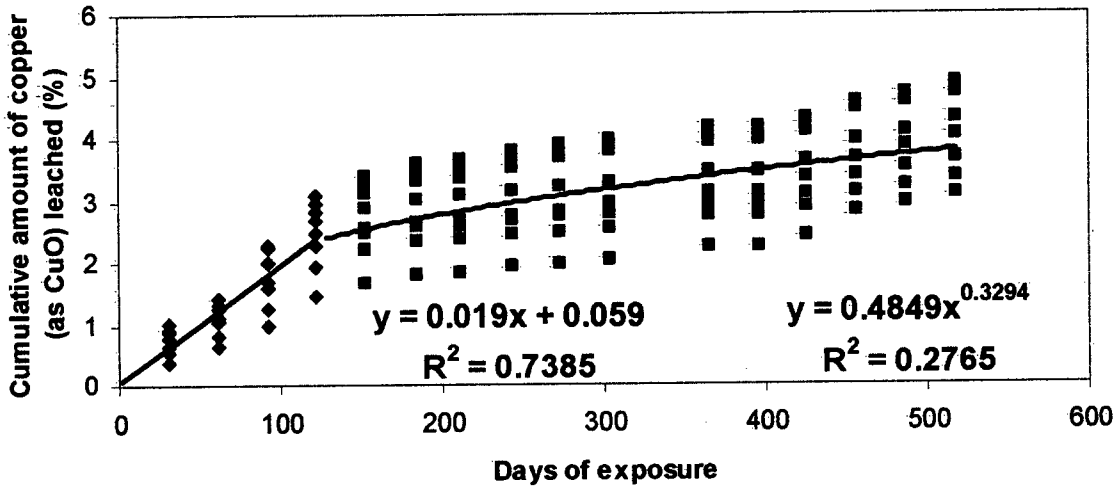

Figure 3-9 Cumulative amount of copper (as CuO) leached (%) from ACQ treated boards during days of exposure (after 17 months)

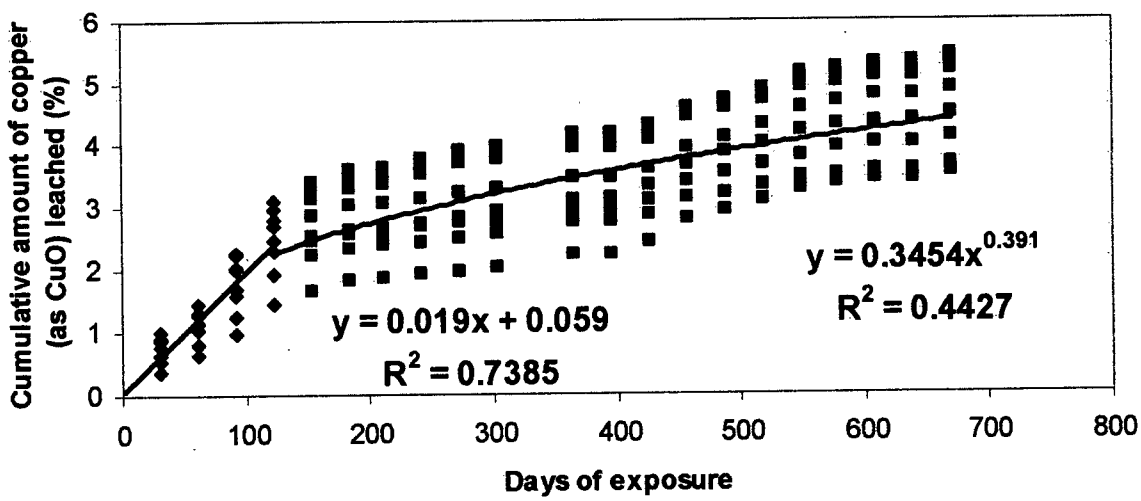

Figure 3-10 Cumulative amount of copper (as CuO) leached (%) from ACQ treated boards during days of exposure (after 22 months)

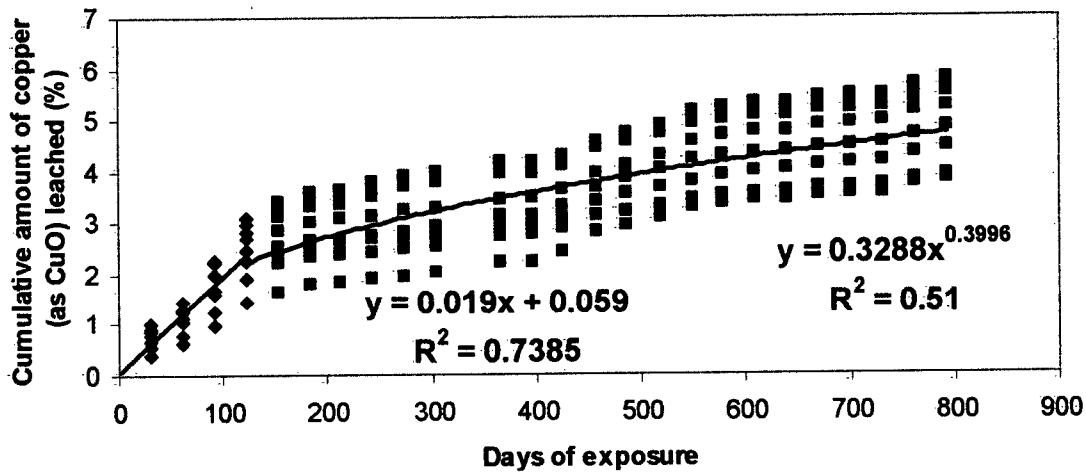

Figure 3-11 Cumulative amount of copper (as CuO) leached (%) from ACQ treated boards during days of exposure (after 26 months) after regression

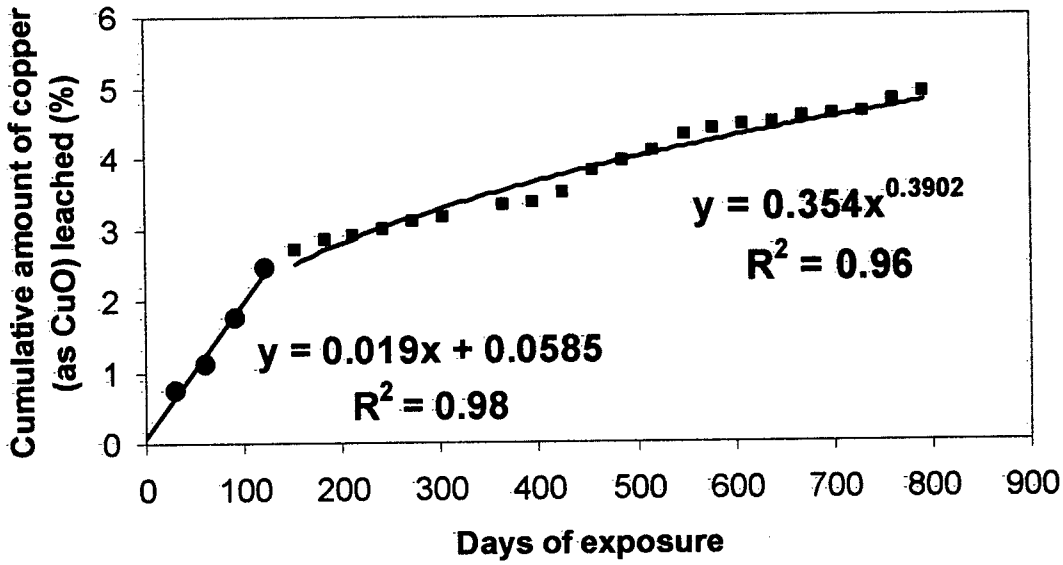

Figure 3-12 Average of cumulative amount of copper (as CuO) leached (%) from ACQ treated boards during days of exposure (after 26 months)

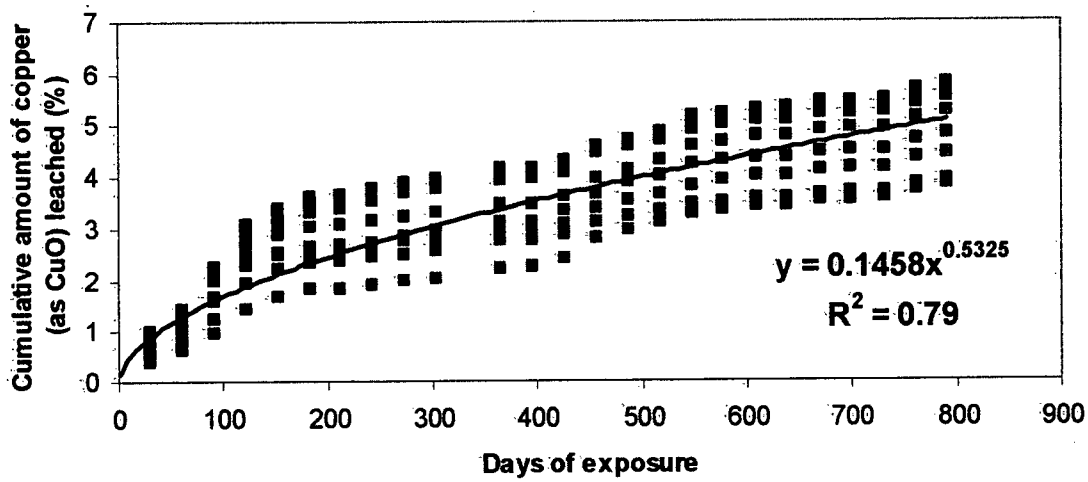

Figure 3-13 Cumulative amount of copper (as CuO) leached (%) from ACQ treated boards during days of exposure (after 26 months) after regression-one fit equation

Table 3-7 Summary of the analysis of regression for the second part of the amount of copper leaching from ACQ treated wood (%) during the time of exposure

Model	Coefficient of correlation (r^2)	Root mean square error	F ratio in lack of Fit analysis	Parameter estimate (coefficients)
Power	0.527646	0.668364	0.2686	Significant

Table 3-8 Comparison of the predicted copper (as CuO) losses values from ACQ treated boards over 20 year period exposure using the equation models

Fit equation	Prediction of the cumulative amount of Copper (CuO) leached (%) over a 20 years period of exposure
8 months	6.14
12 months	6.64
17 months	9.08
22 months	11.19
26 months	11.50
26 months Average	11.39
26 months only one fit	16.63

Scatter plots of the copper losses during of the first month of the exposure versus the corresponding cumulative losses after 26 months of exposure in mg/m² were prepared (Figure 3-

14). It was possible to fit a power relationship between the initial and final copper losses (R^2=0.83). The power relationship was preferred to a linear relationship since it is logical to expert the rate of leaching of copper will decrease after the first months of exposure and with the increasing time will tend to zero. This could be a basis of a tool for identifying problem treatments. It could also used to identify whether different wood species result in different environmental impacts, due to copper leached.

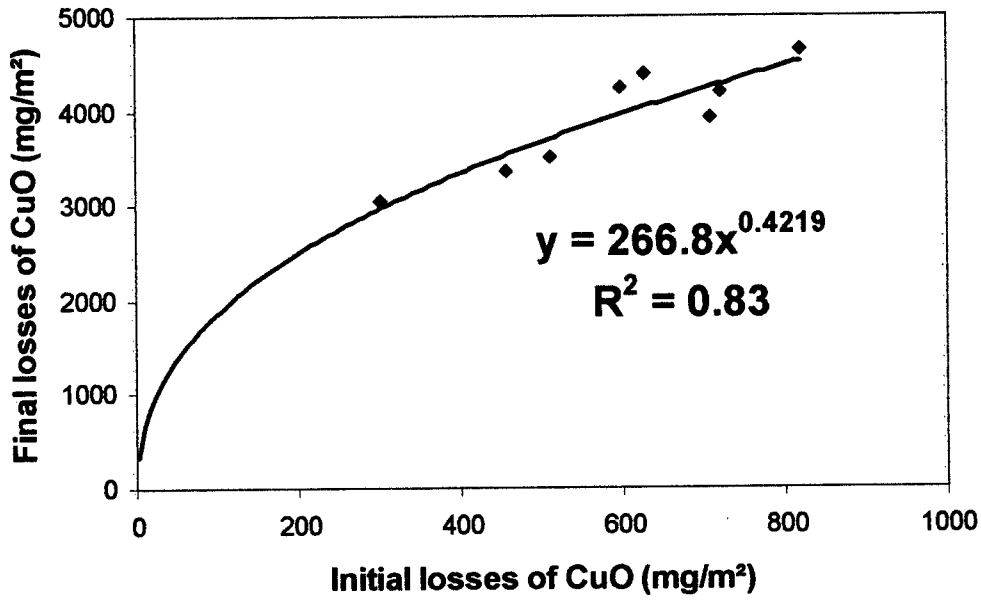

Figure 3-14 Plot of initial losses vs. final losses of copper (as CuO) in mg/m^2 from ACQ treated boards

3.2.5 Leaching of the quaternary compound

No quaternary compound could be detected in either the field or laboratory leaching. This observation agrees with other research done with ACQ with DDAC as a quaternary compound (Jin *et al.*, 1991, and Nicholas *et al.*, 1991). Quaternary compounds ion exchange very rapidly with wood and during wetting can redistribute to other sites where they bind readily (Ruddick *et al*, 1982, Nicholas *et al* 1991), and also they decrease the transport of water through the wood (Hayward et al, 1987). Jin *et al*, (1991) reported that DDAC leachability was negligible, but quat losses were observed when treated wood was in contact with soil and the influence of pH and cation exchange were considered to contribute to the loss of the chemical.

3.2.6 Migration of copper in checks

The long term performance of shell treated wood is dependent on mobile copper being deported from the treated zone onto the untreated newly exposed check surfaces. This has been shown to occur in CCA treated wood, but so far no data to confirm a similar effect in ACQ treated wood is available. To confirm this redistribution, wood samples were recovered from check surfaces as well as further from the check surface (> 2mm). Samples were removed from checks in two different boards exposed during the study. The copper content was measured on the check surface as well as > 2mm from the check surface. In addition, samples were removed from the treated zone adjacent to the check, as well as untreated wood from reference samples, which had not been exposed to leaching. Table 3-9 shows the results of the copper analysis.

Table 3-9 Analysis of copper in checks from ACQ treated boards from the field test

Sample	Zone	Amount of Copper Cu mg / g wood		Tukey-Kramer test
		ACQ 2-1	ACQ 2-4	α= 0.05%
Check	Check surface	0.4711 (0.05)	0.5233 (0.10)	a
	Below check	0.3700 (0.22)	0.3389 (0.22)	a
	Treated zone	1.7172 (0.12)	5.0218 (0.87)	-
Reference	Untreated zone	0.0164 (0.01)	0.0112 (0.00)	b
	Treated zone	5.4125 (0.52)	5.8663 (0.29)	-

* Values within parenthesis standard deviation

An analysis of variance (Appendix 3) and a Tukey-Kramer test of comparison of means were done. The results indicated that at 95% confidence (α = 0.05) there were significant differences between the untreated zone of the reference sample and the check surface and below the check. The results confirm that rainfall causes not only leaching, but also redistribution of the copper onto the check surface. Moreover, because of diffusion, the copper can penetrate below the check surface to a limited extent (see Figure 3-15). During the hot dry summer season, drying of the decking following rain or after initial installation causes movement of mobile copper to the surface and at the same time results in checks formation (Figure 3-15a). Subsequent rain events cause the mobile copper to either be leached or redistributed first onto the inside surface of the checks. With continued rain in winter copper can then diffuse farther from the check surface (Figure 3-15b).

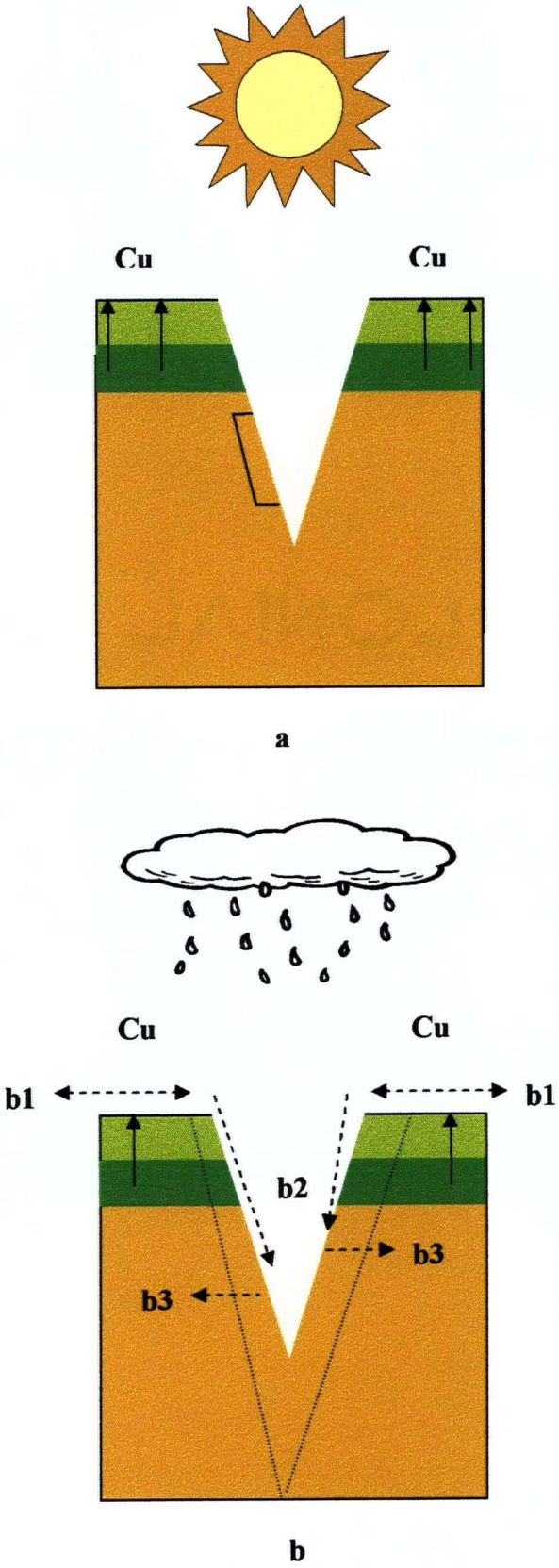

Figure 3-15 Mechanism of migration of copper into the checks: (a) During the summer season (b) Diffusion of copper during subsequent rain: (b1) copper leaching from the surface; (b2) redistribution of copper to the check surface; (b3) diffusion of copper to below the check surface

3.2.7 Effect of post-treatments in copper leaching

To reduce the potential environmental impact of ACQ treated decking, the influence of two post-treatments was studied to determine if the amount of copper depletion could be decreased. It has been observed that the highest amount of copper was leached during the first months of exposure. This was mainly unfixed copper lost from the surface of the wood. One post treatment process was a water pressure wash following treatment designed to remove this unfixed copper from the surface. A second post –treatment focussed on reducing the wetting of the decking during rain. A water repellent finish was applied to the wood surface to reduce water uptake, thereby reducing copper loss.

Table 3-10 shows the penetration and retention measurements for the ACQ treated spruce boards used for this study. It was noted that board # 3 had different penetration and retention from the other three boards. To have a better measure of the retention in board # 3, retention was measured from the 0 to 5 mm depth from the top side of the board. It was considered that a greater amount of copper would be leached from this board. The ACQ penetration of the test boards is illustrated in Figure 3-16; two cross sections per board are shown. The first number corresponds to the source board while the second number corresponds to the location of the section. Boards # 1 and # 4 showed low ACQ penetration in comparison to boards # 2 and # 3. Differences in penetration in section 1 and section 5 of board # 2 were found due to different sapwood content. Board # 3 was found to have an extensive latewood penetration throughout the cross section of the board. In comparison with the hem-fir used in the first experiments, the spruce had much lower penetration and, this likely to impact on copper leaching.

Table 3-10 Initial measurements of the ACQ treated boards before the post-treatments

Board	Penetration (mm)				Retention in 0- 1.5 mm assay (kg/m^3)
	Top	Bottom	Side 1	Side 2	
1	1.33 (0.50)	0.83 (0.25)	1.39 (0.49)	1.00 (0.00)	3.33
2	2.22 (0.97)	1.11 (0.33)	1.94 (1.70)	1.89 (1.96)	4.63
3	8.67 (7.92)	1.22 (0.67)	4.33 (6.22)	6.33 (5.68)	18.92 [14.17]**
4	1.00 (0.00)	1.00 (0.00)	1.61 (1.05)	1.33 (0.71)	3.36

* Values within parenthesis standard deviation

** Value within brackets is the retention value from 0-5 mm depth assay

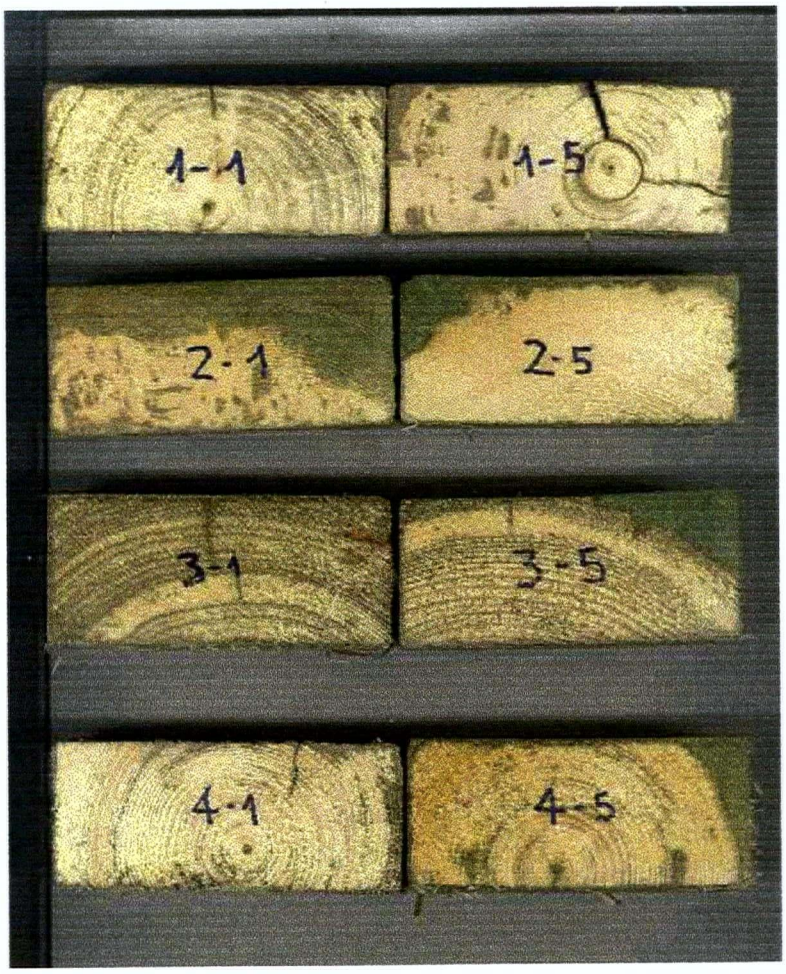

Figure 3-16 Cross section of the ACQ treated spruce boards for post-treatment. First number corresponds to the board and the second number corresponds to the section of the board.

