

**Comparative study of field and laboratory tests for
residual metal content and its distribution in
chromium/copper-treated wood**

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As a native speaker of the English language I find that the Ph.D. Dissertation titled, **Comparative Study of Field and Laboratory Tests for Residual Metal Content and its Distribution in Chromium/Copper-Treated Wood**, authored by Mohsen Bahmani Joneghan has been checked and fulfills requirements for an English dissertation (grammar and dictation).

Regards,

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Abstract

Chemical preservatives are widely used to prolong the service life of wood. Unfortunately, some of the preservative substances can be gradually leached from treated wood into the environment during exterior applications and can be toxic to plants, animals and human health. Most studies on the depletion of preservatives from treated wood were performed with small samples on a laboratory scale. Although these studies provide repeatable conditions and are useful for shorter test durations, they have little applicability to real conditions. These issues raised the consideration of a larger sample (i.e. EN 252) that is more closely associated with commercial sized material for possible improvement of the laboratory tests.

A series of laboratory tests with larger samples (i.e., EN 252 and non-standard) and field tests were conducted to determine the loss of chromium and copper from chromium/copper (CC)-treated wood and evaluate the factors (e.g., exposure time, stake position, wood species and dimension) influencing the residual metal content. The distribution of chromium and copper in the treated wood were also assessed. At the field test, EN 252 pine sapwood, EN 252 spruce and non-standard pine sapwood stakes were installed vertically with half their lengths in ground. In all cases three stakes were sampled after 4, 8, 12, 16, 20 and 24 months of exposure and analyzed according to DIN 52161-7 to determine metal content and its distribution in the wood stakes. Laboratory leaching tests were conducted in accordance to a modified CEN/TS 15119-1 (discontinuous) and CEN/TS 15119-2 (continuous procedure). In addition, wood samples were analyzed after leaching to determine remaining metals and their distribution in the wood specimens. For analyses, Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma Spectrometer-Optical Emission Spectrometry (ICP-OES) were applied.

Result showed that 96, 90 and 95% chromium remained in the EN 252 pine, non-standard pine and EN 252 spruce stakes while the copper content corresponded to 87, 83 and 91% after 24 months outdoor exposure, respectively. The laboratory tests revealed that 97, 96 and 99% chromium remained in the EN 252 pine, non-standard pine and EN 252 spruce stakes whereas the copper content was 96, 97 and 98% after laboratory tests, respectively.

After exposure, both standard and non-standard pine sapwood and spruce stakes contained the highest chromium and copper content in the above ground section. It was found that the wood species had a significant effect on the copper depletion while it had less influence on the chromium losses.

Chromium and copper distribution in the standard and non-standard pine sapwood significantly changed as compared to spruce stakes. However, in all cases the lowest metal content was observed in the soil-air area (groundline) of the treated wood.

Comparison of the laboratory and field tests indicated that metal depletion is greater in field exposure (above and below ground section) in comparison with both laboratory tests (continuous and discontinuous water immersion).

The results have demonstrated that larger specimens like in EN 252 could improve laboratory leaching tests and may provide a better interpretation of the leaching effects of preservatives during outdoor exposure, particularly metal migration.

Zusammenfassung

Weit verbreitet werden chemische Schutzmittel zur Verlängerung der Gebrauchsdauer von Holz verwendet. Leider können einige Schutzmittelsubstanzen bei der Außenverwendung aus behandeltem Holz ausgewaschen und dadurch giftig gegenüber Pflanzen, Tieren und Menschen werden. Die meisten Untersuchungen zur Herauslösung von Wirkstoffen aus behandeltem Holz erfolgten im Labor an kleinen Proben. Zwar liefern sie reproduzierbare Ergebnisse und benötigen weniger Zeit, doch sind die Befunde nur bedingt auf die Praxis übertragbar. Dies führte zu Überlegungen hinsichtlich größerer Proben, wie bei EN 252, die der kommerziellen Anwendung näher kommen und die Laborverfahren möglicherweise verbessern.