The amount of copper leached after the water pressure treatment is shown in Table 3-11. Four sequential vacuum pressure washes were applied to the boards without changing the treatment water between washes. It was found that most of the mobile copper was leached during the first two phases with only one board showing copper leaching after the fourth cycle. As predicted, board # 3 leached much more copper than the other boards. Consequently it was decided to calculate the leaching data for this board separately.

Table 3-11 Amount of copper leached during the water pressure post-treatment in ACQ treated boards

Board	Amount of copper as CuO leached mg				
	1st Treatment	2nd Treatment	3rd Treatment	4th Treatment	Total
1	0	0	15	0	15
2	0	15	0	15	30
3	195	15	15	0	225
4	15	0	0	0	15

The amount of copper leached per month is presented in Table 3-12. For all treatments, the greatest amount of copper leached at the beginning of the rainy season (August-September, 2004). The values for August, 2004 were higher than those for the first month. This was because the samples were placed outside at the end of the rainy season, and only small amounts of precipitation occurred in the following months. Nevertheless significant amounts of copper were leached during the first two months. Table 3-12 compares the effect of the post-treatments on the amount of copper leached, and this comparison is also illustrated in Figures 3-17 and 3-18. Figure 3-17 shows the average values of the basins with boards # 1, # 2 and # 4, while Figure 3-18 shows values of the basins with board # 3. The most effective post-treatment was the water repellent application, which reduced the amount of copper leached by two thirds. The water pressure treatment was not effective in decreasing the amount of copper leaching, according to the Tukey-Kramer test, at 95% of confidence (see Appendix 4), there was no significant difference between the copper leached from the water pressure treatment and the values obtained from the control boards. Although, the water pressure treatment helped to remove the unfixed copper from the surface of the treated board, it did not prevent the migration of copper by diffusion from the inner side of the boards during the summer period. On the other hand, the water repellent treatment decreased the amount of copper leached due to ability of the water repellent to reduce the absorption of rainfall; thereby, decreasing the potential for copper to migrate to the surface of the wood.

Table 3-12 Average of the amount of copper leached (mg) per month from ACQ treated boards with post-treatments exposed at field

Month	Average of the amount of copper CuO leached at the field exposure (mg/basin)					
	Monthly			Cumulative		
	Control	WPT	WRT	Control	WPT	WRT
Apr-04	20.3 (6.9)	13.2 (5.6)	2.8 (0.7)	20.3	13.2	2.8
May-04	17.0 (3.1)	13.0 (1.4)	5.5 (0.6)	37.3	26.1	8.3
Jun-04	5.5 (1.0)	5.5 (0.9)	1.7 (0.6)	42.8	31.6	10.1
Jul-04	4.9 (0.5)	4.8 (0.5)	1.8 (0.5)	47.7	36.4	11.9
Aug-04	24.7 (2.4)	21.4 (4.4)	9.1 (0.7)	72.4	57.8	21.0
Sep-04	15.0 (4.7)	12.7 (1.9)	5.2 (0.8)	87.4	70.5	26.2

* Values within parenthesis standard deviation

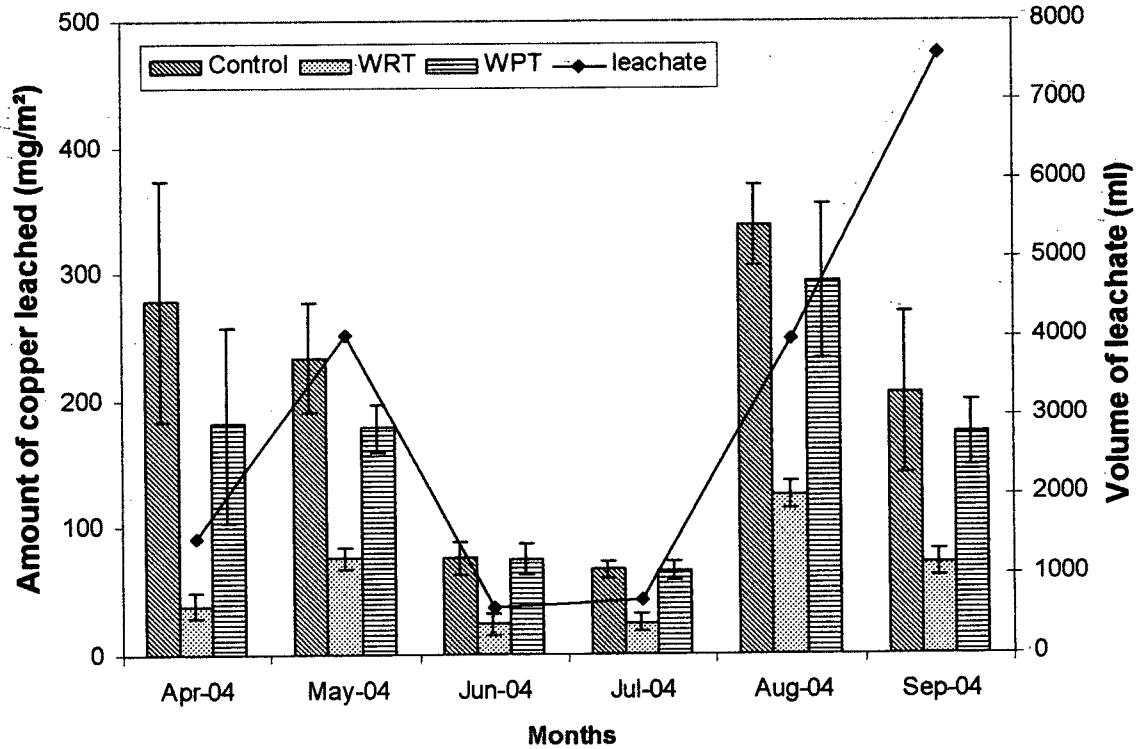

Figure 3-17 Comparison of the post-treatments in the amount of copper leached in mg/m^2 per month from ACQ treated boards

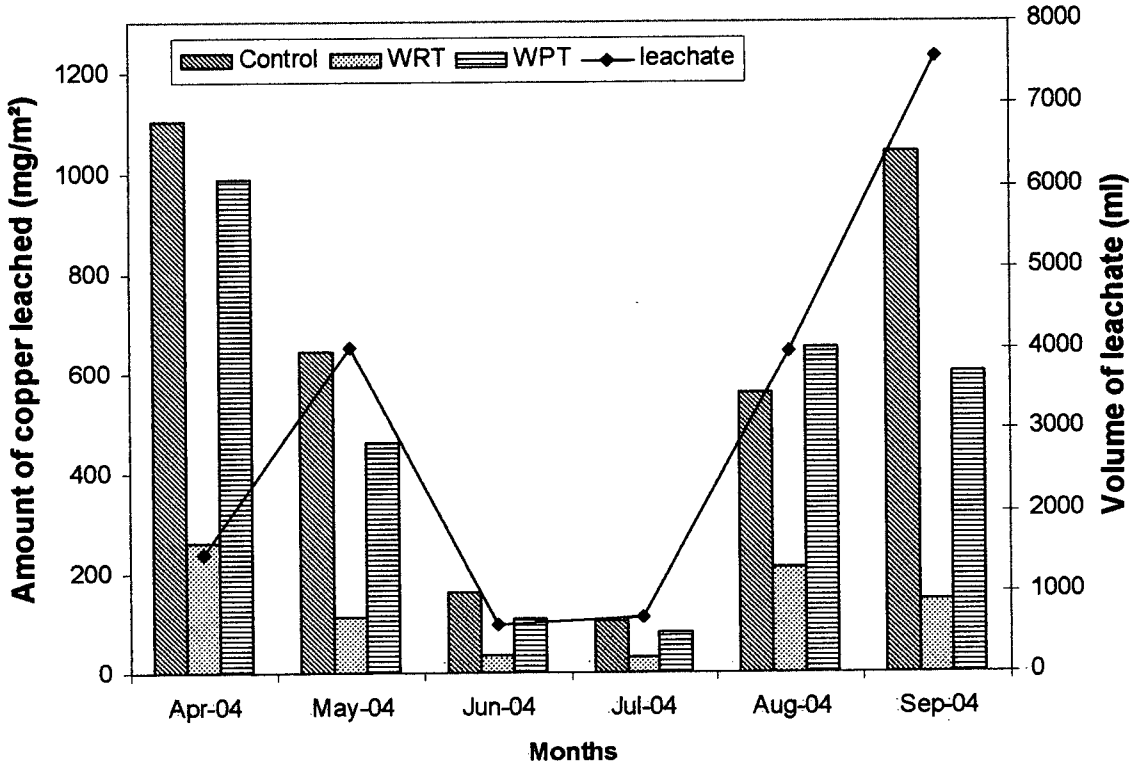

Figure 3-18 Comparison of the post-treatments in the amount of copper leached in mg/m^2 per month for the high penetration ACQ treated board (board # 3)

Table 3-13 presents the percentage of copper leached during the first 6 months. Since there is no information on the weight uptake of the preservative in the treated board, the values were based on the copper present in a calculated treated wood volume. The cumulative amounts of copper leached after 6 months of exposure were 8.2 % and 9.1% for the control and water post-treatments, respectively. The values were similar confirming that the water pressure post-treatment could not reduce the amount of copper leaching over the extended period. The water repellent finish reduced the cumulative copper leaching to 2.9%.

Table 3-13 Average of the amount of copper (as CuO) leached per month from ACQ treated boards with post-treatments exposed at field

Month	Average of the amount of copper CuO leached during the field exposure (%) reference retention at 1.5 mm					
	Monthly			Cumulative		
	Control	WPT	WRT	Control	WPT	WRT
Apr-04	1.8 (0.3)	1.6 (0.5)	0.3 (0.2)	1.8	1.6	0.3
May-04	1.6 (0.5)	1.7 (0.4)	0.6 (0.3)	3.5	3.3	0.9
Jun-04	0.5 (0.1)	0.7 (0.2)	0.2 (0.2)	4.0	4.0	1.1
Jul-04	0.5 (0.2)	0.6 (0.2)	0.2 (0.1)	4.5	4.6	1.3
Aug-04	2.4 (0.8)	2.9 (1.3)	1.0 (0.5)	6.8	7.5	2.3
Sep-04	1.4 (0.2)	1.6 (0.5)	0.6 (0.3)	8.2	9.1	2.9

* Values within parenthesis standard deviation

Table 3-14 and 3-15 shows the amount of copper leached after accelerated leaching in the laboratory. Table 3-14 shows that the first leaching phase had the highest amount of copper leached. The amount of copper leached in mg of CuO per g of wood is different in board # 3 because of the higher retention compared to the other boards. The values of board # 3 were excluded from the statistical analysis to avoid distorting the data (see Appendix 5). The study confirmed that the retention of the boards impacts on the amount of copper leaching; with higher retentions producing greater copper leaching. Comparing the amount of copper leached by percentage, the values obtained for the four boards were not statistically different. The value of copper leached referred as a percentage from the board # 3 was similar to those values of the other three boards, due to the higher amount of treated volume in the board. The average amount of copper leached was 6.19 %, which is lower that the amount obtained in the field leaching. The values of the laboratory leaching should be higher than the values obtained in the field test due to the extreme conditions of leaching. The leaching was done using sawdust which has more surface area contact with the leaching substrate (distilled water) than solid wood. A possible reason for the copper loss in the accelerated leaching is the low and non homogeneous penetration of the treated board surface used to make the sawdust samples. In some boards the copper penetration clearly penetrated extensively into the board, but only in the latewood and so was not considered when the treated volume was calculated. In addition, since the samples used for the accelerated leaching, due to the uneven copper penetration a small percentage of untreated wood which would account for the over estimation of the values.

Table 3-14 Amount of copper (as CuO) leached (mg) per leaching phase using sawdust from spruce ACQ treated boards

Board	Amount of copper leached as CuO (mg)						
	1 hour	3 hours	6 hours	24 hours	48 hours	72 hours	Total
1	1.13	0.01	0.02	0.06	0.09	0.00	1.31
2	1.35	0.02	0.04	0.09	0.15	0.00	1.65
3	4.80	0.49	0.03	0.00	0.22	0.07	5.61
4	0.98	0.10	0.04	0.12	0.07	0.02	1.33
Average	2.07	0.16	0.03	0.07	0.13	0.02	2.48

Table 3-15 Results of the laboratory leaching of the spruce ACQ treated boards before the post-treatments

Board	Retention before leaching (kg/m3)*	g of CuO leached / g of wood (%)*	% of CuO leached*
1	3.33 (0.05)	0.05	6.32 (0.29)
2	4.63 (0.11)	0.07	5.72 (0.22)
3	14.17 (0.20)	0.23	6.35 (0.36)
4	3.36 (0.06)	0.06	6.36 (0.19)
Average			6.19

*Average values

** Values within parenthesis standard deviation

3.3 Conclusions

From this part of the study, the following conclusions can be given:

1) The trend of copper leaching can be divided into two parts. The first part follows a linear regression. The second part follows a power regression.
2) During the first four months of exposure, the treated boards lost higher amounts of copper than the following months. This copper lost is mainly unfixed copper from the wood surface.
3) After four months, the amount of copper leached is mainly mobile copper that migrated to the surface; and decreases and increases depending on the diffusion rate during alternate drying and wetting of the wood.
4) Diffusion of copper in wood takes place in periods of heavy rain.
5) During the leaching, the mobile copper could be fixed in available untreated sites present in wood, for example at the surface of untreated wood exposed during check formation.
6) After 26 months of exposure the total cumulative amount of copper leached in ACQ boards was less than 5%.
7) In the laboratory leaching the total amount leached was around 16%.
8) According to the tendency of copper losses, it could be predicted that after 20 years of exposure, the amount of copper leached would be around 15%.
9) The plot Final losses vs. initial copper losses follow a power relationship.
10) The water pressure post-treatment failed to decrease the amount of copper losses, while the water repellent treatment helped to decrease the amount of copper leached
11) The pH of the first leachates was higher than the pH of the rainfall probably due to the loss of amine from the treated wood.
12) No quaternary compounds in the leachates were found.

Chapter 4

Leaching of Copper in CAz treated wood

4.1 Introduction

Copper Azole (CAz) is an alternative preservative used in the North American market. Since few studies have looked at this preservative, many information gaps exist that affecting the ability to standardise CAz preservative use at the national level. The results obtained from this experiment could provide valuable information that could support the use of CAz in Canada. In this experiment, three species of wood treated with CAz were analysed to determine the degree of copper leaching that occurs from CAz treated wood exposed to field and laboratory leaching. A model was calculated for predicting the loss of copper over time for each. Finally, an analysis of checks was also done to verify the redistribution of copper within treated samples.

4.2 Results and Discussions

4.2.1 Initial Measurements

Table 4-1 shows the initial measurements CAz boards before exposure. The densities shown are the standard values for each species. Penetration was higher in hem-fir (7-9.33 mm) than in pines (1-2.6 mm). Copper content was also found to be higher in hem-fir then in the pines. Between to the two pine species, copper penetrated further into lodgepole pine than jack pine. The low penetration is mainly due to the heartwood content of these species that are refractory (Ruddick, 1985; Choi, 2004). Two measurements of copper content at the top surface are shown in Table 4-2. The first measurement shows the copper content of the sawdust at 1.5 mm from the sample surface while the second measurement represents the copper content of from the outer surfaces of the boards. Because the penetration distances were different for each species, CuO concentrations were also calculated at different depths for each species. For the hem-fir samples, additional sawdust was sampled from 7 mm and analyzed for CuO using X-ray fluorescence. hem-fir sawdust at 7 mm. was expected to have lower amount of copper than that obtained at 1.5 mm, since the concentration of copper typically decreases with the depth of penetration. For lodgepole pine, it was assumed that measurements of copper retention would be similar between the surface depth at 1.71 mm. and at 1.5 mm. and for jack pine was assumed to have higher

copper concentrations at 1 mm. than at 1.5 mm.

Table 4-1 Average of the initial measurements of the CAz treated boards

Species	Density (kg/m^3)	Penetrations (mm)			
		Top	Bottom	Side 1	Side 2
jack pine	420	1.00 (0.00)	1.83 (0.61)	1.00	1.00
hem-fir	380	7.00 (3.84)	9.33 (4.79)	5.00	5.00
lodgepole pine	420	1.71 (0.49)	2.60 (0.70)	1.00	1.00

* Values within parenthesis represent the standard deviation of the measurements

Table 4-2 Average of copper content at different sides of the CAz treated wood

Species	Copper content in wood at 1.5mm (kg/m^3)	Copper content per sides (kg/m^3)			
		Top	Bottom	Side 1	Side 2
jack pine	1.55	2.32	2.32	2.32	2.32
hem-fir	5.58	3.90	4.96	3.90	5.29
lodgepole pine	1.80	1.80	1.80	1.80	1.80

4.2.2 Analysis of Copper Leaching

Based on the penetration and retention of CuO, it was expected that more copper would be leached from hem-fir boards than pine boards. A field test began in June, 2003 and the environmental conditions of the field test are shown in Appendix 1. Table 4-3, Table 4-4 and Table 4-5 show the average leachate collected and the amount of copper leached per month, for jack pine, hem-fir and lodgepole pine, respectively. The trend in copper leaching was comparable to that observed from the analysis of ACQ treated boards. The first months of exposure had the highest amount of copper leached. However, because the CAz boards were installed in the field at the beginning of the summer season (low rain), the period of high leaching was extended until January, 2003 (7 months for hem-fir and lodgepole pine). In the ACQ study, it was found that the high leaching period was only four months because the boards were installed in August, 2002, which is the end of summer. During the summer season, low rainfall and the high temperatures caused resulted in a low amount of leachate collection; as a consequence, leachate collected in July, 2003 was the cumulative for June and July, 2003. During the following months, September, 2003 to January, 2004, an increase in copper leaching

was observed due to the start of the rainy season. From February, 2004 until April, 2004 the amount of copper leaching began to decrease as the amount of unfixed copper at the surface of the samples was depleted. April, 2004 was a dry period in which little rainfall occurred. In this dry period, diffusion of copper from the inner part of the wood to the surface occurred. During May, 2004, rainfall increased which corresponded with an increase in the amount of copper leached. Increased leaching occurred due to the increase in mobile copper at the surface of the board available for leaching. After May, the summer season started and with it less rainfall was observed. During these months, the amount of copper leached decreased until the start of the next rain season (August-September, 2004). This observation agrees with the research done by Taylor *et al.*, 2003 and Choi *et* al., 2004 working with CCA treated wood.

The trend in pH was similar to that exhibited by copper leaching. When the amount of copper leached is higher, the pH of the leachate has higher values (approximately 6) and when the amount of copper leached is lower, the pH lower. This is probably caused by the small amount of ammonia (NH_3) that is leached with copper. This was reported by Ruddick (1992) found the relationship between the copper leaching and pH, in which higher amounts of copper leached, higher pH values. When the pH of the leachate was lower than the pH of the rainfall, it is possibly due to no more ammonia is being leached and also to the possibility that the wood is buffering the pH of the rainfall, since the pH of the wood is lightly acid (5-6). Figure 4-1 shows the comparison of the pH of the rainfall with the average of the pH of the leachates per month. It shows that the leachate from hem-fir boards are usually higher than the pH of the rainfall, it seems that they are losing ammonia. In the case of jack pine and lodgepole pine, the first months of exposure the pH of the leachate was higher than the pH of the rainfall, from February, 2004 the values of pH of the leachate were lower than the pH of the water, however in September 2004 a higher values were observed mainly due to the increase of the ammonia leaching after the drying period and the starting of the rain season.

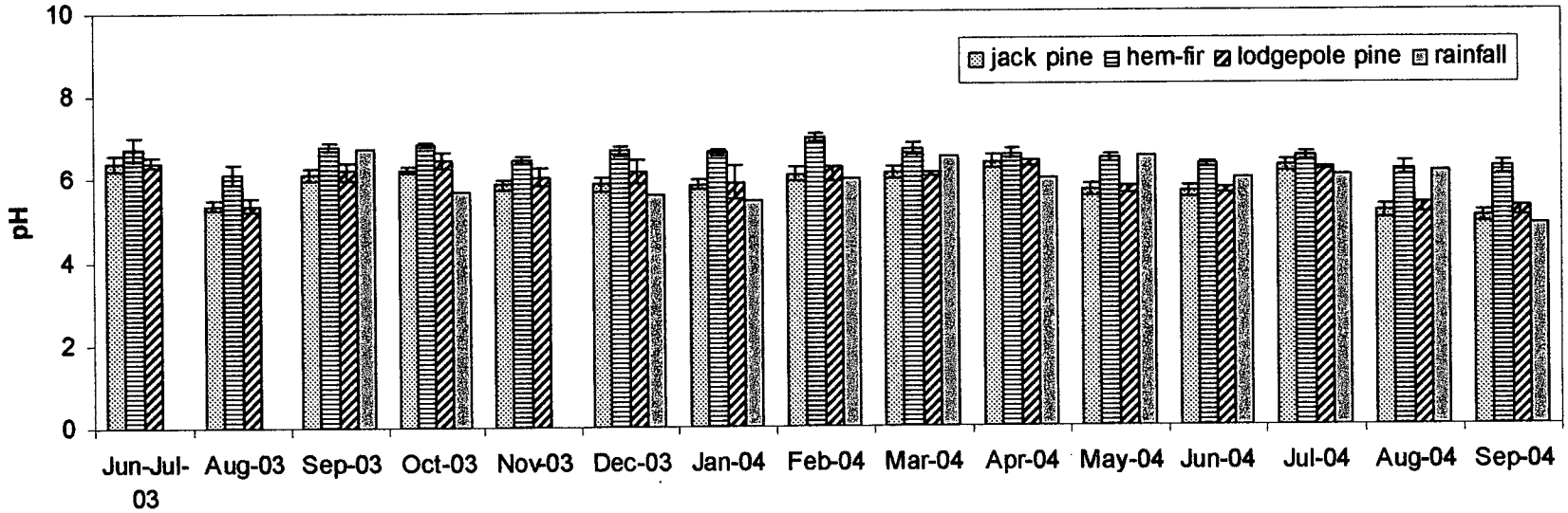

Figure 4-1 Comparison of the pH of the leachate from the jack pine, hem-fir, lodgepole pine CAz boards and rainfall

After 16 months of exposure the cumulative amount of copper leached was 37.17 mg for jack pine, 194.84 mg for hem-fir and 56.21 mg for lodgepole pine. It appears that the retention ability of the wood may have an influence on the amount of copper leached. The higher the retention, the more unfixed copper would be present in the wood and thus an increase in the amount of copper leached. Hem-fir boards had the highest retention and the highest amount of copper leached, while jack pine boards, with the lowest retention, had the lowest amount of copper leached.

Table 4-3 Monthly evaluations of jack pine CAz treated boards exposed above ground*

Month	Volume of leachate (L)	Amount of copper (CuO) leached (mg)	Cumulative amount of copper (CuO) leached (mg)
Jun/Jul-03	3.16 (1.76)	4.64 (1.38)	4.64
Aug-03	0.06 (0.02)	0.63 (0.20)	5.27
Sep-03	0.92 (0.40)	5.62 (1.69)	10.88
Oct-03	16.23 (1.83)	5.09 (1.83)	15.98
Nov-03	15.71 (1.86)	2.10 (0.80)	18.07
Dec-03	13.14 (1.53)	2.56 (1.10)	20.63
Jan-04	11.67 (1.01)	1.69 (0.65)	22.32
Feb-04	6.42 (0.50)	0.88 (0.21)	23.20
Mar-04	6.97 (0.46)	1.48 (0.57)	24.68
Apr-04	0.25 (0.00)	0.63 (0.13)	25.31
May-04	3.90 (0.27)	3.40 (0.63)	28.71
Jun-04	0.43 (0.08)	0.92 (0.21)	29.62
Jul-04	0.57 (0.05)	0.92 (0.24)	30.54
Aug-04	4.03 (0.36)	4.59 (1.03)	35.14
Sep-04	7.70 (0.56)	2.03 (0.56)	37.17

* Average of the evaluations
** Values within parenthesis is the standard deviation

Table 4-4 Monthly evaluations of hem-fir CAz treated boards exposed above ground*

Month	Volume of leachate (L)	Amount of copper (CuO) leached (mg)	Cumulative amount of copper (CuO) leached (mg)
Jun/Jul-03	3.27 (1.50)	19.16 (5.24)	19.16
Aug-03	0.03 (0.02)	0.55 (0.38)	17.69
Sep-03	0.58 (0.36)	17.13 (8.28)	34.82
Oct-03	15.07 (2.27)	57.69 (37.55)	92.51
Nov-03	14.94 (1.74)	23.71 (13.79)	116.21
Dec-03	12.09 (1.34)	23.10 (14.47)	139.32
Jan-04	10.81 (0.97)	15.72 (10.52)	155.03
Feb-04	6.04 (0.38)	7.64 (5.78)	162.68
Mar-04	6.45 (0.32)	6.77 (4.38)	169.45
Apr-04	0.25 (0.00)	0.95 (0.29)	170.40
May-04	3.31 (0.25)	6.47 (1.26)	176.87
Jun-04	0.36 (0.73)	1.64 (0.53)	178.51
Jul-04	0.50 (0.06)	1.20 (0.30)	179.70
Aug-04	3.57 (0.24)	8.72 (2.13)	188.42
Sep-04	7.46 (0.31)	6.42 (2.60)	194.84

* Values of the evaluations
** Values within parenthesis is the standard deviation

Table 4-5 Monthly evaluations of lodgepole pine CAz treated boards exposed above ground*

Month	Volume of leachate (L)	Amount of copper (CuO) leached (mg)	Cumulative amount of copper (CuO) leached (mg)
Jun/Jul-03	2.81 (1.64)	9.33 (2.79)	9.33
Aug-03	0.08 (0.02)	1.06 (0.21)	10.39
Sep-03	0.90 (0.39)	7.48 (1.65)	17.88
Oct-03	15.66 (1.24)	8.14 (2.75)	26.01
Nov-03	14.35 (1.26)	3.59 (1.75)	29.60
Dec-03	12.54 (1.65)	4.99 (2.33)	34.59
Jan-04	11.21 (1.16)	3.76 (2.46)	38.34
Feb-04	6.24 (0.58)	1.69 (0.99)	40.03
Mar-04	6.61 (0.73)	1.84 (0.65)	41.87
Apr-04	0.25 (0.00)	0.77 (0.23)	42.65
May-04	3.75 (0.41)	4.04 (0.84)	46.69
Jun-04	0.40 (0.14)	0.84 (0.34)	47.53
Jul-04	0.55 (0.05)	1.04 (0.17)	48.56
Aug-04	3.68 (0.40)	5.20 (1.38)	53.76
Sep-04	7.42 (0.72)	2.45 (0.79)	56.21

* Values of the evaluations
** Values within parenthesis is the standard deviation

From the statistical analysis, it was observed that the treated ends of the samples had an influence on the amount of copper leached. Table 4-6 shows the average values of copper leached per month for the treated end of the sample boards. The results showed that statistical differences exist for hem-fir and lodgepole pine boards but not for jack pine boards. The penetration and retention of the boards could be a key determinant in the influence of the treated board end on copper leaching. For hem-fir and lodgepole pine, with treated ends, it is expected that higher values of copper leaching will occur due to this additional source of leachable copper. Also, untreated ends could be available zones for mobile copper to bond, decreasing the amount of copper leaching. The lack of a statistical difference for jack pine suggests that lower penetration and retention at the treated board end provides less unfixed copper for leaching.

Table 4-6 Average of the amount of copper leached (mg) per month considering the end treated part from CAz treated boards

Month	Jack pine		Hem-fir		Lodgepole pine	
	With end treated part (mg)	Without end treated part (mg)	With end treated part (mg)	Without end treated part (mg)	With end treated part (mg)	Without end treated part (mg)
Jun/Jul-03	5.40 (0.98)	3.87 (1.36)	19.06 (5.18)	19.25 (5.90)	9.83 (3.41)	8.82 (2.28)
Aug-03	0.52 (0.20)	0.74 (0.16)	0.50 (0.33)	0.59 (0.47)	1.12 (0.13)	1.01 (0.27)
Sep-03	6.13 (0.72)	5.10 (2.30)	19.82 (10.36)	14.44 (5.36)	8.32 (1.13)	6.65 (1.76)
Oct-03	5.12 (1.00)	5.07 (2.55)	73.88 (46.57)	41.49 (18.68)	9.05 (2.69)	7.22 (2.77)
Nov-03	2.28 (0.51)	1.91 (1.05)	29.59 (17.87)	17.82 (4.68)	3.74 (1.47)	3.43 (2.15)
Dec-03	2.62 (1.07)	2.50 (1.26)	28.02 (18.97)	18.19 (7.15)	5.62 (2.26)	4.35 (2.47)
Jan-04	1.94 (0.71)	1.44 (0.55)	20.47 (13.27)	10.97 (4.06)	4.53 (2.04)	2.98 (2.83)
Feb-04	0.83 (0.05)	0.92 (0.30)	10.42 (7.21)	4.87 (2.00)	2.10 (0.44)	1.29 (1.27)
Mar-04	1.42 (0.53)	1.53 (0.67)	8.62 (5.65)	4.92 (1.65)	2.05 (0.49)	1.63 (0.78)
Apr-04	0.70 (0.08)	0.56 (0.15)	1.10 (0.29)	0.80 (0.23)	0.77 (0.24)	0.78 (0.26)
May-04	3.65 (0.59)	3.15 (0.61)	7.00 (1.54)	5.94 (0.71)	4.27 (0.76)	3.81 (0.93)
Jun-04	0.96 (0.13)	0.87 (0.28)	1.87 (0.64)	1.41 (0.31)	0.94 (0.21)	0.74 (0.43)
Jul-04	1.10 (0.13)	0.73 (0.18)	1.29 (0.29)	1.11 (0.31)	1.02 (0.10)	1.05 (0.23)
Aug-04	4.29 (0.74)	4.90 (1.27)	9.35 (2.63)	8.08 (1.50)	6.14 (1.14)	4.26 (0.88)
Sep-04	1.77 (0.53)	2.29 (0.51)	7.62 (3.16)	5.22 (1.24)	2.88 (0.69)	2.10 (0.66)
Tukey test	a	a	b	c	d	e

* Values within parenthesis is the standard deviation

Using the same methodology as was used in the ACQ study, the relative loss of copper was determined in three different ways: related to the top surface area, to the exposed area and reference to the treated volume. The amount of copper loss, based on weight uptake, could not be calculated because information on the weight uptake of the CAz preservative in boards after the treatment was not provided. The first approach considered the amount of copper leached related to the deck surface area (top surface area). The decking simulated area in this part was 0.0812 m^2 (Table 4-7). According to this approach the trend of copper in losses remained the same for each species. During the later months of exposure, the differences between species started to decrease. After 16 months of exposure, the cumulative amount of copper leached were 457.74 mg/m^2 for jack pine boards, 2219.85 mg/m^2 for hem-fir, and 692.22 mg/m^2 for lodgepole pine. Figure 4-2, 4-3 and 4-4 show the average of amount of copper leached (mg/m^2) and the amount of leachate collected from jack pine, hem-fir and lodgepole pine, respectively. The highest amount of copper leachate was collected in Jun-July, September, and October for jack pine and lodgepole pine treated boards and June and July for hem-fir treated boards. The following months showed a decrease in the amount of copper leached, except for May, 2004 and August, 2004, in which the amount of copper leached increased after dry periods, due to the process of CuO diffusion.

Table 4-7 Average of copper leached per month in mg/m^2 of decking area from CAz treated boards at field exposure

Month	jack pine		hem-fir		lodgepole pine	
	Amount of copper (CuO) leached per month (mg/m^2)	Amount of copper (CuO) leached per month (mg/m^2) cumulative	Amount of copper (CuO) leached per month (mg/m^2)	Amount of copper (CuO) leached per month (mg/m^2) cumulative	Amount of copper (CuO) leached per month (mg/m^2)	Amount of copper (CuO) leached per month (mg/m^2) cumulative
Jun/Jul-03	57.11	57.11	236.02	236.02	114.89	114.89
Aug-03	7.76	64.87	6.73	241.86	13.10	127.99
Sep-03	69.17	134.04	210.98	452.49	92.18	220.16
Oct-03	62.74	196.77	710.46	1073.46	100.20	320.37
Nov-03	25.81	222.59	291.94	1339.55	44.17	364.54
Dec-03	31.54	254.12	284.52	1604.77	61.41	425.95
Jan-04	20.81	274.94	193.58	1768.66	46.25	472.19
Feb-04	10.79	285.73	94.13	1847.33	20.85	493.04
Mar-04	18.19	303.92	83.37	1920.04	22.64	515.68
Apr-04	7.79	311.70	11.72	1931.56	9.52	525.20
May-04	41.84	353.54	79.68	2008.05	49.80	575.00
Jun-04	11.28	364.82	20.17	2027.42	10.30	585.30
Jul-04	11.32	376.14	14.77	2042.12	12.75	598.05
Aug-04	56.57	432.71	107.35	2146.69	64.06	662.11
Sep-04	25.02	457.74	79.05	2219.85	30.12	692.22

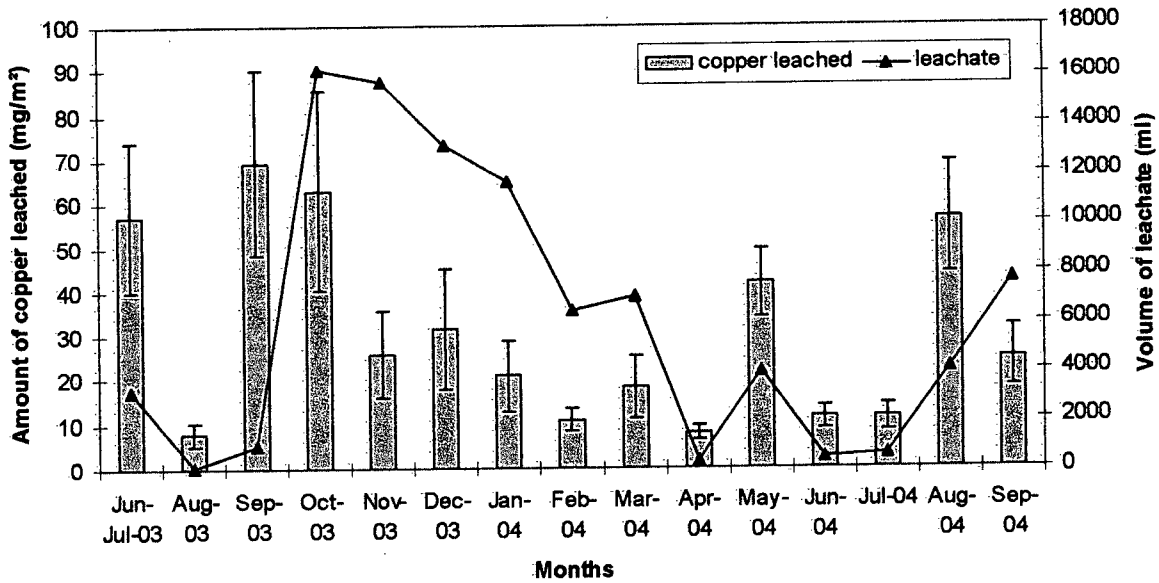

Figure 4-2 Average of the amount of copper leached (mg/m^2) from jack pine CAz treated boards after 16 months of exposure

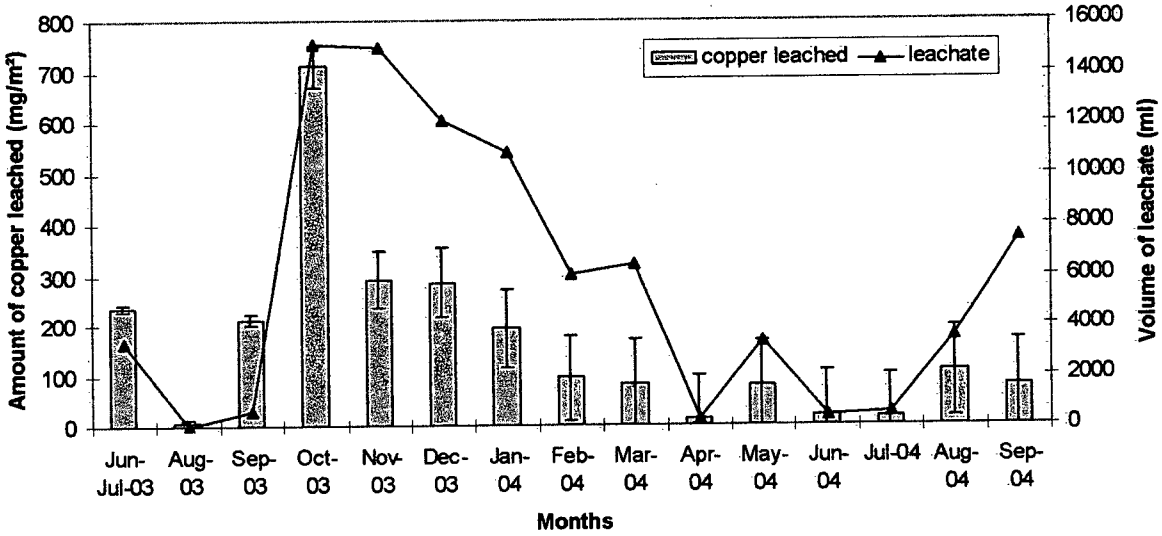

Figure 4-3 Average of the amount of copper leached (mg/m^2) from hem-fir CAz treated boards after 16 months of exposure

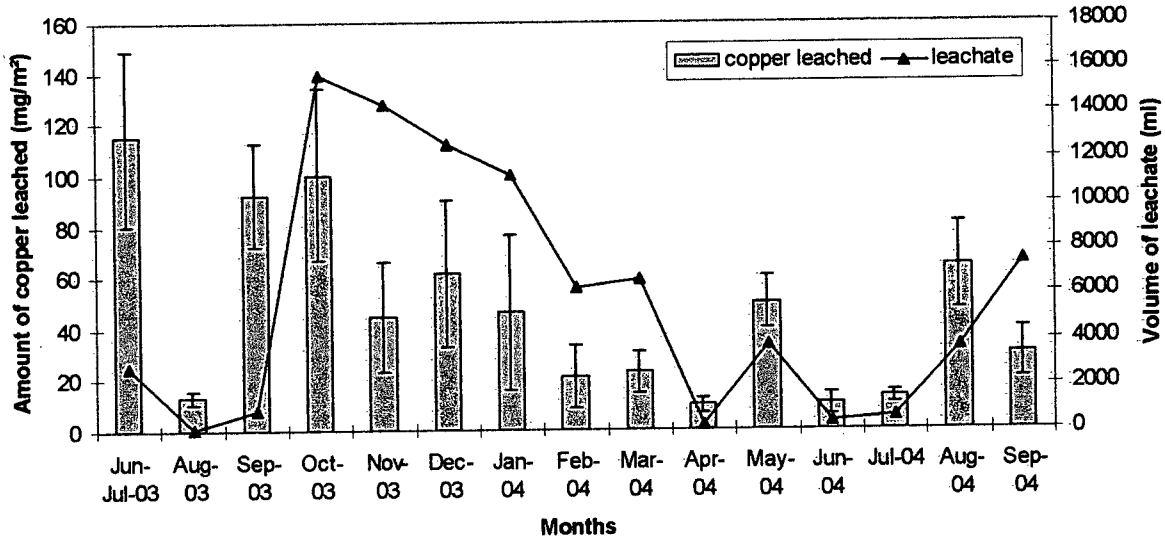

Figure 4-4 Average of the amount of copper leached (mg/m^2) from lodgepole pine CAz treated boards after 16 months of exposure

The second approach was to relate the amount of copper losses to the exposed area (Table 4-8). In this case the exposed area considers the top surface and two sides per board. The exposed area was 0.1253 m^2 which included two boards per basin. The tendency of copper losses remains the same as it was observed for copper losses in mg. After 16 months of exposure, the cumulative copper losses were 296.68 mg/m^2 for jack pine, 1555.23 mg/m^2 for hem-fir and 448.66 mg/m^2 for lodgepole pine.

Table 4-8 Average of copper leached per month in mg/m^2 of exposed area from CAz treated boards at field exposure

Month	jack pine		hem-fir		lodgepole pine	
	Amount of copper (CuO) leached per month (mg/m^2)	Cumulative amount of copper (CuO) leached per month (mg/m^2)	Amount of copper (CuO) leached per month (mg/m^2)	Cumulative amount of copper (CuO) leached per month (mg/m^2)	Amount of copper (CuO) leached per month (mg/m^2)	Cumulative amount of copper (CuO) leached per month (mg/m^2)
Jun/Jul-03	37.01	37.01	152.98	152.98	78.63	78.63
Aug-03	5.03	42.04	4.36	148.78	8.60	84.56
Sep-03	44.83	86.88	136.75	277.92	59.74	142.70
Oct-03	40.66	127.54	460.49	738.40	64.95	207.65
Nov-03	16.73	144.27	189.22	927.62	28.63	236.27
Dec-03	20.44	164.71	184.41	1112.03	39.80	276.08
Jan-04	13.49	178.20	125.47	1237.50	29.97	306.05
Feb-04	7.00	185.20	61.01	1298.50	13.51	319.56
Mar-04	11.79	196.98	54.03	1352.54	14.68	334.24
Apr-04	5.05	202.03	7.59	1360.13	6.17	340.41
May-04	27.12	229.15	51.64	1411.78	32.28	372.69
Jun-04	7.31	236.46	13.07	1424.85	6.67	379.36
Jul-04	7.34	243.80	9.57	1434.42	8.27	387.63
Aug-04	36.66	280.46	69.58	1504.00	41.52	429.14
Sep-04	16.22	296.68	51.23	1555.23	19.52	448.66

The third method used to express the relative loss of copper is in the percentage of copper over the total amount of copper in the boards. The amount of copper in the boards was calculated from the amount copper retention and from the total volume of treated wood. This approach gives an approximation of the total amount of copper present. As was mentioned in the ACQ study, errors arise due to the varying penetration of copper along the surface of the board. Table 4-9 shows the average of the percentage of copper leached per basin. The lowest percentage of copper leached was found in hem-fir. This is due to the highest penetration and

retention of copper found in hem-fir. The tendency of copper to leach can be explained by the same mechanism that was identified for the amount of copper (as CuO) leached in mg. The highest amount of copper leached was found in the first months of the exposure (with the exception of August, 2003, due to the low precipitation). Also, it was observed that a small increase in copper leachate occurred in the May and August, 2004. The highest percentage of copper leached was found from lodgepole pine. After 16 months of exposure, the cumulative percentage of copper leached was 2.69% for hem-fir, 4.38 % for jack pine, and 7.84% for lodgepole pine.

Table 4-9 Average of copper leached from CAz treated boards per month in percentage

Month	jack pine		hem-fir		lodgepole pine	
	Amount of copper (CuO) leached per month (%)	Amount of copper (CuO) leached per month (%) cumulative	Amount of copper (CuO) leached per month (%)	Amount of copper (CuO) leached per month (%) cumulative	Amount of copper (CuO) leached per month (%)	Amount of copper (CuO) leached per month (%) cumulative
Jun/Jul-03	0.40 (0.52)	0.52	0.29 (0.13)	0.29	1.34 (1.09)	1.34
Aug-03	0.09 (0.09)	0.60	0.01 (0.01)	0.30	0.15 (0.10)	1.49
Sep-03	0.64 (0.39)	1.25	0.24 (0.11)	0.55	1.03 (0.70)	2.52
Oct-03	0.60 (0.42)	1.85	0.76 (0.40)	1.28	1.13 (0.89)	3.65
Nov-03	0.23 (0.14)	2.09	0.33 (0.16)	1.60	0.52 (0.50)	4.17
Dec-03	0.30 (0.22)	2.39	0.32 (0.18)	1.93	0.70 (0.65)	4.87
Jan-04	0.20 (0.13)	2.58	0.22 (0.13)	2.14	0.50 (0.53)	5.37
Feb-04	0.11 (0.08)	2.69	0.10 (0.05)	2.23	0.21 (0.22)	5.58
Mar-04	0.18 (0.12)	2.87	0.09 (0.04)	2.32	0.26 (0.21)	5.84
Apr-04	0.07 (0.03)	2.94	0.01 (0.00)	2.33	0.12 (0.11)	5.96
May-04	0.39 (0.20)	3.33	0.10 (0.04)	2.43	0.59 (0.47)	6.54
Jun-04	0.12 (0.10)	3.45	0.02 (0.01)	2.45	0.12 (0.10)	6.66
Jul-04	0.10 (0.04)	3.55	0.02 (0.01)	2.47	0.16 (0.13)	6.82
Aug-04	0.57 (0.40)	4.12	0.13 (0.07)	2.60	0.70 (0.49)	7.52
Sep-04	0.26 (0.19)	4.38	0.09 (0.05)	2.69	0.32 (0.21)	7.84

* Values within parenthesis is the standard deviation

4.2.3 Effect of species treated board on copper leaching

Species have different effects on copper leaching. The amount of copper that is leached depends on the amount of copper that is available in the treated wood. Typically the higher the amount of copper in the wood, the higher amount of unfixed copper is available for leaching. Higher amounts of copper are found when copper penetrates deeper into a board. The penetration depth of the preservatives depends on the species being treated. According to the treated boards used for this experiment, hem-fir treated boards showed the highest retention and the deepest penetration, therefore highest amount of copper was leached. Jack pine and lodgepole pine showed lower penetration than hem-fir and significant differences in the amount of copper leached (Figure 4-5). After 16 months of exposure, hem-fir boards had a cumulative amount of copper leached of 2219.85 mg/m^2, the pines had a cumulative amount of copper leached no higher than 700 mg/m^2.