Zur vergleichenden Untersuchung von Feld- und Labortests erfolgten daher Versuchsserien mit größeren Proben, die sowohl den Maßen von EN 252 entsprachen (Standardproben) als auch mit davon abweichendem Zuschnitt (Nicht-Standard-Proben). Im Freilandversuch wurden der Verlust an Chrom und Kupfer aus Chrom-Kupfer (CC)-behandeltem Holz gemessen und die den Restmetallgehalt beeinflussenden Faktoren bewertet, nämlich Verweildauer, Probenposition, Holzart und Probengröße. Ferner wurde die Verteilung von Chrom und Kupfer im behandelten Holz bestimmt. Bei dem Feldversuch wurden EN 252-Kiefernspiltholzstäbe, EN 252-Fichtenholzstäbe und Nicht-Standard-Kiefernspiltholzstäbe senkrecht je zur Hälfte in den Erdboden gebracht. Jeweils drei Stäbe wurden nach 4, 8, 12, 16, 20 und 24 Monaten entnommen und gemäß DIN 52161-7 hinsichtlich Gehalt und Verteilung der Metalle im Holz untersucht. Auswaschversuche im Labor erfolgten nach einem modifizierten CEN/TS 15119-1- (diskontinuierlich) und CEN/TS 15119-2-Verfahren (kontinuierlich). Danach wurden schließlich Restgehalt und Verteilung der Metalle im Holz gemessen.

Die Ergebnisse zeigten, dass bei den Stäben nach 24 Monaten noch 96% (EN 252-Kiefer), 90% (Nichtstandard-Kiefer) und 95% (EN 252-Fichte) Chrom vorhanden waren sowie entsprechend 87, 83 und 91% Kupfer. Die Laborversuche ergaben 97, 97 und 99% Restchrom sowie 96, 97 und 98% Restkupfer. Die Verteilung von Chrom und Kupfer in dem Standard- und Nicht-Standard-Kiefernholz änderte sich im Vergleich mit Fichte deutlich. In allen Fällen wurde der geringste Metallgehalt in der Erdluftzone und der höchste Gehalt im oberen Bereich der Stäbe

gemessen. Es zeigte sich, dass die Holzart den Verlust an Kupfer deutlich und denjenigen an Chrom nur wenig beeinflusste. Der Metallverlust war im Feldversuch, sowohl in der Luftzone als auch im Erdbereich, größer als bei beiden (diskontinuierlich, kontinuierlich) Laborversuchen.

Insgesamt haben die Ergebnisse gezeigt, dass größere Proben, wie bei EN 252, die Auswaschversuche im Labor verbessern und eventuell eine bessere Deutung der Auswaschvariablen von Schutzmitteln im Freilandversuch ermöglichen, besonders hinsichtlich der Metallverschiebung.

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1. Introduction

1.1 General

Wood is one of the most commonly used raw material in a wide variety of applications such as poles, fences, decks, masts, constructional timber, children playgrounds etc. Wood is susceptible to decay in conditions that are suitable for the growth of fungi. Chemicals are used to treat the wood to prolong the service life against fungal and insect attacks. For example, untreated railway ties that are used in North America would have an average life of five years (Konasewich and Henning, 1998) whereas treated ties with creosote under service conditions are estimated to serve 30 years (Webb, 1990).

Chromated copper arsenate (CCA) was the main water-based preservative formulation for residential and industrial applications for decades. CCA is no longer permitted to be used in Europe due to the concern of the arsenic exposure that could potentially be a health hazard. In Europe, Germany was the first country where the use of arsenic in preservatives was forbidden and formulations such as chromated copper borate (CCB) and chromium copper (CC) were introduced. The waterborne preservative containing Cr, Cu and B in its formulation is considered to be less toxic than CCA, because of the absence of arsenic, but it is more susceptible to leaching (Fox et al., 1994).

Despite the fact that copper-based solutions have been widely used as fungicides for many biocidal products, their main disadvantage is insufficient fixation. It is important that copper present in the treating solution is fixed within the wood cells to reduce its depletion from treated wood. It has been documented that the copper leaching from treated wood with the new generation of copper based preservatives like copper-HDO and copper-ethanolamine is still higher than that of the chromium-copper-based wood preservative (Habicht et al., 2003, Temiz et al., 2006).

Chromium compounds have been applied as fixing agents for decades and they are still the most important commercial fixing agent to reduce copper leaching from the treated wood.

After the implementation of "European Commission concerning the placing of biocidal products on the market in 1998 (BPD 98/8/EC) ", the application of chrome-containing preservative formulations was accepted based on the following requirements:

- Products containing chromic acid, the active substance must be a copper compound, such as copper (II) oxide or copper hydroxide.
- The mass ratio of chromic acid to copper (II) oxide in all products must be no more than 3:1.

Also, there are requirements regarding the use of the chrome-containing products:

- Treated wood should not be used in Use Class 1 or Class 2 applications as there are other chromium-free alternative products available presenting a lesser risk for these uses and should not be used in Use Class 5 (marine) applications as no data on efficacy against marine organisms is available.
- To be applied only via vacuum pressure processes.
- Treated wood must undergo appropriate procedures to ensure fixation has been fully completed and that full reduction of hexavalent chromium to the safer chromium trivalent form has been achieved.
- There should be no hexavalent chromium in leachates or on the surface of treated wood when it is placed on the market.