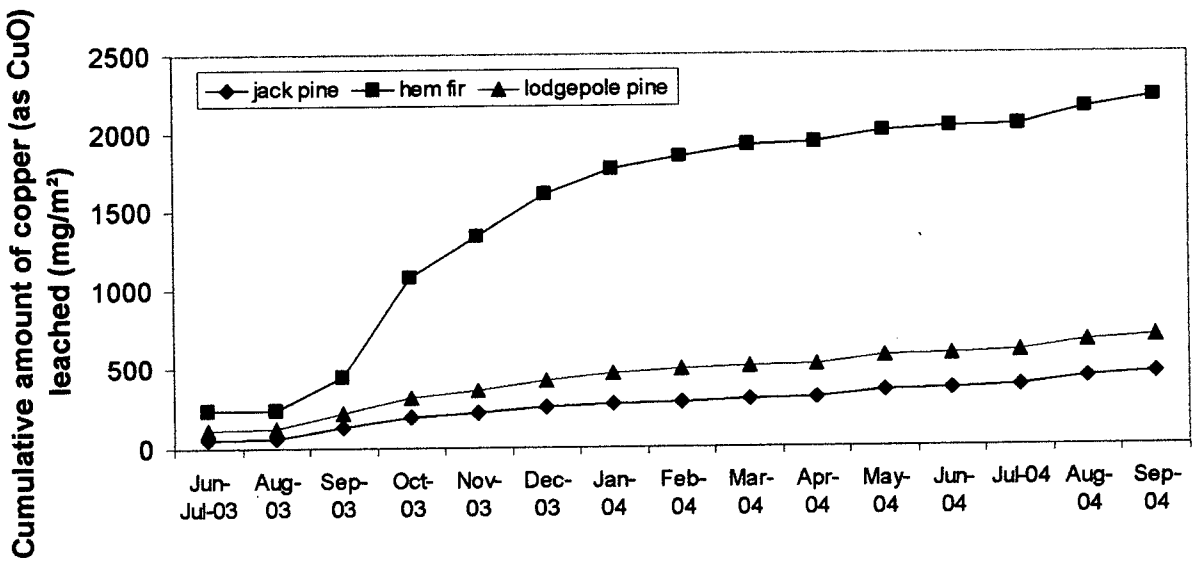

Figure 4-5 Comparison of the cumulative amount of copper leached (mg/m^2) after 16 months of field exposure

4.2.4 Laboratory Leaching

Accelerated laboratory leaching was conducted on reference samples of each board that were exposed in the field test. This test was used to asses the amount of total mobile copper in the CAz boards. In this test, a method was designed to model the amount of copper leached at determined time intervals during the leaching process. Table 4-10, 4-11, and 4-12 show the amount of copper leached in period intervals during the accelerated laboratory leaching, for jack pine, hem–fir and lodgepole pine, respectively. For the three species, the greatest amount of copper leached occurred during the first hour of leaching, during the following time periods only very small amounts of copper were leached. In some cases, no copper was leached or none was detectable by the Atomic Absorption Spectroscopy. Due to the small amount of copper leached, modeling the copper losses was not possible.

Table 4-10 shows the amount of copper leached from jack pine treated sawdust per board. It was observed that retention and penetration had an influence on the total amount of copper leached. The boards JP 5, JP 10, JP 7, and JP 2 had highest retention and as a result, had a higher amount of copper leached compared to the rest of the boards. Board JP 12 was an exception since it had the highest retention (2.14 kg/m^3) compared to the other boards, but the lowest amount of copper leached (0.21 mg). An explanation for this observation can be seen from Figure 4-6, in which the cross section of the references samples of the jack pine boards are shown. The top part of the board JP 12 was not very well penetrated compared to the other samples. Boards with high penetration had higher amounts of copper leached. Boards JP 5, JP10 and JP 7 showed deeper penetration than other boards. A deeper penetration assured that the sawdust samples for leaching had no untreated sawdust in them. Since penetration is not homogeneous within a board; deeper penetration increases the probability that all sawdust collected by a router from the base depth of 1.5 mm has been treated. Samples from boards with low penetration certainly have a higher probability of having untreated sawdust in them. This is apparently the reason why Board JP 12 and other boards with higher retention had lower amounts of copper leached.

Table 4-10 Amount of copper leached from jack pine CAz treated sawdust during the accelerated laboratory leaching

Board	Retention (kg/m^3)	Amount of copper leached as CuO (mg)						
		1 hour	3 hours	6 hours	24 hours	48 hours	72 hours	Total
JP 1	1.37	0.10	0.02	0.04	0.01	0.03	0.01	0.21
JP 2	2.23	0.20	0.02	0.02	0.05	0.03	0.03	0.35
JP 3	1.20	0.11	0.01	0.02	0.02	0.03	0.02	0.22
JP 4	1.37	0.16	0.02	0.02	0.03	0.03	0.02	0.28
JP 5	1.87	0.32	0.02	0.02	0.07	0.05	0.02	0.51
JP 7	1.62	0.28	0.01	0.01	0.05	0.04	0.00	0.40
JP 8	1.00	0.24	0.00	0.01	0.05	0.04	0.01	0.36
JP 10	1.27	0.30	0.01	0.00	0.07	0.05	0.04	0.47
JP 12	2.14	0.11	0.02	0.02	0.04	0.02	0.01	0.21
JP 14	1.39	0.19	0.01	0.00	0.05	0.03	0.03	0.30
Average	1.55	0.20	0.01	0.02	0.05	0.03	0.02	0.33

Figure 4-6 Cross section of the references samples of the jack pine CAz treated boards

Table 4-11 shows the amount of copper leached from hem-fir treated sawdust per board. The amount of copper leached is higher compared to jack pine; due to the higher retention of the hem-fir boards. As it was observed in jack pine, the first hour of the leaching process caused the highest amount of copper to be leached. In this one hour-period leaching, almost all the unfixed copper was leached from the surface of the wood. During the subsequent periods of leaching, the amount of copper being leached decreased substantially. As was the case with jack pine, the higher retention of the boards the higher the amount of copper leached. Board HF 1, with the highest retention, leached the greatest amount of copper while boards HF 4 and HF 21, with the lowest retention, leached the smallest amount of copper. However, there were some boards with high retention that did not leached as much as it was expected i.e. board HF 24 with retention 5.50 kg/m^3, leached only 1.85 mg of copper, while board, while boards HF 2 and HF5 with similar retention 5.39 kg/m^3 and 5.42 kg/m^3 respectively, leached 2.69 mg and 3.05 mg of copper. The answer could be in the top side of the boards. Figure 4-7 shows the cross section of the boards. Differences in the top side of the boards can be observed. The penetration of the boards was irregular in some boards. HF 24 had irregular penetration than HF 2 and HF 5. Also, differences in proportion of radial and tangential part in the top side of the board could influence the amount of copper leached.

Table 4-11 Amount of copper leached from hem-fir CAz treated sawdust during the accelerated laboratory leaching

Board	Retention	Amount of copper leached as CuO (mg)						
	(kg/m^3)	1 hour	3 hours	6 hours	24 hours	48 hours	72 hours	Total
HF 1	6.71	7.56	0.03	0.12	0.02	0.18	0.00	7.90
HF 2	5.39	1.89	0.22	0.05	0.20	0.20	0.13	2.69
HF 4	4.10	1.07	0.07	0.05	0.10	0.09	0.06	1.44
HF 5	5.42	2.87	0.00	0.01	0.02	0.08	0.07	3.05
HF 6	6.09	2.45	0.00	0.00	0.00	0.08	0.08	2.62
HF 8	6.03	1.89	0.04	0.00	0.12	0.10	0.08	2.22
HF 11	6.42	3.15	0.05	0.01	0.00	0.04	0.14	3.40
HF 18	6.22	2.55	0.09	0.06	0.00	0.11	0.07	2.89
HF 21	3.92	1.54	0.03	0.03	0.08	0.11	0.10	1.89
HF 24	5.50	1.47	0.00	0.05	0.11	0.15	0.07	1.85
Average	5.58	2.64	0.05	0.04	0.06	0.11	0.08	2.99

Figure 4-7 Cross section of the references samples of the hem- fir CAz treated boards

Table 4-12 shows the average of amount of copper leached per board during accelerated laboratory leaching for lodgepole pine. The trend for the amount of copper leached for was the same as observed for the other two species. The highest amount of copper leached was in the first hour, with lower amounts of leaching in subsequent time periods. The amount of copper leached was lower than that observed in the hem-fir boards but was a little higher than that observed in jack pine boards, though the losses were similar. The similar amounts of copper leached were due to the samples having similar copper retention and penetration. The penetration of copper is shown in Figure 4-8. Shell penetration, showed by the jack pine boards, was also observed in the lodgepole pine boards. The highest amount of copper leached was found for board LP 2 and board LP 4, which had the highest copper retention (2.72 kg/m^3 and 2.53 kg/m^3, respectively), also, these boards were different then the other sample boards. Board LP 17 and board LP 1, with the lowest copper retention (1.00 kg/m^3 and 1.24 kg/m^3, respectively) had the lowest amount of copper leached and were different then the other boards.

Table 4-12 Amount of copper leached from lodgepole pine CAz treated sawdust during the accelerated laboratory leaching

Board	Retention (kg/m^3)	Amount of copper leached as CuO (mg)						
		1 hour	3 hours	6 hours	24 hours	48 hours	72 hours	Total
LP 1	1.24	0.15	0.00	0.01	0.03	0.02	0.01	0.23
LP 2	2.72	0.77	0.00	0.16	0.09	0.07	0.05	1.14
LP 3	2.28	0.62	0.03	0.05	0.09	0.08	0.03	0.90
LP 4	2.53	0.80	0.00	0.16	0.09	0.06	0.08	1.19
LP 5	1.63	0.18	0.01	0.02	0.07	0.06	0.01	0.35
LP 6	1.54	0.23	0.01	0.01	0.09	0.06	0.03	0.42
LP 8	1.28	0.26	0.02	0.02	0.06	0.04	0.01	0.42
LP 11	1.65	0.60	0.03	0.02	0.11	0.05	0.01	0.84
LP 17	1.00	0.20	0.01	0.01	0.04	0.02	0.01	0.29
LP 20	2.11	0.66	0.04	0.02	0.08	0.07	0.05	0.91
Average	1.80	0.45	0.02	0.05	0.08	0.05	0.03	0.67

Figure 4-8 Cross section of the references samples of the Lodgepole pine CAz treated boards

4.2.5 Prediction of copper leaching

As it was mentioned in the ACQ study, it is important to observe the rate of copper leaching as a measure of the mobile copper in wood. This is possible comparing this copper depletion during 20 year service life with the known total amount of mobile copper. The average of copper leached monthly per basin expressed as a percentage of the total amount of copper present in the treated wood volume was plotted against the time of exposure. The basins with boards with treated ends were used for this part due to the less variability in copper leaching among the basins.

For this part two fit equations were considered. The first one was to divide the data into two different trends. Figure 4-9 to 4-11 show the trend of cumulative losses after 8, 12 and 16 months of exposure for jack pine boards. The first four months showed the rapid copper losses fit a linear trend (r^2 = 0.6999). It is in this period that the most unfixed copper from the surface is leached. After this first 4 months of exposure, the rate of copper leached decreased. It was in this part that the leaching depended in the amount of mobile copper is transported to the surface of the wood. This process was slow and the copper losses decreased. In the second part of the exposure, the cumulative amount of copper leached may be fitted in a power equation (r^2=0.3778). The coefficient of correlation (r^2) increases with more data of exposure is added. It is expected that with more data of cumulative copper leaching the correlation would increase. Slight increase in the rate of copper leaching was observed in the 12th month May, 2004 (365 days), in which the rainfall increased after a dry period (Figure 4-10) and in the 15th month August, 2004 (458 days), at the beginning of the rainy season (Figure 4-11). Those slight increases in cumulative amount of copper leaching can be seen in Figure 4-12 in which the average of the cumulative of copper leached after 16 months of exposure is shown in Figure 4-12. In addition, one fit equation was also considered (Figure 4-13). The logarithm fit was the best equation with a coefficient of correlation r^2=0.6768.

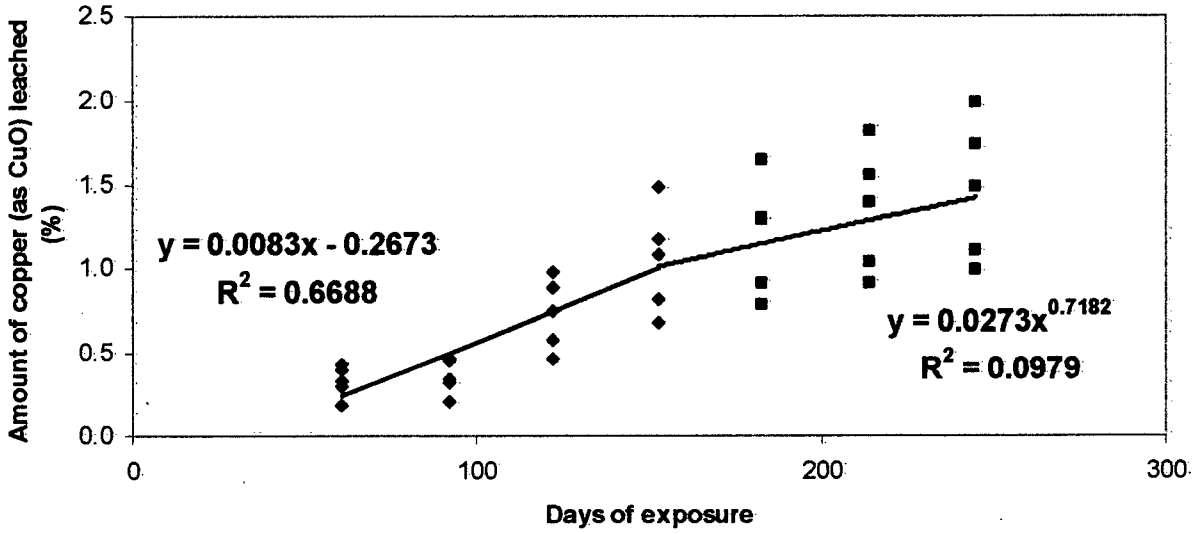

Figure 4-9 Cumulative amount of copper (as CuO) leached (%) from jack pine CAz treated boards with treated ends after 8 months of exposure

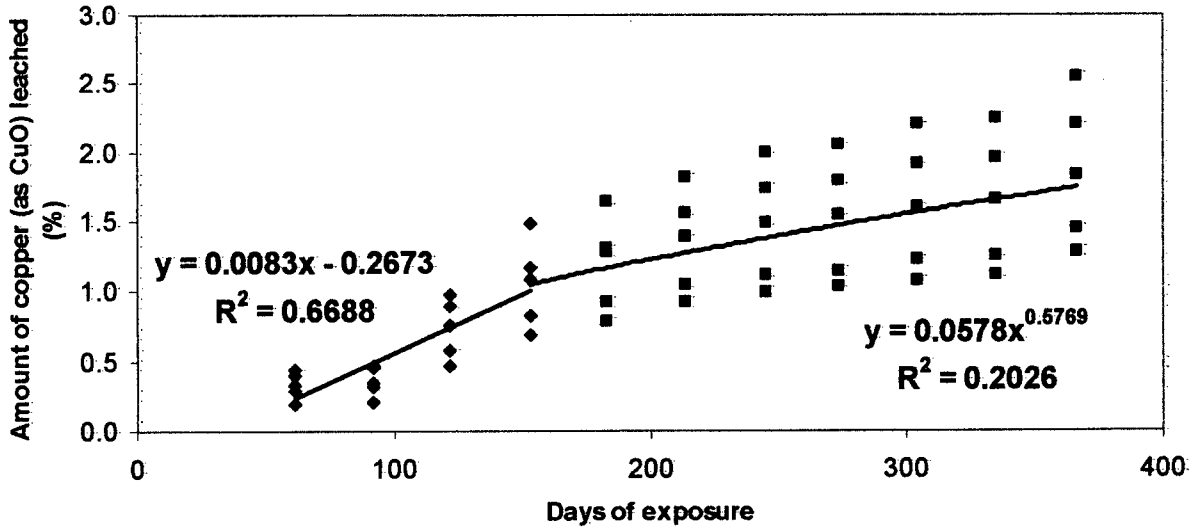

Figure 4-10 Cumulative amount of copper (as CuO) leached (%) from jack pine CAz treated boards with treated ends after 12 months of exposure

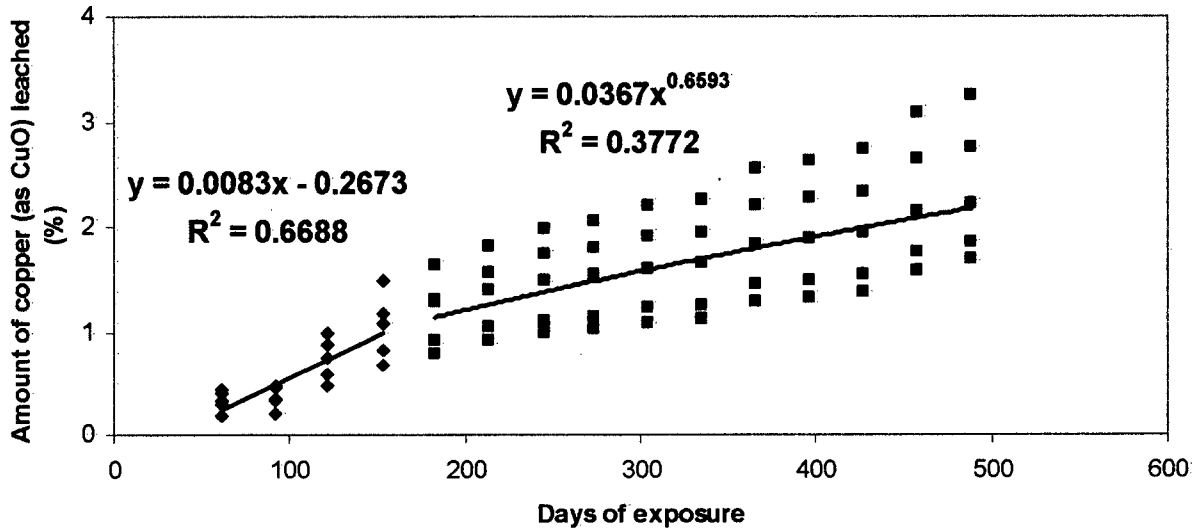

Figure 4-11 Cumulative amount of copper (as CuO) leached (%) from jack pine CAz treated boards with treated ends after 16 months of exposure

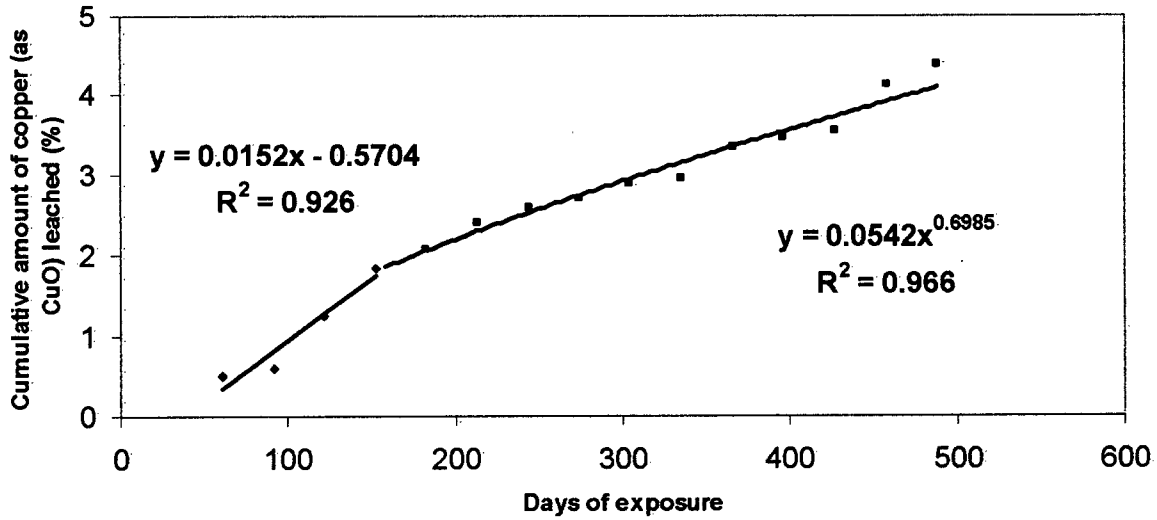

Figure 4-12 Average of the cumulative amount of copper (as CuO) leached (%) from jack pine CAz treated boards with treated ends after 16 months of exposure.

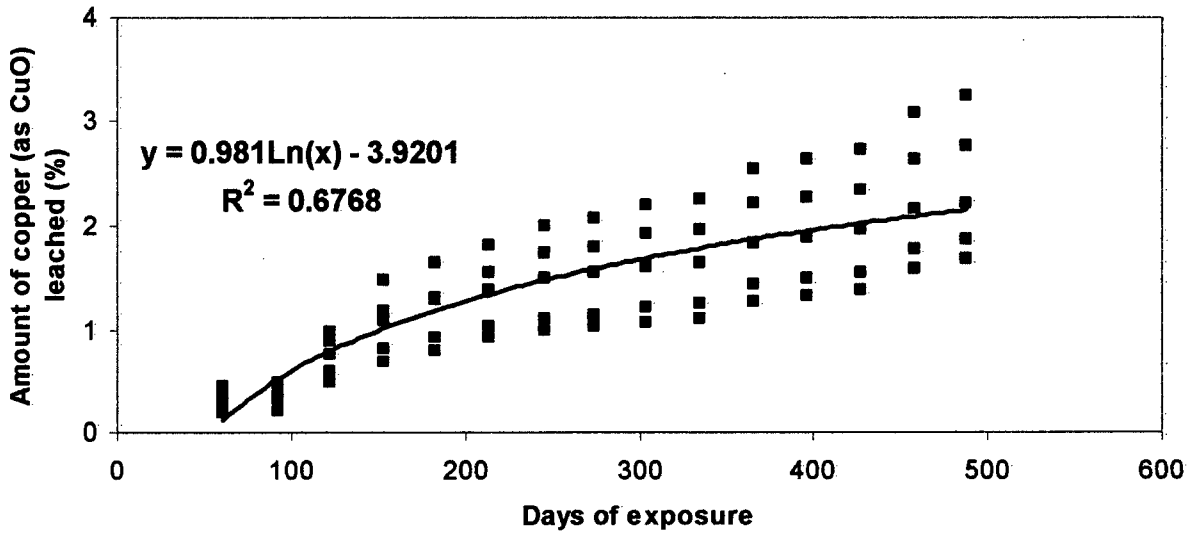

Figure 4-13 Cumulative amount of copper (as CuO) leached (%) from jack pine CAz treated boards with treated ends after 16 months of exposure – one fit

Using the regression equations from the Figures 4-9 to 4-13, prediction of the cumulative amount of copper leached were calculated for a 20 years life. The results are shown in Table 4-13. For the 8-month equation, the prediction was 16.25%. This value is higher that the 12-moth and 16-month's predicted values. This is due to the values from the values had higher rate of losses than the following periods. The values calculated from the 12 month equation had the lowest prediction 9.79% of copper losses. This is due to that the in the 12-month period the amount of copper being leached was decreasing in the last days of exposure. A small increase in the amount of copper leached in the last days of exposure was observed in the 16-month period, therefore an increased in the predicted value was expected (12.93%) compared with the 12-month predicted value. The 16-month average showed higher values of cumulative amount of copper losses (27%). This is due to the rapid high copper losses of the first 4 month of exposure are taking in count in these equations. Using the 16-month one equation, the predict value of copper leached was 4.81%, a value much lower than the other predicted values calculated with other equations.

Table 4-13 Comparison of the predicted copper (as CuO) losses values from jack pine CAz treated boards with treated ends over 20 year period exposure using the fit equations

Fit equation	Prediction of the cumulative amount of Copper (CuO) leached (%) over a 20 years period of exposure*
8 months	16.25
12 months	9.79
16 months	12.93
16 months average	27.07
16 months only one fit	4.81

* Prediction was done with equation calculated with boards with treated ends

A similar analysis was done for hem-fir boards. Figures 4-14 and 4-15 show the cumulative amount of copper leached after 12 and 16 months of exposure. The plots indicated that the cumulative copper loss could group into two fit equations. Also, the trends of the equation were divided into two. The first was the rapid copper leaching that fit in a linear regression (r^2=0.9184 and r^2=0.7915). This rapid loss of copper at the beginning of the exposure was extended until the 8th month because the basins were installed at the beginning of the summer season, and during this period not enough rain occurred to remove the unfixed copper from the surface. The following months, the rate copper leaching was slow and depending on the migration amount of mobile copper to the surface. This second part of the copper leaching it was fit in a power regression (Figure 4-14 and Figure 4-15). No remarkable small increases could be observed as was seen in the jack pine boards, this is may be due to the higher amount of copper leached in hem-fir and the rainy season just started in the last month of data observed in this study. Figure 4-16 shows the average of the cumulative amount of copper per basin and no small increases have been observed until the 16th month of exposure (488 days). Figure 4-17 shows the cumulative amount of copper leached after 16 months of exposure with only one fit. The best fit was a logarithmical equation (r^2=0.8516 and r^2=0.7551), which give a better projection of anticipated copper losses over extended time than the power fit. Predictions of the cumulative amount of copper leached calculated for a 20 years life are shown in Table 4-14. The values calculated vary between 2 % to 9 % of copper losses. Using the average values, for the 12 and 16 months of exposure, the cumulative values of copper losses were approximately 4.34% and 5%, respectively; and for the 16 month average and 16 month with only one fit, the predicted copper losses were 5.87 % and 5.94 %, respectively.

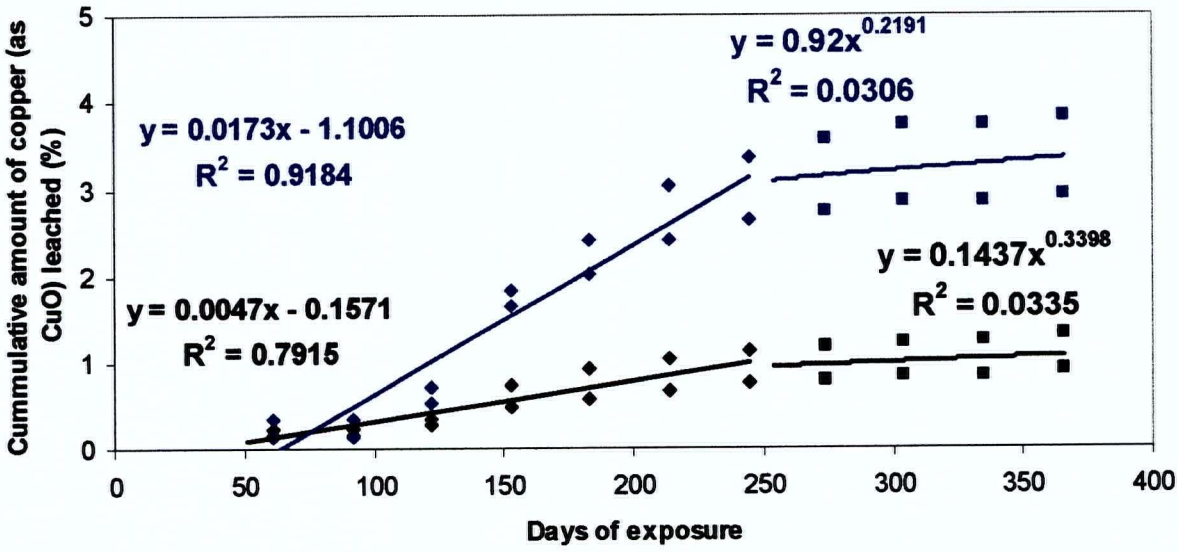

Figure 4-14 Cumulative amount of copper (as CuO) leached (%) from hem-fir CAz treated boards with treated ends after 12 months of exposure and trend in two models

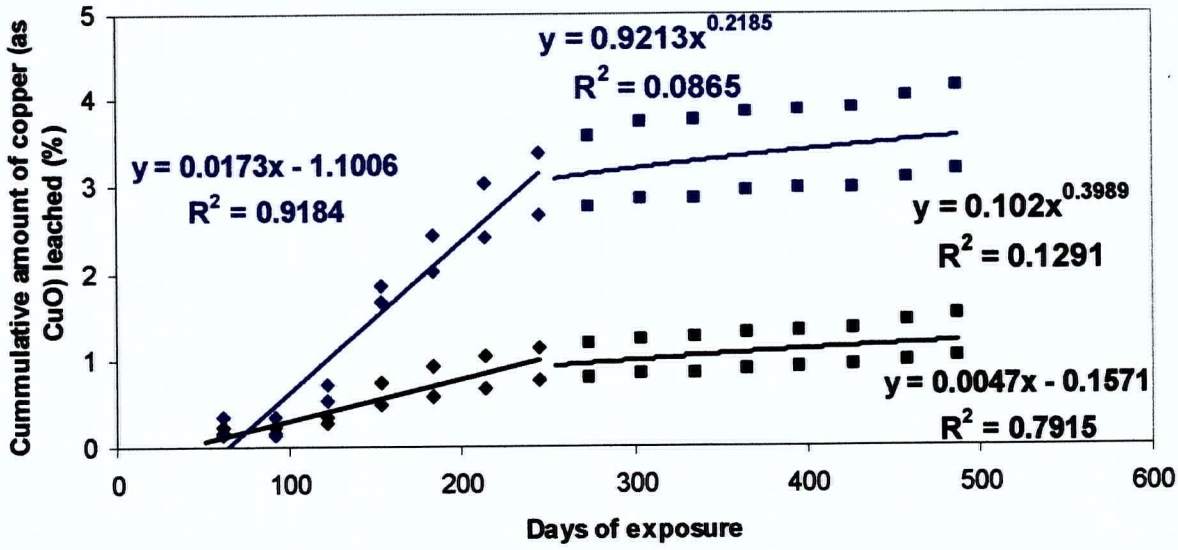

Figure 4-15 Cumulative amount of copper (as CuO) leached (%) from hem-fir CAz treated boards with treated end after 16 months of exposure and trend in two models

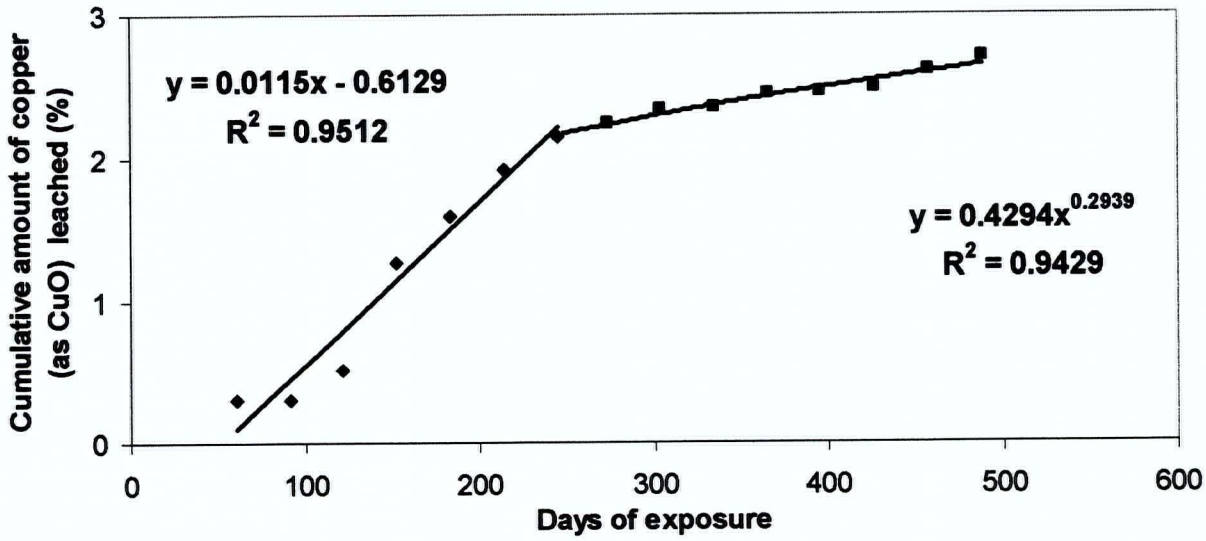

Figure 4-16 Average of cumulative amount of copper (as CuO) leached (%) from hem-fir CAz treated boards with treated ends

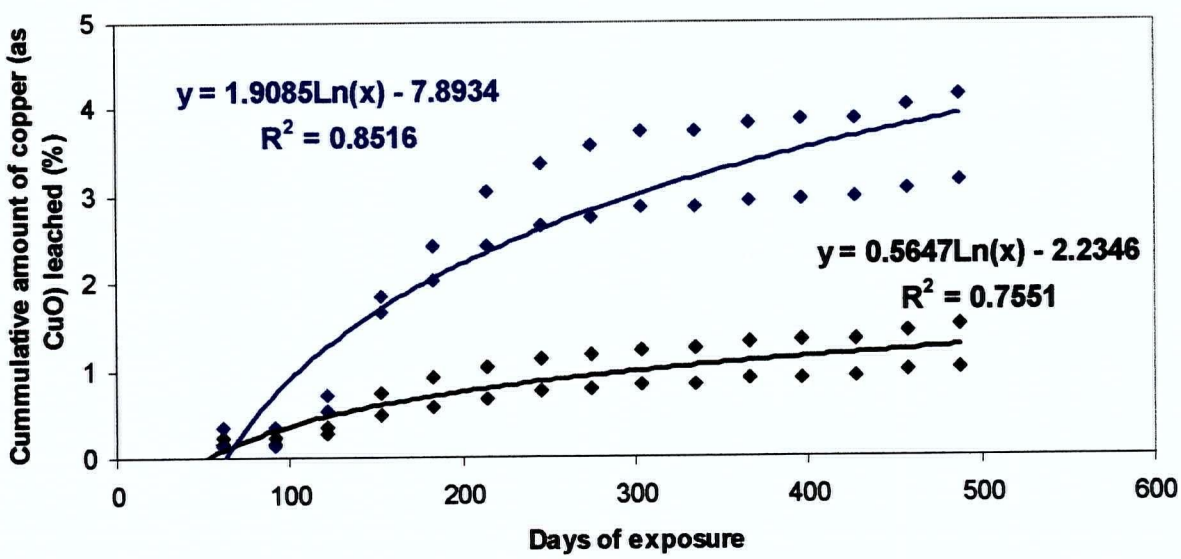

Figure 4-17 Cumulative amount of copper (as CuO) leached (%) from hem-fir CAz treated boards with treated ends – one fit

Table 4-14 Comparison of the predicted copper (as CuO) losses values from hem-fir CAz treated boards with treated ends over 20 year period exposure using the fit equations

Fit equation	Equation	Prediction of the cumulative amount of Copper (CuO) leached (%) over a 20 years period of exposure	
		Per equation	Average
12 months	a	6.46	4.34
	b	2.29	
16 months	a	6.44	5.00
	b	3.55	
16 months average		5.87	5.87
16 months only one fit	a	9.08	5.94
	b	2.79	

Finally, the same analysis was conducted on the lodgepole pine boards. The amount of copper leached monthly expressed as a percentage of the total treated volume in the wood, was plotted against the time of exposure. Figures 4-18 to 4-21 show the trend of the cumulative losses of copper after 12 and 16 months of exposure. Again, two trends were considered to fit the cumulative losses. The first trend is the rapid losses of copper that fits in a linear regression. (r^2=0.723). This trend took place the first 7 months of exposure. This part was longer than the jack pine or ACQ treated boards experiment because the period of installation was at the beginning of the summer season, in which only small rainfall occurred and it was not enough to remove the unfixed copper from the surface of the board. Once the unfixed copper was removed, the leaching was limited to the migration of copper to the surface by diffusion and wetting and drying of the wood. The process was slower and the rate of the copper leaching decreased. This decreasing of the copper leaching rate changed the trend to a power fit. Figure 4-18 and 4-19 shows the two trends in copper leaching after 12 (365 days) and 16 months (488 days) of exposure. No small increases of copper leaching were observed after the 7th month, this is due to the in this period no high rainfall was involved and the rainy season started after the 16th month data that is using for this study. Also, using the average of copper leaching, no small increase is observed (Figure 4-20). Figure 4-21 shows the cumulative values of copper leaching vs. the time of exposure with only one fit equation. The best equation was the logarithmical equation due to provide a reasonable projection of anticipated copper losses over a period of time. Based on the regression equations, predictions of total copper losses after 20 year life period of exposure were calculated. The results are shown in Table 4-15. The value calculated from the 12-month equation period was 11.91 % copper loss. For the 16-month equation

period and the 16-month average equation, the predicted amount of copper leached was 16 % and 17.54 %, respectively. Finally, the amount of copper loss predicted for the one fit equation was 7.75 %.

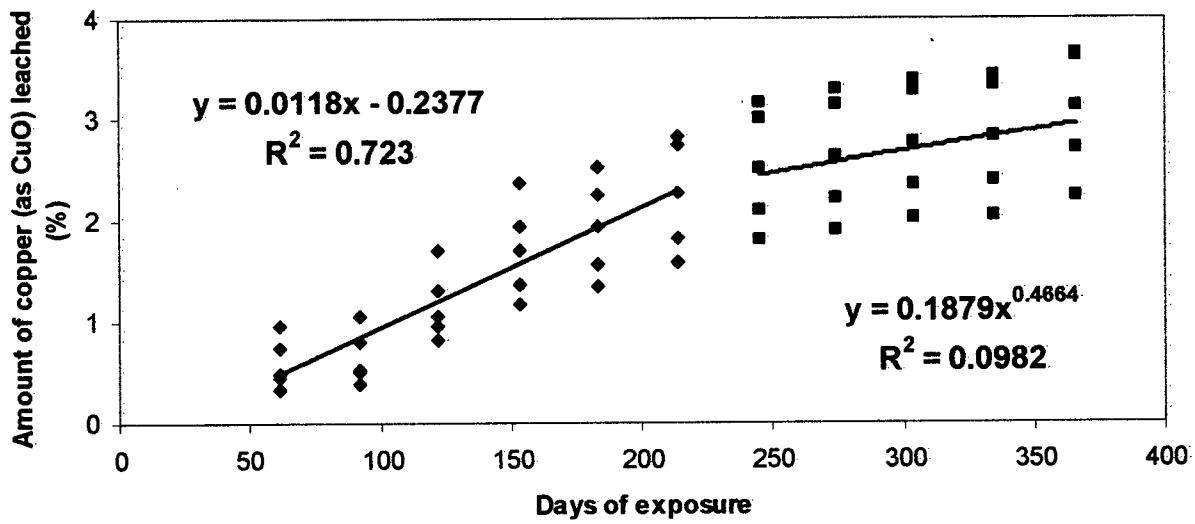

Figure 4-18 Cumulative amount of copper (as CuO) leached (%) from lodgepole pine CAz treated boards with treated ends after 12 months of exposure and trend in two models

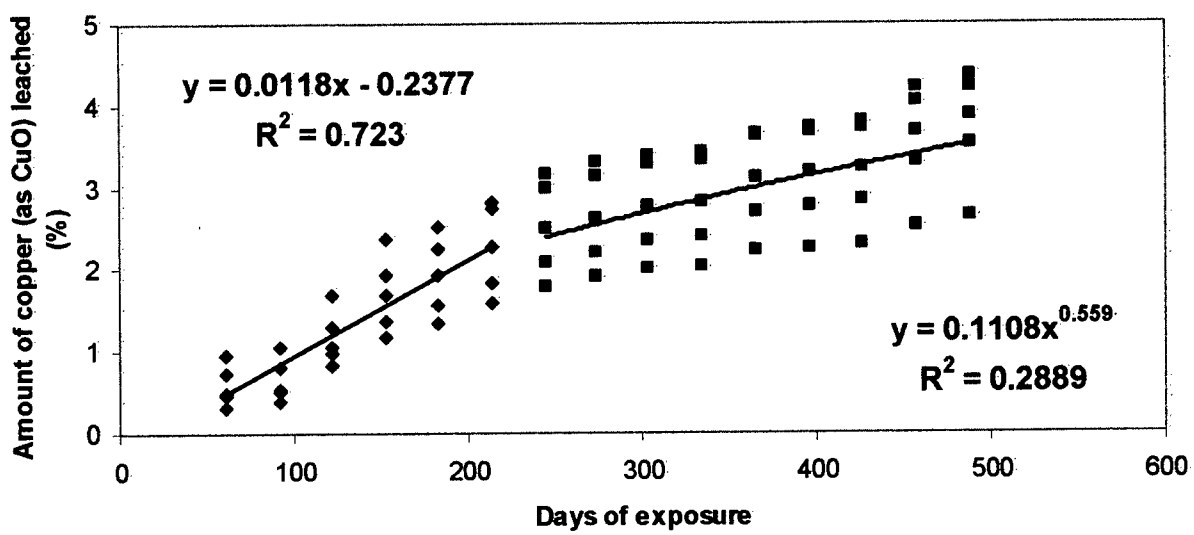

Figure 4-19 Cumulative amount of copper (as CuO) leached (%) from lodgepole pine CAz treated boards with treated ends after 16 months of exposure and trend in two models

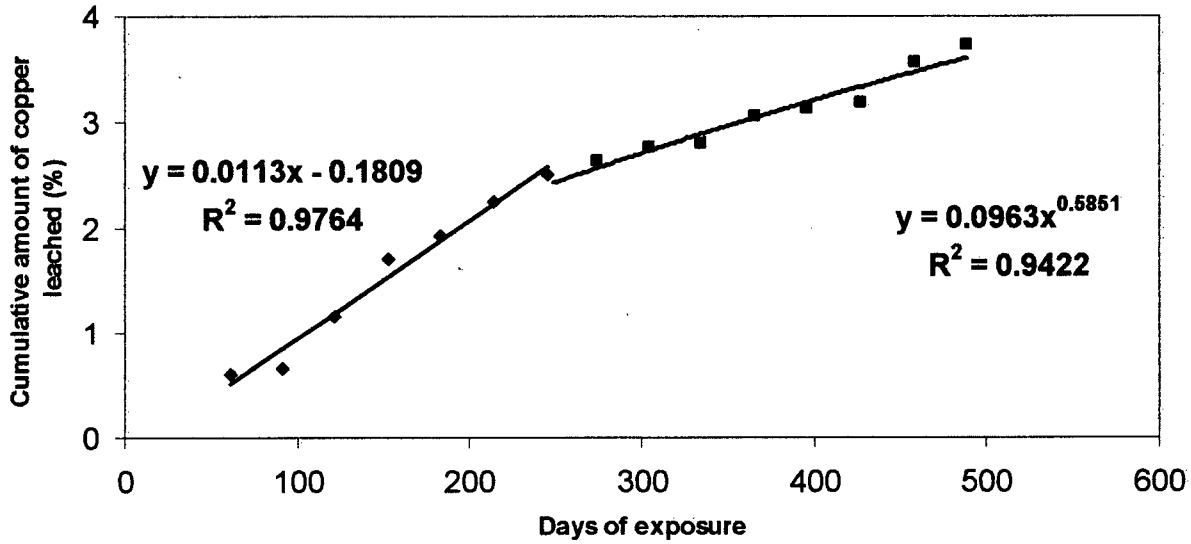

Figure 4-20 Average cumulative amount of copper (as CuO) leached (%) from lodgepole pine CAz treated boards with treated ends after 16 months of exposure and trend in two models

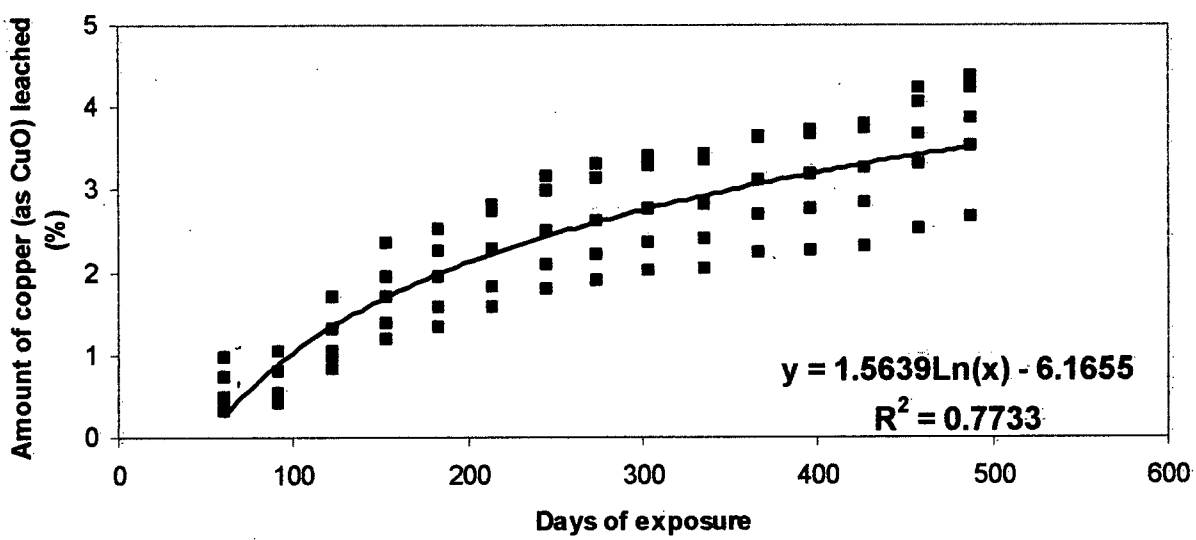

Figure 4-21 Cumulative amount of copper (as CuO) leached (%) from lodgepole pine CAz treated boards with treated ends after 16 months of exposure one fit

Table 4-15 Comparison of the predicted copper (as CuO) losses values from lodgepole pine CAz treated boards with end treated part over 20 year period exposure using the fit equations

Fit equation	Prediction of the cumulative amount of Copper (CuO) leached (%) over a 20 years period of exposure
12 months	11.91
16 months	16.00
16 months average	17.54
16 months only one fit	7.75

Finally, a comparison of copper losses from laboratory, field leaching, and prediction after 20 years of exposure was conducted (see Table 4-16). The field data and the predictions were divided in boards with and without treated ends. The values for samples with treated ends were lower due to the larger total treated volume calculated. Although, the amount of laboratory leaching were supposed to be the highest (because it reflexes the total amount of copper available to be leached), the amounts calculated for the boards without treated ends part in pines were higher. This could be explained by the fact that the total treated volume of wood was calculated based on an approximation of the amount of copper that the treated board could retain and a under estimation of the total treated volume could occur. Since no information on the weight uptake of the preservative was provided, the calculated volume was used. According to the calculations a higher percentage of copper was leached from lodgepole pine boards exposed the field test and also for the predicted amount of copper leached after 20 years of exposure. This problem was not found for hem-fir boards, which have deeper penetration, therefore higher treated volume than the pines. Thus, the lowest percentage of copper loss was observed for hem-fir boards, due to the highest total volume of treated wood.

Table 4-16 Comparison of the amount of copper leached in percentage from CAz treated wood

Specie	Laboratory	Field – 16 months			Prediction 20 years
		Boards with end treated part	Boards without end treated part	Average	Boards with end treated part
jack pine	3.00	2.35	6.41	4.38	4.81
hem-fir	6.58	2.70	2.83	2.69	5.94
lodgepole pine	4.91	3.73	11.96	7.84	7.75

***Calculated from average**

4.2.6 Migration of copper into checks

Analysis on the relocation of mobile copper was also done for the CAz treated boards. For this study, three hem-fir boards were selected because they had the deepest checks, which exposed the untreated zone of the wood. No check samples for the pine species were used because these wood species did not develop deep enough checks that could be analysed. The analysis was done in a similar way as the sample checks from ACQ boards. The results are presented in Table 4-17. The boards HF 5D and HF 18D had similar values of copper, while board HF 11C had dramatically higher values. This is could be explained by the higher copper content found in this board. It was observed that approximately 0.4 mg of copper per gram of wood was present at the surface of the check. This indicates that mobile copper had relocated to the surface of the check, since the amount of copper at the surface in the reference sample was never more than 0.02 gram of copper per gram of wood. Also, copper was found on the below the check surface (approximately 0.1 gram of copper per gram of wood). These results show that mobile copper could relocate from the surface of the check to the inside of the check by diffusion. A statistical comparison of means using the Tukey-Kramer test was done to compare the amount of copper found in the different zones (Appendix 6). The Tukey-Kramer test showed that there was a redistribution of copper into the checks. Statistical differences between the untreated reference samples and the surface of the check and the part below check sample, confirmed the redistribution of copper from the treated parts into the surface checks and closer zones to them (below part of the check). Differences between the surface check and the outside of the check sample, analysed in the Tukey-Kramer test, that indicated higher amounts of copper occurred on the check surface compare to the inside part of the check sample. This suggests that the copper

leached from the treated part relocates to the check surface and then the mobile copper moves to the inside part. The fact that the untreated part remained statistically different from the below part of the check and the surface of the check, respectively allows for the conclusion that copper is redistributed over time within treated boards that are exposed over time.

Table 4-17 Analysis of copper in checks from CAz treated boards from the field test

Sample	Zone	Amount of Copper Cu mg / g wood			Tukey-Kramer test
		HF 5D	HF 11C	HF 18D	ά:= 0.05%
Check	Surface check	0.4594 (0.00)	0.4882 (0.07)	0.3552 (0.13)	a
	below check	0.1375 (0.02)	0.7116 (0.64)	0.1159 (0.04)	b
	Treated zone	2.4630 (0.35)	6.6254 (0.15)	1.4486 (0.34)	-
Reference	Untreated zone	0.0159 (0.01)	0.0056 (0.01)	0.0113 (0.00)	c
	Treated zone	4.5157 (0.22)	3.6162 (1.09)	3.5945 (1.58)	-

* Values within parenthesis is the standard deviation

4.2.7 Leaching of tebuconazole

Preliminary analysis of the first two months of leaching reveals that no more that 1 mg. of tebuconazole was leached per basin (Table 4-18). Since the first two months are the period with highest amount of leaching, it was assumed that the following months the amount of tebuconazole decreased.

Table 4-18 Amount of tebuconazole leached per basin in the first two month of exposure

Specie	Average of the amount of tebuconazole leached per basin in the first two months (mg)
jack pine	0.34
hem-fir	0.22
lodgepole pine	0.24

4.3 Conclusions

From this part of the study, the following conclusions could be given:

1) As it was observed for the ACQ boards study, the pH of the first leachates were higher than the pH of the rainfall
2) As was in the case with the ACQ boards, the trend of copper losses in CAz treated boards could be divided in two parts: the first part fits in a linear regression, in which copper losses were higher and after a second part that fits a power regression in which the copper losses decrease.
3) Higher amount of copper were leached in the first months of exposure (4-8 months). However, this is depending on the amount rainfall and the season when the boards were installed. In this part most of the copper lost was not fixed to the surface of the board.
4) Increases of copper leached were observed after a dry period and at the beginning of the rain season
5) In hem-fir and lodgepole pine, the boards with treated ends leached more copper than the boards without treated ends, this is due to the higher retention and/or penetration
6) Hem-fir had higher amount of copper leached than the pine species. This is due to the higher retention of copper.
7) In the laboratory leaching, a higher amount of copper was leached from boards with higher retention.
8) Modelling of copper losses from accelerated laboratory leaching was not possible due to the high copper leaching that occurred within the fist hour. In subsequent time periods the amount of copper was very low and almost undetectable.
9) Modelling of the copper leaching trend was difficult due the variability of the retention and penetration of the boards.
10) After 16 months of exposure, the cumulative amounts of copper leached were 4.38% for jack pine boards, 2.69% for hem-fir boards and 7.84% for lodgepole pine boards.
11) Lower cumulative amount of copper leached in percentage in the laboratory leaching for jack pine (3.00%) and Lodgepole pine (4.91%) treated boards than that observed in the field leaching test (4.38% and 7.84%, respectively), this is due to the low treated volume of wood observed in these boards that made difficult to calculate the treated volume.

12) For hem-fir treated boards, the cumulative amount of copper leached after the accelerated leaching test was 6.58%. In the laboratory leaching the cumulative amount of copper leached was 2.69%.

13) During the field leaching test, it was found that unfixed copper, located below the surface of the board, could relocate into the surface and close areas of the checks that were formed during the exposure.

Chapter 5

Leaching of Copper in CX™ treated wood

5.1 Introduction

CX™, also know as Copper HDO, is the final alternative preservative analysed in this study. This preservative is currently completing regulations in the US-Environmental Protection Agency (EPA) for introduction into the North America market. In this part of the study, two different sizes of hem-fir boards, treated with three different treatment charges of CX™ preservative were used. The analysis of copper leaching after 10 months of exposure is discussed in this chapter. The influence of the charge (type) of the treatment and the dimension of the boards were studied. Finally, comparisons of laboratory and field leaching were also done.

5.2 Results and Discussions

5.2.1 Initial Measurements

The copper content of the boards, measured by X-ray, and the penetration of the preservative in the boards presented in Table 5-1. According to Dr. Wolman GmbH, the boards were treated in three different ways. The copper content for the boards treated with Charge 2 (Modified Full Cell A) appears to be lower than that observed for Charge 1 (Full cell) and Charge 3 (Modified Full Cell B). The penetration of copper was deep in all the boards and in some cases full penetration was achieved. The cross sections of the boards are shown in Figure 5-1.

Table 5-1 Initial measurements of the CX™ treated boards

Charge	Board	Copper content (kg/m^3)	Penetration (mm)			
			Top	Bottom	Side 1	Side 2
1	A-3	3.074	12	11	25	44
	A-10	4.129		Full		
	A-11	3.426	5	10	6	5
	A-56	4.348	15	11	47	8
	A-58	4.549	12	15	41	12
2	2-B	2.805	5	7	14	37
	6-B	2.439	2	8	2	3
	14-B	3.800		Full		
	51-B	3.882		Full		
	53-B	3.267	14	12	11	13
3	15-A	2.922	6	9	9	4
	18-A	5.994		Full		
	19-A	4.126	17	7	12	19
	59-A	4.178	10	9	7	12
	63-A	4.548	11	13	16	12
Aver.		3.832				

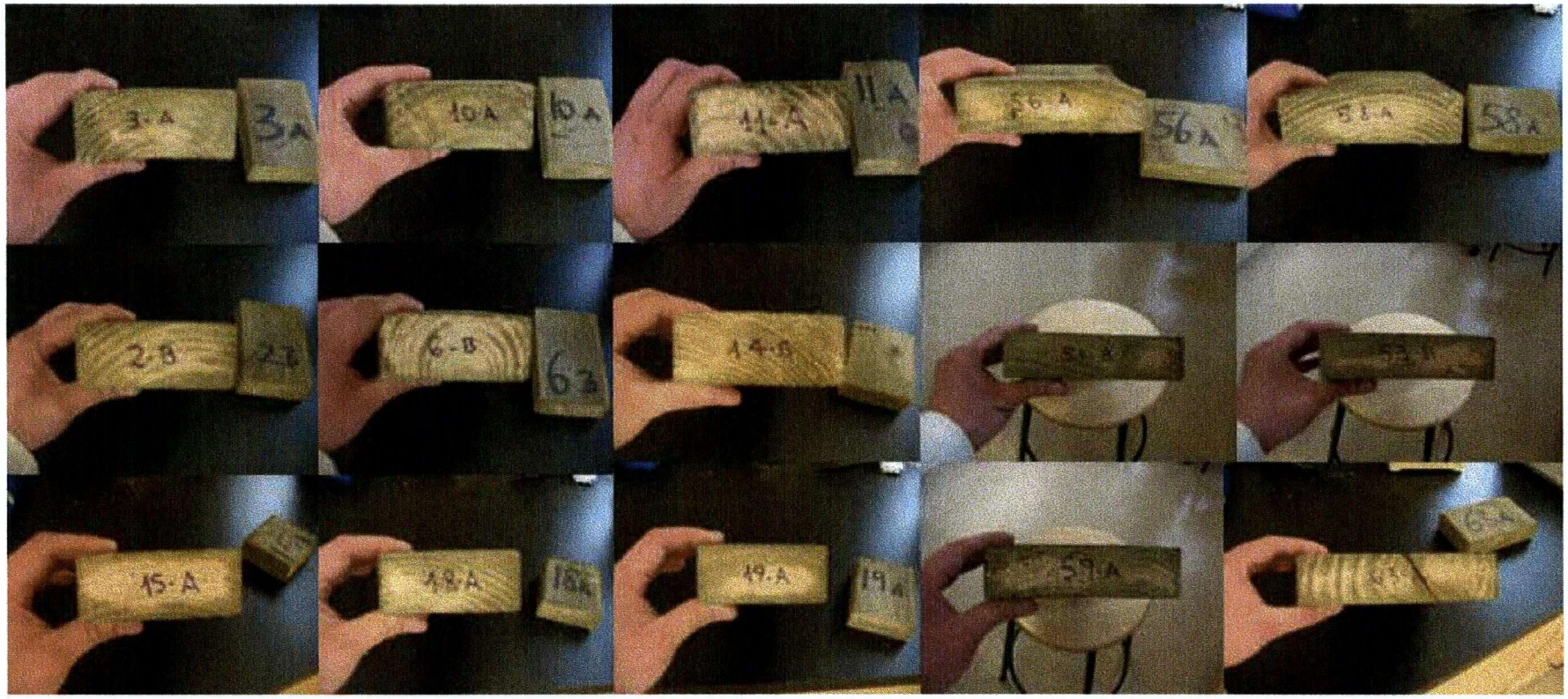

Figure 5-1 Cross section of the CX™ treated boards

5.2.2 Analysis of copper leaching

Table 5-2 presents the average amount of copper leached per month. As it was observed in ACQ and CAz treated boards, the first month of exposure (March, 2004) had the highest amount of copper leached, the next month was expected to see continually high leaching, however a low amount of rain occurred in this month (April, 2004) resulting in only a small amount of copper to be leached. In May, 2004, an increase of copper losses was observed due to the increase in rainfall. However, leaching decreased again over the next two months, coinciding with the start of the summer season. The amount of copper losses began to increase in August, 2004, when the rain season started. After 10 months of exposure a cumulative averaged amount of copper of 242 mg of copper was leached.

Table 5-2 Average of monthly evaluations of hem-fir CX™ treated boards exposed above ground*

Month	Volume of leachate (L)	Amount of copper (CuO) leached (mg)	Cumulative amount of copper (CuO) leached (mg)
Mar-04	3044	50 (38)	50
Apr-04	147	6 (5)	56
May-04	3596	26 (12)	82
Jun-04	502	7 (3)	89
Jul-04	627	4 (1)	92
Aug-04	3842	26 (8)	118
Sep-04	7093	22 (11)	141
Oct-04	9713	38 (18)	178
Nov-04	15642	31 (15)	209
Dec-04	15943	34 (17)	242

* Average of the evaluations
** Values within parenthesis is the standard deviation

The amount of copper leached appears to be the same during the months of exposure, with the exception of June, April, and July in which the lowest precipitation occurred. Table 5-3 shows the average amount of copper leached in mg per month and classified per charge of treatment and per dimension of board. The values per month were tested in a 3 x 2 factorial experiment design (Appendix 7). The result of this test was that no significant differences exist among treatment types (charge) and board dimensions (all $p > 0.05$ at $\alpha = 0.05$). In addition, a test was conducted with the cumulative amount of copper leached (mg) at the end of the exposure period.

No significant difference was found among the amounts of copper leached. Table 5-4 shows the values in percentage of the total treated volume and the cumulative amount of copper leached after 10 months of exposure was from 2.52 % to 3.87 %.

Table 5-3 Average of amount of copper leached (mg) per month

Month	Charge 1		Charge 2		Charge 3	
	2 x 4	2 x 6	2 x 4	2 x 6	2 x 4	2 x 6
Mar-04	80 (73)	59 (36)	18 (8)	41 (0)	54 (29)	48 (11)
Apr-04	7 (5)	5 (3)	3 (1)	3 (1)	9 (9)	7 (4)
May-04	27 (12)	33 (12)	14 (7)	29 (4)	31 (22)	27 (1)
Jun-04	6 (4)	9 (4)	4 (2)	6 (1)	9 (4)	7 (1)
Jul-04	4 (1)	4 (1)	3 (0)	3 (0)	4 (1)	4 (1)
Aug-04	26 (6)	30 (4)	18 (5)	33 (2)	30 (13)	25 (3)
Sep-04	22 (13)	35 (12)	12 (4)	34 (7)	21 (11)	17 (1)
Oct-04	34 (16)	51 (2)	24 (5)	62 (13)	39 (23)	24 (6)
Nov-04	26 (13)	45 (0)	17 (5)	54 (7)	31 (15)	19 (4)
Dec-04	30 (20)	47 (2)	21 (8)	61 (12)	30 (14)	22 (6)
Cumulative	263 (138)	317 (69)	133 (39)	323 (44)	257 (133)	199 (15)

* Values within parenthesis represent the standard deviation of the measurements

Table 5-4 Average of amount of copper leached (%) per month

Month	Charge 1		Charge 2		Charge 3	
	2 x 4	2 x 6	2 x 4	2 x 6	2 x 4	2 x 6
Mar-04	0.99 (0.56)	0.58 (0.37)	0.36 (0.14)	0.48 (0.16)	0.70 (0.51)	0.60 (0.01)
Apr-04	0.08 (0.03)	0.05 (0.04)	0.07 (0.06)	0.03 (0.00)	0.17 (0.26)	0.09 (0.04)
May-04	0.38 (0.14)	0.32 (0.13)	0.30 (0.16)	0.34 (0.16)	0.39 (0.31)	0.34 (0.08)
Jun-04	0.08 (0.02)	0.08 (0.04)	0.10 (0. 06)	0.07 (0.02)	0.11 (0.04)	0.09 (0.04)
Jul-04	0.06 (0.04)	0.04 (0.01)	0.08 (0.06)	0.04 (0.01)	0.05 (0.04)	0.05 (0.02)
Aug-04	0.37 (0.14)	0.29 (0.05)	0.39 (0.19)	0.39 (0.15)	0.42 (0.34)	0.33 (0.11)
Sep-04	0.39 (0.39)	0.33 (0.13)	0.26 (0.13)	0.41 (0.21)	0.31 (0.28)	0.22 (0.06)
Oct-04	0.44 (0.02)	0.49 (0.00)	0.55 (0.34)	0.75 (0.39)	0.52 (0.43)	0.30 (0.01)
Nov-04	0.35 (0.08)	0.44 (0.02)	0.38 (0.20)	0.64 (0.29)	0.45 (0.40)	0.25 (0.11)
Dec-04	0.38 (0.11)	0.45 (0.00)	0.43 (0.17)	0.74 (0.38)	0.42 (0.34)	0.27 (0.02)
Cumulative	3.52	3.06	2.92	3.87	3.55	2.52

*** Values within parenthesis represent the standard deviation of the measurements**

5.2.3 Effect of the dimensions of the wood and the treatment type in copper leaching

It was hypothesised that the size of the board would have an influence on the amount of chemical being leached, since in the decking area the narrow size of board could have more treated sides exposed than the wide-size boards. However, the results of the statistical analysis show that no significant differences were found between the leachate from the basins with 2 x 4 boards and the basins with 2 x 6 boards (Appendix 7). This was mainly due to the area of exposure in the basins not being large enough to involve more boards with treated sides. This would have made a difference in the amount of copper leached. In the basins with 2 x 6 boards, four treated sides were exposed, while in the basins with 2 x 4 boards, six treated sides were exposed. The two extra treated sides per basin did not make a difference in the amount of copper leached. Figure 5-2 shows the comparison of the amount of copper leached from 2 x 4 and 2 x 6 boards after 10 months of exposure. The values were similar between the boards and the small differences were not significant. However, if the surface area exposed was greater, the treated sides could result in a different amount of copper leached. Also, cumulative values per area could make a difference. In Table 5-5 shows the values of copper leached in mg/m^2, the cumulative amount of copper leached after 10 months of exposure was (1756 – 4278 mg/m^2).

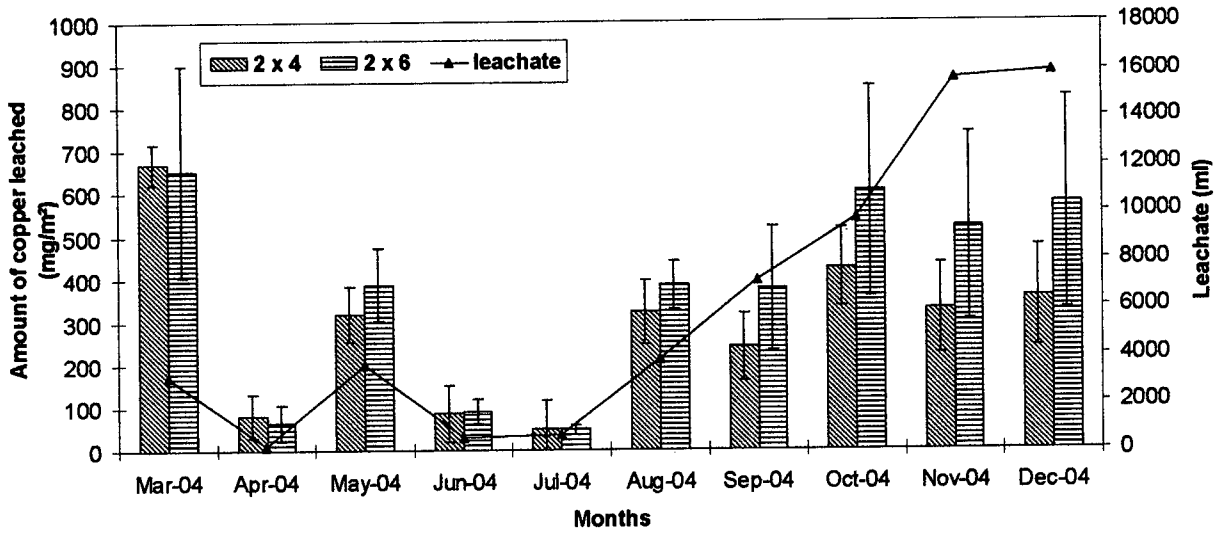

Figure 5-2 Comparison of the amount of copper leached (mg) from 2 x 4 and 2 x 6 CX™ treated boards after 10 months of exposure

Table 5-5 Average of amount of copper leached (mg/m^2) per month

Month	Charge 1		Charge 2		Charge 3	
	2 x 4	2 x 6	2 x 4	2 x 6	2 x 4	2 x 6
Mar-04	1063	784	234	540	709	635
Apr-04	89	66	37	32	114	94
May-04	363	432	182	377	407	353
Jun-04	82	111	59	73	119	90
Jul-04	51	53	42	40	51	49
Aug-04	342	394	233	430	391	331
Sep-04	287	453	153	452	281	226
Oct-04	448	678	316	817	513	314
Nov-04	350	600	225	708	413	252
Dec-04	403	624	274	809	397	294
Cumulative	3478	4195	1756	4278	3396	2636

* Values within parenthesis represent the standard deviation of the measurements

On the other hand, the type of charge/ treatment did not have an influence on the amount of copper leached. Figure 5-3 shows the comparison of the amount of copper leached from the three different charges during the 10 months of exposure. The values were very similar, resulting in small differences that were not significant at $\alpha = 0.05$ $p > 0.4009$ (see Appendix 7).

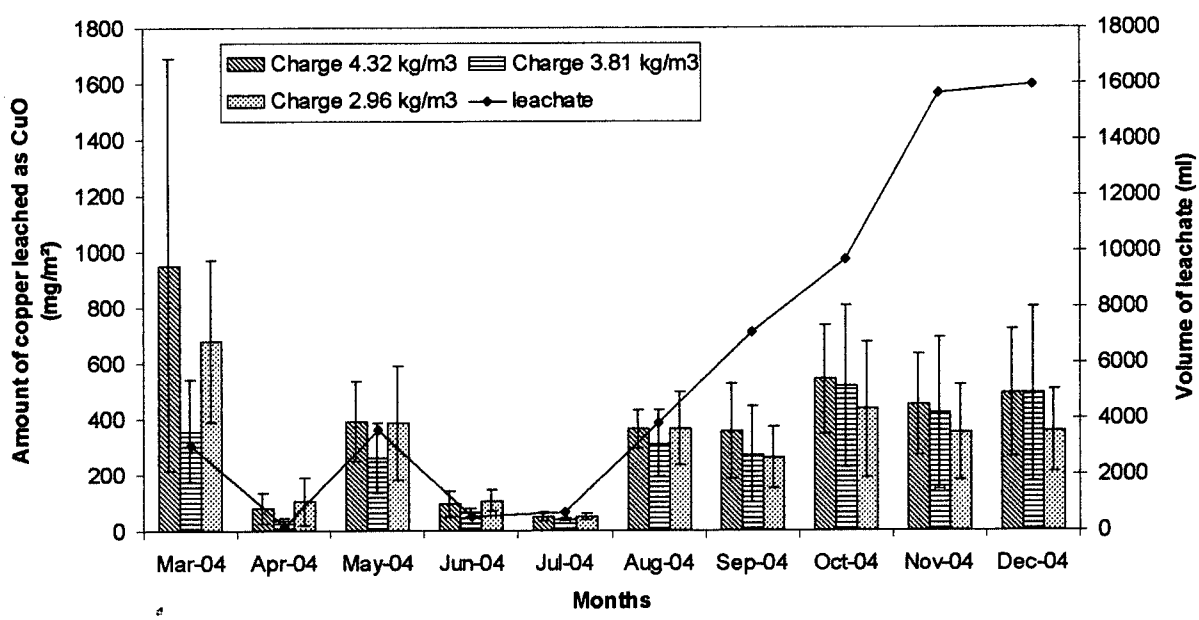

Figure 5-3 Comparison of the amount of copper leached (mg) from 2 x 4 and 2 x 6 CX™ treated boards after 10 months of exposure

5.2.4 Comparison of copper leaching between laboratory and field leaching

Accelerated leaching was conducted in the laboratory using the same methodology applied in the CAz treatment experiment. The objective was to model the loss of copper over time. The results of the leaching test are presented in Table 5-6. As expected, the greatest amount of copper was leached during the first hour. In subsequent time periods, the amount of copper leached was reduced. Because the amounts of copper leached in these intervals were very low and sometimes undetectable, no modelling could be done. Sample boards with the highest retention had the greatest amount of total copper leached. Boards 51 B (retention=3.88 kg/m^3), A 58 (retention = 4.55 kg/m^3), and A56 (retention = 4.35 kg/m^3) exhibited the greatest amount of copper leaching (5-6 mg of copper) while boards 2B (retention = 2.81 kg/m^3) and B6 (retention = 2.44 kg/m^3) leached the lowest amount of copper (< 2 mg).

Table 5-6 Amount of copper leached from CX™ treated sawdust during the accelerated laboratory leaching

Board	Retention	Amount of copper leached as CuO (mg)						
	(kg/m^3)	1 hour	3 hours	6 hours	24 hours	48 hours	72 hours	Total
A 3	3.074	2.39	0.07	0.15	0.13	0.03	0.13	2.90
A 10	4.129	3.20	0.47	0.23	0.16	0.23	0.09	4.39
A 11	3.426	3.13	0.19	0.09	0.03	0.18	0.04	3.67
A 56	4.348	4.43	0.11	0.16	0.22	0.10	0.06	5.09
A 58	4.549	5.40	0.12	0.07	0.05	0.21	0.00	5.85
2 B	2.805	1.42	0.12	0.08	0.11	0.11	0.03	1.87
6 B	2.439	1.29	0.11	0.07	0.07	0.10	0.00	1.64
14 B	3.800	1.88	0.17	0.03	0.12	0.24	0.05	2.49
51 B	3.882	5.63	0.29	0.07	0.17	0.10	0.13	6.39
53 B	3.267	1.73	0.19	0.06	0.06	0.12	0.01	2.17
15 A	2.922	1.95	0.21	0.00	0.11	0.08	0.01	2.36
18 A	5.994	3.65	0.27	0.23	0.15	0.15	0.00	4.45
19 A	4.126	3.00	0.09	0.18	0.04	0.05	0.02	3.39
59 A	4.178	2.63	0.12	0.16	0.10	0.07	0.04	3.11
63 A	4.548	2.65	0.14	0.18	0.00	0.09	0.11	3.17
Average	3.833	2.96	0.18	0.12	0.10	0.13	0.05	3.53

Table 5-7 shows the comparison of the amount of copper leached in laboratory and the cumulative amount of copper leached after 10 months of exposure in the field. The values of the laboratory averaged 10.83 %, while values from the field averaged 3.26 %. It appears that the retention capability of the boards may be the most important factor in the laboratory leaching.

Boards with higher retention (boards A56, A58, 51B, 19A, and 59A) were the samples with that exhibited the highest amount of copper leaching. However, this trend was not reflected in the same manner in the field test. Most of the field tested samples had the same or lower amounts of copper leached compared to the samples with lower retention. An explanation for this could be that the amount of copper available for leaching (that could be reflected in higher retentions) is not the only important factor governing copper loss. The process in which copper becomes accessible for leaching also appears to be a very important mechanism. The accessibility of unfixed copper to be leached in the field test is caused by the wetting and drying of the board and the diffusion of copper. Depending on the orientation, permeability and density of boards (e.g. tangential faced, higher permeability and lower density boards are more easily subjected to wetting and drying), the diffusion of copper to the surface could be facilitated in a faster and easier manner (Lebow *et al.*, 2004).

Table 5-7 Comparison of the average amount of copper (as CuO) leached in percentage from CX™ treated wood

Charge	Board	Copper (as CuO) Retention Kg/m^3	Copper leached (CuO) Laboratory (%)			Copper leached (CuO) Field - 10 months (%)	
			Per board (%)	Per charge (%)	Tukey-Kramer Test	Per board (%)	Per charge (%)
1	A 3	3.07	10.67	13.12	a	2.26	3.34
	A 10	4.13	12.04			3.79	
	A 11	3.43	12.13			4.50	
	A 56	4.35	13.24			3.62	
	A 58	4.55	17.53			2.51	
2	2 B	2.80	7.54	10.05	b	2.83	3.30
	6 B	2.44	7.61			4.39	
	14 B	3.80	7.40			1.54	
	51 B	3.88	18.62			2.62	
	53 B	3.27	9.07			5.12	
3	15 A	2.92	9.15	9.33	b	6.90	3.14
	18 A	6.15	10.14			2.34	
	19 A	4.13	9.30			1.42	
	59 A	4.18	10.17			2.77	
	63 A	4.55	7.88			2.28	
Average			10.83 (3.39)			3.26 (1.48)	

5.2.5 Prediction of copper leaching

Plots of the cumulative amount of copper leached vs. the time of exposure are shown in the Figure 5-4. The plot shows an increasing trend of copper leaching. In the first months, a slow loss of copper was observed from March, 04 to July, 04. Then, from August, 04 to December, 04 coinciding with the rainy season, the amount of copper being leached increased. The plot fit in a logarithm equation and prediction of copper losses in a 20 year life was calculated. Based in this logarithm equation, it was calculated that 5.92 % of copper would be lost after 20 years of exposure.

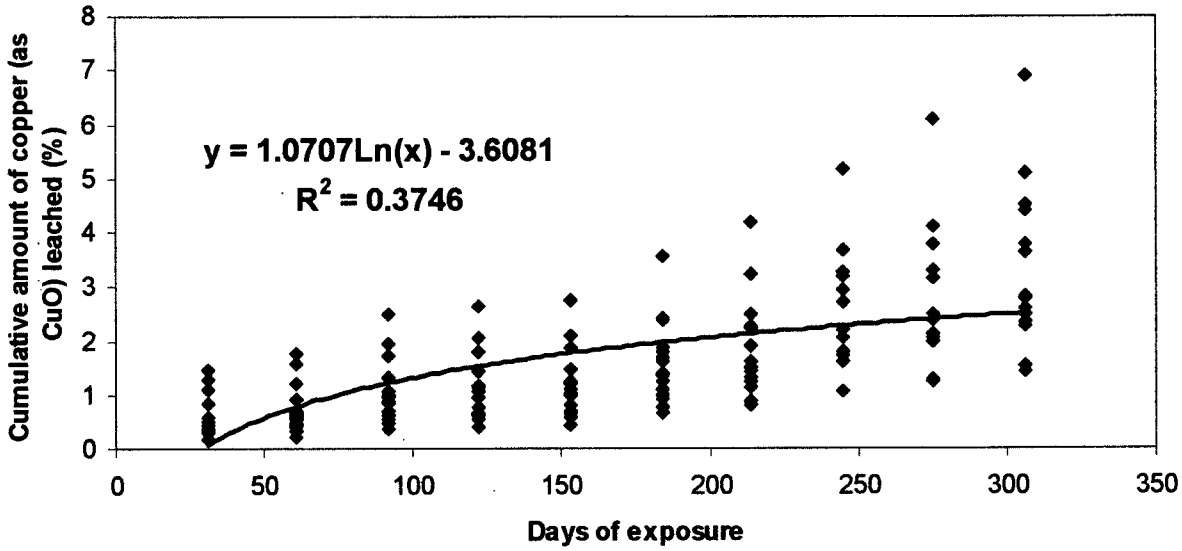

Figure 5-4 Cumulative amount of copper (as CuO) leached (%) from CX™ treated boards during the days of exposure (after 10 months)

5.3 Conclusions

From this part of the study, the following conclusion could be given:

1) As it was observed for the ACQ and CAz treated boards, the amount of copper leached was higher in the first months of the exposure, but this trend depends on the amount of rainfall.
2) No differences in copper leaching were found among the charge treatments.
3) No differences in copper leaching were found between the sizes of the boards used in a basin area (0.078 m^2).
4) In the field leaching test, it was found that boards with high copper retention did not necessarily have the highest amounts of copper leached.
5) The average copper leached from the samples in the field test was 3.26 %.
6) Less than 4 % of copper was leached from the boards after 10 months of exposure.
7) No modelling of copper losses was achieved in the accelerated leaching due to a very high percentage of the unfixed copper being leached during the first hour of the process.
8) In the accelerated laboratory leaching test, higher amounts of copper were leached from boards with higher retention.
9) The average copper leached from the samples in the laboratory test was 10.83 %.

Chapter 6

Summary

The goal of this project was to evaluate the leaching of copper from three different copper–based preservative systems that are currently in use (ACQ and CAz) or are waiting approval (CX™) to be used for residential purposes in North America. Board samples were installed over basins and exposed to environmental conditions to simulate their use as decking. Several factors influence leaching under environmental conditions that are not reproducible in accelerated leaching tests conducted in a laboratory. Therefore, an important aspect of this project was to evaluate leaching under environmental conditions in order to gain an understanding of the mechanisms that determine the amount of copper that may be leached over time. A comparison between field testing and accelerated laboratory testing was conducted to verify that differences do exist in regards to the degree of leaching and the causal mechanisms.

The leaching of copper from treated boards occurs in two separate parts. During the first part, unfixed copper is removed from the surface of the board. This part is directly influence by the amount of rainfall. Depending on the amount of the rainfall, this process can be extended from four months (as seen in ACQ treated boards that were installed at the beginning of the rainy season) or eight months (as seen in CAz treated boards and CX™ that were installed at the beginning of the dry season, causing some months to have low amount of copper leached). These increases in copper leaching can be explained using a linear model.

The second part of the copper leaching occurs due to the removal of unfixed copper from the zones near the surface of the board. This process was slow and was controlled by the diffusion of copper to the surface. The diffusion of copper was perpetuated by the wetting and drying of the sample. After the majority of unfixed copper from the surface was leached and the wood was wet, copper diffused to the surface due to the low concentration in this zone. When the board started to dry, the moisture located inside of the board moved to the surface carrying the unfixed copper to the surface. Since the process depends on the wetting and drying of the board, the leaching process in this part had small increases in copper leaching after dry periods, prior to the onset of the rainy season, and reduced copper leaching after the rainy season. These increases in copper leaching with time can be described using a power and/or logarithmic model.

From the species used, hem-fir had highest retention and penetration, which resulted in the highest amount of copper being leached. As a result, it was easier to predict the amount of copper leached over a specific period of time due to the quantity of copper leached. Jack pine and lodgepole pine had lower penetration and retention, which resulted in decreased copper leaching from both these species.

Since the majority of copper being leached was unfixed copper located at the surface of the samples, two post-treatments were designed to decrease the amount of copper being leached. Using commercial ACQ treated wood; the post-treatments were applied to the boards before exposure. The first post-treatment was a water pressure treatment that consisted of four wash phases. The first wash leached the highest amount of copper, the next washes leached less copper compare to the first wash. Unfortunately, when the boards were placed to the field for exposure, the amount of copper leached by the rainfall was similar to the control boards.

The second post-treatment tested was a water repellent finish. A commercial water repellent was applied to the boards before exposure. After 10 months of exposure, the results showed that the water repellent was able to protect the wood from getting wet during rainfall, which resulted in less amount of copper being leached. Also, since the wood was protected from wetting, very little diffusion occurred.

During exposure, the wetting and drying of the board created checks. Check formation was more frequent in the hem-fir boards. These checks exposed untreated wood to a potential attack by fungi and other organisms. During the leaching process, unfixed copper was removed from the surface and relocated to the untreated surfaces in the checks. Check samples from ACQ and CAz treated hem-fir boards were exposed in the field test and analyzed. Small amounts of copper were observed in the surface of the checks and in the surrounding area of the checks, confirming that relocation of unfixed copper in to the checks had occurred.

For the CX™ treated board experiment the objective was to compare the influence of the size and the width of the samples at different charges. Two different sizes of boards were used: 2 x 4 and 2 x 6; and three different treatment charges of retention: Full Cell treatment (4.32 kg/m^3), Modified Full Cell A (3.81 kg/m^3), and Modified Full Cell B (2.86 kg/m^3). It was hypothesized that the smaller size samples would have more copper leached per basin, since the 2 x 4 samples

had more surface area[2] exposed then the 2 x 6 samples. No differences were found in the amount of copper leached, probably due to the difference in surface area having a minimal effect on the amount of copper being leached. Also, no differences in copper leaching were found among the three treatments. Though, the retention of charge 2 was a little lower than the other charges, no significant differences could be found.

In addition to the field leaching test, an accelerated leaching test was done on reference samples taken from the treated board. This was done to find the total amount of copper that can be removed from the treated wood and compare it to the amount leached during the field test. Two different methods were used. For ACQ, ultrasonic and static leaching were used in three different phases. During the first phase almost all of the unfixed copper was leached; consequently during the other two phases the amount of copper leached was significantly decreased. The total amount leached was on average 16.85%. For CAz and CX™ boards a magnetic stirring method was used with the leachate measured at specific time intervals to with the objective of being able to model the loss of copper. A model could not be developed because the majority of unfixed copper was leached during the first interval. The average amount of copper leached was 3.00% for jack pine CAz treated boards, 6.58% for hem-fir CAz treated boards, 4.91% for lodgepole pine CAz treated boards, and 10.83% for hem-fir CX™ treated boards.

It was observed that not only the higher retention caused high copper leaching in the field. Differences between field and laboratory leaching, showed that the high retention of copper not always have the highest amount of copper leached. CX™ boards with high retention had lower amount of copper leached in the field than lower retention boards. Factors such as wood properties, section of the boards exposed, can have an important role in the influence in the diffusion and at therefore in copper leaching.

The two trends observed in copper leaching allowed for the development of two models that could be used for predicting copper loss over time. The first model fits a linear regression, while the second model fits a power (square root) structure. Fitting the models to the monthly average data resulted in a high correlation coefficients (e.g. $r^2 = 0.98$). However, when the data collected

[2] Three 2" x 4" samples and two 2" x 6" samples were exposed. Because three 2" x 4" samples were used there were 2 more sides exposed then for the 2" x 6" samples.

from each basin was used the coefficient of correlation decreased. This is due to the variability in the amount of copper being leached between samples. With these two models, prediction of copper loss was calculated for a specific time period. For ACQ treated boards, 11 % of copper was predicted by the model to be leached (r^2 = 0.51) over a projected exposure period of 20 years. In addition, a power relationship in copper leaching between initial losses and cumulative final losses was found. This relationship could be used to predict the amount of copper that can be leached over a predetermined period of time, having the information of the first month of copper leaching.

For CAz treated boards, the analysis was more difficult due to the differences in copper leached per board. This resulted because samples from the same board were placed together over a basin causing more variation among the basins, since different retention were found per board. Although the variation among the basins was high, they all followed a similar trend. Using the average measurements from each month a trend with a higher coefficient of correlation could be defined. Using a model built from 16 months of data, predictions for copper loss over a projected exposure period of 20 years was calculated for each species. For jack pine projected copper losses were 4.81% from boards with treated ends. For hem-fir samples, projected copper losses were 5.94% on average, while for lodgepole pine, projected copper losses were 7.55%.

In conclusion, the leaching of copper from treated wood in service has different mechanism from laboratory accelerated leaching. It is depending on two mechanisms: the first one is defined rapid lost originated by the amount of rainfall that is taking the unfixed copper from the surface of the board and a rapid lost in the first months, and the second is defined by diffusion of copper with a decrease in the amount of copper. The most amount of copper lost was in the first month. A way to decrease the amount of copper leached is to apply a water repellent finish. ACQ, CAz and CX™ have the same trend and prediction of copper losses over a period of time could be made. Higher amount of copper would be expected from higher copper retention boards, although other factors would be involved. Relocation of copper was confirmed in checks from hem-fir boards that gives protection to untreated part of the check.

Chapter 7

Recommendations for Future Research

1. Continue to evaluate the leaching of copper from the treated boards and verify how the trends of leaching change. The longest duration of the experiment could give better information of the copper leaching.

2. Verify the diffusion and mobility of copper during the exposure of the boards in the field. Samples of the surface of the board should be taken in the dry season and after the rainy season for copper analysis to proof the mobility of copper by wetting and drying of the board and diffusion.

3. Since the water pressure wash application failed in decreasing the copper of leaching, modified the post treatments including change of water load and include a pre-drying at low temperature to simulate diffusion inside the board.

4. Water repellent application as a finish in ACQ treated spruce boards had good results in decreasing the amount of copper leaching. This application should be tested if it would have the same effect in a deeper penetrated species such a hem-fir or/and using others preservatives systems such as CAz and CX™

5. Further studies should compare the copper leaching among the three different preservative systems installed wood samples at the same time and using the same species.

6. Modelling of copper losses involve environmental factors (precipitation, sun hours, temperature, etc.) and wood properties that directly influence the copper diffusion in wood. Further studies should done analyzing all this factors to construct a model of leaching.

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Appendices

Appendix 1 Environmental conditions during the time of exposure*

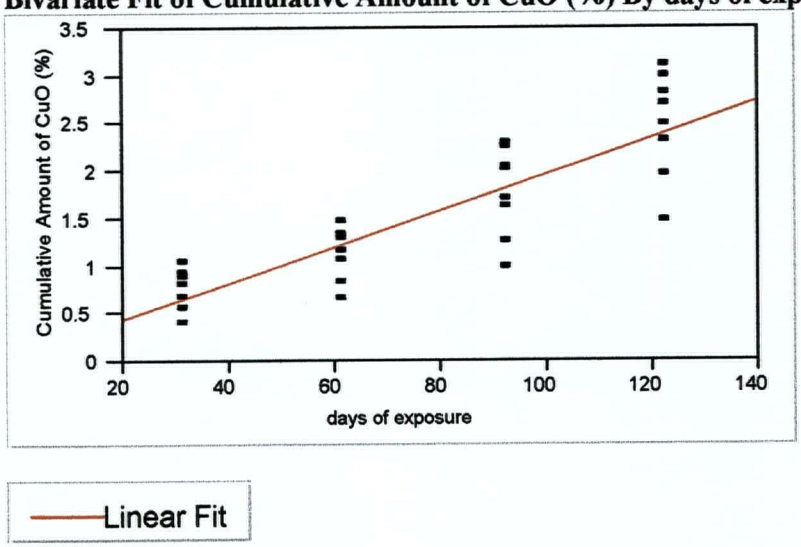
Month	Monthly precipitation (mm)	Mean Temperature monthly (°C)	Monthly sun hours
Aug-02	5.8	17.9	287
Sep-02	34.6	15.0	239
Oct-02	18.3	9.7	151
Nov-02	147.7	7.7	77
Dec-02	139.5	5.3	40
Jan-03	151.1	6.3	70
Feb-03	27.1	4.6	106
Mar-03	130.0	7.3	91
Apr-03	139.6	9.3	124
May-03	49.3	12.6	210
Jun-03	12.8	16.8	243
Jul-03	19.8	19.1	354
Aug-03	4.1	18.6	301
Sep-03	40.2	15.8	229
Oct-03	248.2	11.6	100
Nov-03	167.4	4.6	116
Dec-03	113.2	4.4	38
Jan-04	161.4	4.1	36
Feb-04	83.4	5.9	94
Mar-04	101.2	8.1	149
Apr-04	15.0	11.1	277
May-04	60.8	14.1	220
Jun-04	22.8	17.3	271
Jul-04	16.6	19.7	309
Aug-04	75.0	19.3	218
Sept-04	169.4	14.4	150
Oct-04	117.2	10.8	126
Nov-04	199.6	6.8	59
Dec-04	314.4	5.3	44

***Data obtained from Environment Canada. Vancouver International Airport Station**

Appendix 2 Multiple regression of the copper leaching from ACQ treated wood expressed in percentage

First part: first four months

Response Cumulative Amount of CuO (%)
Bivariate Fit of Cumulative Amount of CuO (%) By days of exposure



Linear Fit

Cumulative Amount of CuO (%) = 0.0589671 + 0.019029 days of exposure

Summary of Fit

RSquare	0.738454
RSquare Adj	0.729736
Root Mean Square Error	0.39754
Mean of Response	1.514688
Observations (or Sum Wgts)	32

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	2	0.2367812	0.118391	0.7359
Pure Error	28	4.5043625	0.160870	Prob > F
Total Error	30	4.7411437		0.4881
				Max RSq
				0.7515

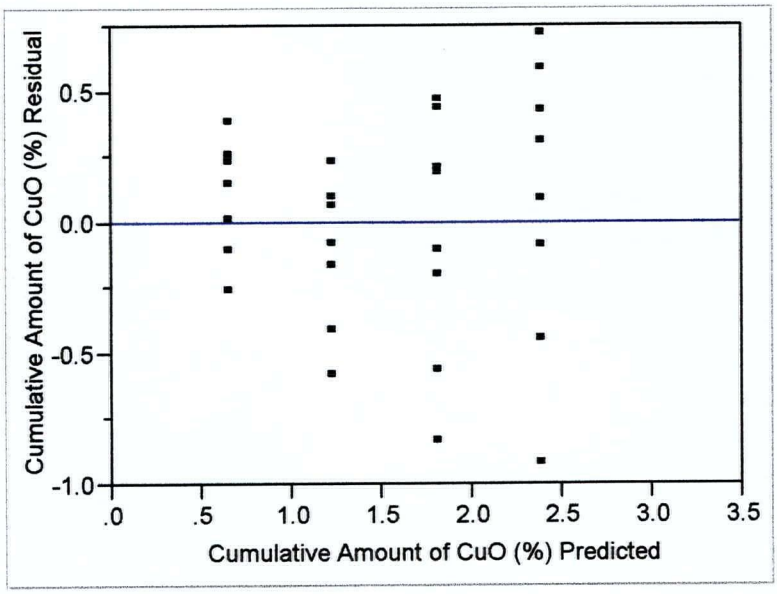
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	13.386253	13.3863	84.7027
Error	30	4.741144	0.1580	Prob > F
C. Total	31	18.127397		<.0001

Parameter Estimates

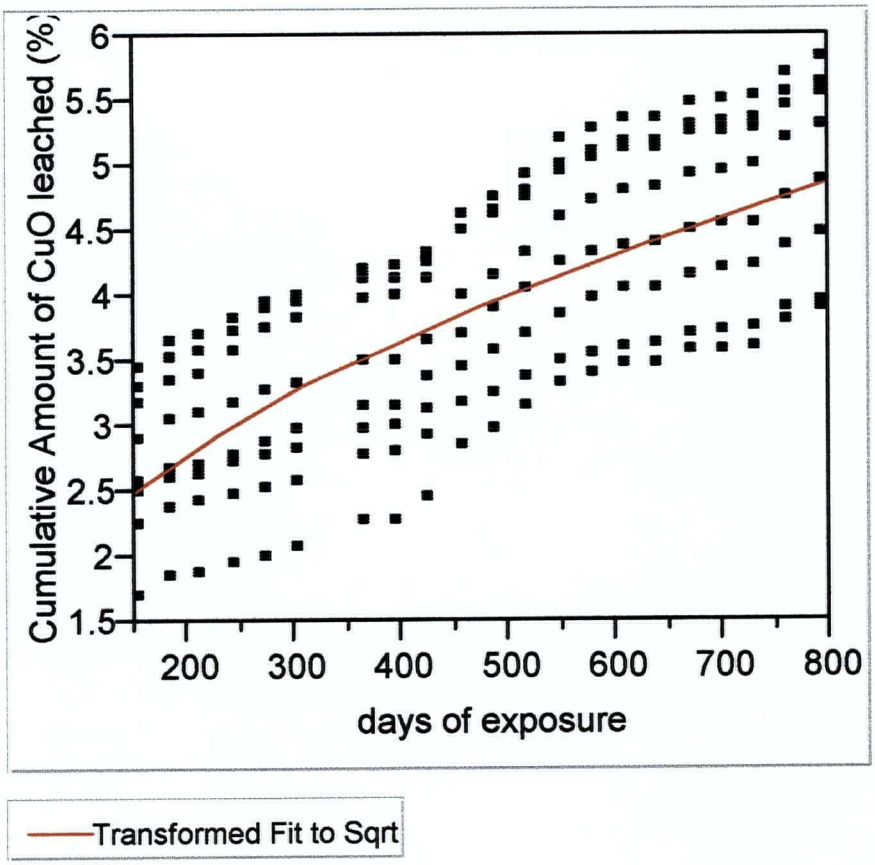
Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	0.0589671	0.173081	0.34	0.7357
days of exposure	0.019029	0.002068	9.20	<.0001

Residual by Predicted Plot



Second part

Bivariate Fit of Cumulative Amount of CuO leached (%) By days of exposure



Transformed Fit to Sqrt (power)

Cumulative Amount of CuO leached (%) = 0.6822678 + 0.1481644 Sqrt(days of exposure)

Summary of Fit

RSquare	0.527646
RSquare Adj	0.524801
Root Mean Square Error	0.668364
Mean of Response	3.84625
Observations (or Sum Wgts)	168

Lack of Fit

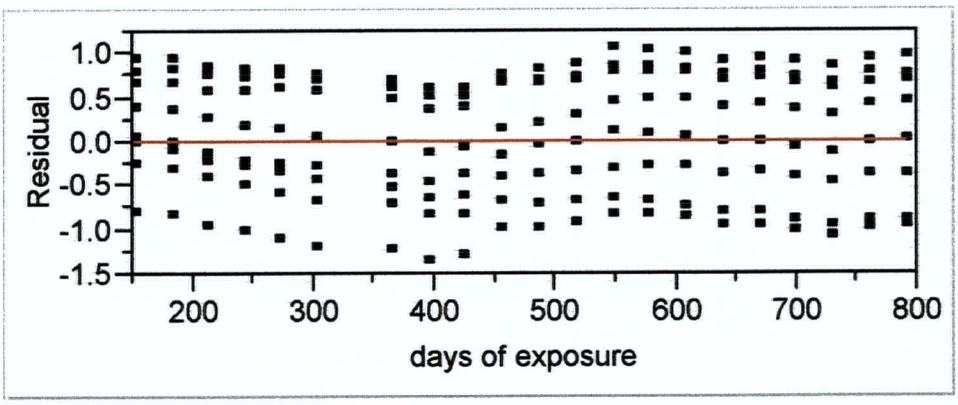
Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	19	2.487895	0.130942	0.2686
Pure Error	147	71.666037	0.487524	Prob > F
Total Error	166	74.153933		0.9991
				Max RSq
				0.5435

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	82.83420	82.8342	185.4315
Error	166	74.15393	0.4467	Prob > F
C. Total	167	156.98814		<.0001

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	0.6822678	0.238003	2.87	0.0047
Sqrt(days of exposure)	0.1481644	0.010881	13.62	<.0001



Appendix 3 Statistical analysis of the migration of copper in checks in ACQ treated wood

One-way Analysis of log (mg CuO/g wood) By Section

One-way Anova

Analysis of Variance

Ho: the amount of CuO leached of the leachates phases are similar
H1: the amount of CuO leached of the leachates phases are different
$\alpha = 0.05$

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Section	2	5.8680593	2.93403	104.1572	<.0001
Sample	1	0.0082595	0.00826	0.2932	0.6029
Error	8	0.2253539	0.02817		
C. Total	11	6.1016727			

H1 is accepted. Different amount of copper in sections but not in samples (boards).

Positive values show pairs of means that are significantly different.

Abs(Dif)-LSD	check	outside check	Ref. untreated part
check	-	-	+
outside check	-	-	+
Ref. untreated part	+	+	-

Appendix 4 Statistical analysis per month of the amount of copper leached in ACQ with post treatments treated boards exposed in field

Month 1: April 2004
Distributions
CuO leached (mg)

Analysis of Variance

Ho: the amount of CuO leached from the different post-treatments is similar
H1: the amount of CuO leached from the different post-treatments is different
$\acute{\alpha} = 0.05$

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Treatment	2	438.00000	219.000	12.2804	0.0196
Board	2	88.66667	44.333	2.4860	0.1988
Error	4	71.33333	17.833		
C. Total	8	598.00000			

H1 is accepted. Different amount of copper leached in the post-treatments but there are not differences among the boards.

Positive values show pairs of means that are significantly different.

Abs(Dif)-LSD	Control	WPT	WRT
Control	-	-	+
WPT	-	-	-
WRT	+	-	-

Month 2: May 2004

Analysis of Variance

Ho: the amount of CuO leached from the different post-treatments is similar
H1: the amount of CuO leached from the different post-treatments is different
$\acute{\alpha} = 0.05$

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Treatment	2	198.22222	99.1111	22.3000	0.0068
Board	2	14.88889	7.4444	1.6750	0.2962
Error	4	17.77778	4.4444		
C. Total	8	230.88889			

H1 is accepted. Different amount of copper leached in the post-treatments but there are not differences among the boards.

Positive values show pairs of means that are significantly different.

Abs(Dif)-LSD	Control	WPT	WRT
Control	-	-	+
WPT	-	-	+
WRT	+	+	-

Month 3: June 2004

Analysis of Variance

Ho: the amount of CuO leached from the different post-treatments is similar
H1: the amount of CuO leached from the different post-treatments is different
$\acute{\alpha} = 0.05$

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Treatment	2	34.888889	17.4444	62.8000	0.0010
Board	2	0.888889	0.4444	1.6000	0.3086
Error	4	1.111111	0.2778		
C. Total	8	36.888889			

H1 is accepted. Different amount of copper leached in the post-treatments but not in differences in boards.

Positive values show pairs of means that are significantly different.

Abs(Dif)-LSD	Control	WPT	WRT
Control	-	-	+
WPT	-	-	+
WRT	+	+	-

Month 4: July 2004

Analysis of Variance

Ho: the amount of CuO leached from the different post-treatments is similar
H1: the amount of CuO leached from the different post-treatments is different
$\acute{\alpha} = 0.05$

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Treatment	2	18.000000	9.00000	27.0000	0.0048
Board	2	0.666667	0.33333	1.0000	0.4444
Error	4	1.333333	0.33333		
C. Total	8	20.000000			

H1 is accepted. Different amount of copper leached in the post-treatments but not in differences in boards.

Positive values show pairs of means that are significantly different.

Abs(Dif)-LSD	Control	WPT	WRT
Control	-	-	+
WPT	-	-	+
WRT	+	+	-

Month 5: August 2004

Analysis of Variance

Ho: the amount of CuO leached from the different post-treatments is similar
H1: the amount of CuO leached from the different post-treatments is different
$\alpha = 0.05$

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Treatment	2	408.66667	204.333	38.3125	0.0025
Board	2	26.00000	13.000	2.4375	0.2031
Error	4	21.33333	5.333		
C. Total	8	456.00000			

H1 is accepted. Different amount of copper leached in the post-treatments but not in differences in boards.

Positive values show pairs of means that are significantly different.

Abs(Dif)-LSD	Control	WPT	WRT
Control	-	-	+
WPT	-	-	+
WRT	+	+	-

Month 6: September 2004

Analysis of Variance

Ho: the amount of CuO leached from the different post-treatments is similar
H1: the amount of CuO leached from the different post-treatments is different
$\alpha = 0.05$

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Treatment	2	152.66667	76.3333	13.4706	0.0167
Board	2	20.66667	10.3333	1.8235	0.2736
Error	4	22.66667	5.6667		
C. Total	8	196.00000			

H1 is accepted. Different amount of copper leached in the post-treatments but not in differences in boards.

Positive values show pairs of means that are significantly different.

Abs(Dif)-LSD	Control	WPT	WRT
Control	-	-	+
WPT	-	-	+
WRT	+	+	-

Appendix 5: Statistical analysis of the amount of copper leached in mg CuO/g wood (%) in laboratory from ACQ-t treated sawdust of the boards

Tests that the Variances are Equal

Ho: The variances of the amount of Cu leached (mg /g wood) from the different boards are similar
H1: The variances of the amount of Cu leached (mg /g wood) from the different boards are different
ά = 0.05

Level	Count	Std Dev	Mean Abs Dif to Mean	Mean Abs Dif to Median
1	3	0.0026858	0.0020444	0.0019333
2	3	0.0027791	0.0021111	0.0020333
4	3	0.0013279	0.0010222	0.0007667

Test	F Ratio	DFNum	DFDen	Prob>F
O'Brien[.5]	0.5071	2	6	0.6259
Brown-Forsythe	0.4713	2	6	0.6455
Levene	1.5395	2	6	0.2886
Bartlett	0.4606	2	.	0.6309

Ho is accepted

Welch Anova testing Means Equal, allowing Std Devs Not Equal

F Ratio	DFNum	DFDen	Prob>F
25.1804	2	3.5259	0.0082

Analysis of Variance

Ho: the amount of CuO leached (mg /g wood) from the different boards is similar
H1: the amount of CuO leached (mg /g wood) from the different boards is different
ά = 0.05

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Board	2	0.00037934	0.000190	34.0725	0.0005
Error	6	0.00003340	0.000006		
C. Total	8	0.00041274			

H1 is accepted.

Means for One-way Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
1	3	0.054667	0.00136	0.05133	0.05800
2	3	0.068867	0.00136	0.06553	0.07220
4	3	0.055567	0.00136	0.05223	0.05890

Std Error uses a pooled estimate of error variance

Means Comparisons

Dif=Mean[i]-Mean[j]	2	4	1
2	0.000000	0.013300	0.014200
4	-0.0133	0.000000	0.000900
1	-0.0142	-0.0009	0.000000

ά = 0.05

Comparisons for all pairs using Tukey-Kramer HSD

q*
3.06815

Abs(Dif)-LSD	2	4	1
2	-0.00591	0.007389	0.008289
4	0.007389	-0.00591	-0.00501
1	0.008289	-0.00501	-0.00591

Positive values show pairs of means that are significantly different.

Abs(Dif)-LSD	2	4	1
2	-	+	+
4	+	-	-
1	+	-	-

Appendix 6 Statistical analysis of the migration of copper in checks in CAz treated wood

Analysis of Variance

Ho: the amount of CuO leached of the leachates phases are similar
H1: the amount of CuO leached of the leachates phases are different
α: 0.05

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Section	2	0.80366333	0.401832	97.9528	<.0001
Error	13	0.05332986	0.004102		
C. Total	15	0.85699319			

H1 is accepted.

Positive values show pairs of means that are significantly different.

Abs(Dif)-LSD	Surface check	Below check	Ref. untreated part
Surface check	-	+	+
Below check	+	-	+
Ref. untreated part	+	+	-

Appendix 7 Statistical analysis of the amount of copper leached per month CX™ treated wood

First Month March

Analysis of Variance

Ho: The amount of CuO leached by board size and treatment type is similar
H1: The amount of CuO leached by board size and treatment type is different
ά: 0.05

Source	DF	SS	MS	Fcal	Ftab	significance
Treatment	5	0.626655	0.125331	1.8185	3.48	ns
Charge	2	0.427429	0.213714	3.100905	4.26	ns
Board	1	0.044	0.044	0.638419	5.12	ns
ChxB	2	0.155227	0.077613	1.126137	4.26	ns
Error	9	0.62028	0.06892			
Total	14	1.246935				

Ho is accepted. There is no significant difference in the amount of copper leached between board size and treatment type.

Second Month April

Analysis of Variance

Ho: The amount of CuO leached by board size and treatment type is similar
H1: The amount of CuO leached by board size and treatment type is different
ά: 0.05

Source	DF	SS	MS	Fcal	Ftab	significance
Treatment	5	0.338813	0.067763	0.507291	3.48	ns
Charge	2	0.305606	0.152803	1.143931	4.26	ns
Board	1	0.002668	0.002668	0.019972	5.12	ns
ChxB	2	0.030539	0.015269	0.114311	4.26	ns
Error	9	1.202195	0.133577			
Total	14	1.541008				

Ho is accepted. There is no significant difference in the amount of copper leached between board size and treatment type.

Third Month May

Analysis of Variance

Ho: The amount of CuO leached by board size and treatment type is similar
H1: The amount of CuO leached by board size and treatment type is different
ά: 0.05

Source	DF	SS	MS	Fcal	Ftab	significance
Treatment	5	0.258726	0.051745	1.103561	3.48	ns
Charge	2	0.110917	0.055459	1.182757	4.26	ns
Board	1	0.07795	0.07795	1.662437	5.12	ns
ChxB	2	0.069858	0.034929	0.744927	4.26	ns
Error	9	0.422004	0.046889			
Total	14	0.680729				

Ho is accepted. There is no significant difference in the amount of copper leached between board size and treatment type.

Fourth Month June

Analysis of Variance

Ho: The amount of CuO leached by board size and treatment type is similar
H1: The amount of CuO leached by board size and treatment type is different
ά: 0.05

Source	DF	SS	MS	Fcal	Ftab	significance
Treatment	5	42.6	8.52	1.090237	3.48	ns
Charge	2	30.53333	15.266667	1.953555	4.26	ns
Board	1	0.711111	0.7111111	0.090995	5.12	ns
ChxB	2	11.35556	5.6777778	0.72654	4.26	ns
Error	9	70.33333	7.8148148			
Total	14	112.9333				

Ho is accepted. There is no significant difference in the amount of copper leached between board size and treatment type.

Fifth Month July

Analysis of Variance

Ho: The amount of CuO leached by board size and treatment type is similar
H1: The amount of CuO leached by board size and treatment type is different
ά: 0.05

Source	DF	SS	MS	Fcal	Ftab	significance
Treatment	5	2.566667	0.5133333	0.894194	3.48	ns
Charge	2	2.133333	1.0666667	1.858065	4.26	ns
Board	1	0.011111	0.0111111	0.019355	5.12	ns
ChxB	2	0.422222	0.2111111	0.367742	4.26	ns
Error	9	5.166667	0.5740741			
Total	14	7.733333				

Ho is accepted. There is no significant difference in the amount of copper leached between board size and treatment type.

Sixth Month August

Analysis of Variance

Ho: The amount of CuO leached by board size and treatment type is similar
H1: The amount of CuO leached by board size and treatment type is different
ά: 0.05

Source	DF	SS	MS	Fcal	Ftab	significance
Treatment	5	365.5	73.1	1.321527	3.48	ns
Charge	2	56.13333	28.066667	0.507399	4.26	ns
Board	1	80.27778	80.277778	1.451289	5.12	ns
ChxB	2	229.0889	114.54444	2.070773	4.26	ns
Error	9	497.8333	55.314815			
Total	14	863.3333				

Ho is accepted. There is no significant difference in the amount of copper leached between board size and treatment type.

Seventh Month September

Analysis of Variance

Ho: The amount of CuO leached by board size and treatment type is similar
H1: The amount of CuO leached by board size and treatment type is different
ά: 0.05

Source	DF	SS	MS	Fcal	Ftab	significance
Treatment	5	0.39829	0.079658	2.039982	3.48	ns
Charge	2	0.059654	0.029827	0.763849	4.26	ns
Board	1	0.176329	0.176329	4.515664	5.12	ns
ChxB	2	0.162306	0.081153	2.078275	4.26	ns
Error	9	0.351435	0.039048			
Total	14	0.749725				

Ho is accepted. There is no significant difference in the amount of copper leached between board size and treatment type.

Eighth Month October

Analysis of Variance

Ho: The amount of CuO leached by board size and treatment type is similar
H1: The amount of CuO leached by board size and treatment type is different
ά: 0.05

Source	DF	SS	MS	Fcal	Ftab	significance
Treatment	5	0.324858	0.064972	1.97853	3.48	ns
Charge	2	0.03523	0.017615	0.536412	4.26	ns
Board	1	0.087345	0.087345	2.659866	5.12	ns
ChxB	2	0.202282	0.101141	3.07998	4.26	significance
Error	9	0.295544	0.032838			
Total	14	0.620402				

Ho is accepted. There is no significant difference in the amount of copper leached between board size and treatment type.

Ninth Month November

Analysis of Variance

Ho: The amount of CuO leached by board size and treatment type is similar
H1: The amount of CuO leached by board size and treatment type is different
ά: 0.05

Source	DF	SS	MS	Fcal	Ftab	significance
Treatment	5	0.465758	0.093152	3.355408	3.48	ns
Charge	2	0.036079	0.01804	0.649807	4.26	ns
Board	1	0.142043	0.142043	5.116536	5.12	ns
ChxB	2	0.287635	0.143818	5.180446	4.26	ns
Error	9	0.249855	0.027762			
Total	14	0.715612				

Ho is accepted. There is no significant difference in the amount of copper leached between board size and treatment type.

Tenth Month December

Analysis of Variance

Ho: The amount of CuO leached by board size and treatment type is similar
H1: The amount of CuO leached by board size and treatment type is different
ά: 0.05

Source	DF	SS	MS	Fcal	Ftab	significance
Treatment	5	0.417194	0.083439	2.218537	3.48	ns
Charge	2	0.040591	0.020296	0.539634	4.26	ns
Board	1	0.161317	0.161317	4.289235	5.12	ns
ChxB	2	0.215285	0.107643	2.862091	4.26	ns
Error	9	0.338488	0.03761			
Total	14	0.755682				

Ho is accepted. There is no significant difference in the amount of copper leached between board size and treatment type.

December Cumulative

Analysis of Variance

Ho: The amount of CuO leached by board size and treatment type is similar
H1: The amount of CuO leached by board size and treatment type is different
ά: 0.05

Source	DF	SS	MS	Fcal	Ftab	significance
Treatment	5	0.275997	0.055199	1.798694	3.48	ns
Charge	2	0.064688	0.032344	1.053936	4.26	ns
Board	1	0.08019	0.08019	2.61302	5.12	ns
ChxB	2	0.131119	0.06556	2.13629	4.26	ns
Error	9	0.276197	0.030689			
Total	14	0.552194				

Ho is accepted. There is no significant difference in the amount of copper leached between board size and treatment type.