It was demonstrated that some of the biocide substances can gradually migrated from treated wood into the environment during outdoor exposure and could be toxic to plants and animals (Lebow, 1996). In order to determine the leaching of wood preservative components from treated wood, there are two major approaches: laboratory and field tests.

A considerable amount of literature has been published on laboratory evaluations of the factors that can influence the depletion of preservative chemicals from treated wood (e.g., Smith and Williams, 1973a,b; Cooper, 1994; Haloui and Vergnaud, 1997; Schoknecht et al., 2004). Laboratory leaching tests are reproducible. A challenge of laboratory tests is their inability to compare to the situations found in real conditions and also their results are hardly transformable to real conditions. Laboratory tests are usually conducted with small samples to magnify the

leaching conditions and accelerate the acquisition of results. Small sized samples should not be used to estimate the depletion of wood preservative in service conditions (Lebow, 1996); since larger samples (EN 252:1990) are comparable to commercial-size material in development and evaluation of laboratory methods rather than lab scale tests. Rapid comparable data in a natural outdoor exposure is a key component to reliable information. Field exposure testing, while being more time-consuming, has advantages over lab scale studies since treated wood is subjected to actual climatic environmental conditions. Results from field exposure tests may vary due to different soil and climatic conditions among field test sites. It should also be considered that the wood specimens, although being chemically treated, are supposed to the influence of soil fungi and bacteria, particularly during long exposure over years, and that the microbial flora differs among test fields. Soft-rot fungi are generally rather tolerant to harsh environmental conditions (Dickinson et al., 1976; Liese and Peters, 1977; Greaves and Nilsson, 1982). Like with antibiotics and bacteria, resistance against the chemical may develop, i.e. at low concentrations, with the possible consequence that the fixation of the chemicals is attacked. Comparative studies on the laboratory and field tests are needed to evaluate whether laboratory test results are able to accurately estimate the depletion of wood preservative components during in-service conditions. Besides the type of preservative, retention and wood species (Hingston et al., 2001), the effectiveness of a preservative treatment is influenced by the distribution and penetration of the preservative in the wood (Ibach, 1999). Therefore, information on distribution of preservative chemicals within wood is important in developing and understanding of all phases of preservatives from impregnation to outdoor performance.

However, the stakes are usually not analyzed during outdoor exposure and at the end of experiment to assess residual chemical content and its distribution in the stakes. Treated wood during exterior applications is affected by long-term weathering and soil composition (Lebow, 1996; Schultz et al., 2002) thereby causing changes in metal contents and their distribution within the wood. These changes may affect the effectiveness of the treated wood against biodegradation. Knowing the residual chemical content and its distribution can provide useful information on the preservative performance in real conditions, environmental issues, and future reuse of wood.

1.2 Aim of the study

The objectives of this study were to determine:

- the distribution of chromium and copper in the stakes prior and after different exposure times,
- the residual content of chromium and copper in CC-treated wood after different exposure time intervals,
- the influence of wood species and sample size on distribution and left over metal content,
- the comparison of chromium and copper leaching potential in the field versus laboratory protocol tests.

1.3 Literature review

1.3.1 Composition and structure of wood

Wood is made up of cells which contain many different polymer molecules. The wood cell wall is composed of three major components; cellulose, lignin, and hemicelluloses. In addition, wood contains small amounts (5% to 10%) of extractives (Miller, 1999). General description of the wood components is described below:

- Cellulose, the major component, is a linear polymer of 10.000 to 15.000 β -D-linked glucose anhydride units and constitutes approximately 50% of wood's dry weight. In "native cellulose", hydrogen bonds exist between the OH-groups of neighboring glucose units and neighboring cellulose molecules. Regions of crystalline cellulose and areas of lower order (amorphous, paracrystalline cellulose) alternate (Schmidt, 2006).
- Lignin constitutes 26 to 39% of the wood substance in softwoods and 18 to 39% in hardwoods. Lignin is a complex, three-dimensional macromolecule in the range of 100 kDa and is highly hydrophobic reducing the hygroscopicity of wood and improving its resistance to microorganisms. It functions as a binding and encrusting material in the cell wall distributed with hemicelluloses in the spaces of inter-cellulose microfibrils. Most softwood lignins are as guaiacyl lignins (G-lignins) polymers predominantly made of coniferyl alcohol (C). Hardwood lignins are guaiacyl-syringyl lignins (GS-lignins) and consist predominantly of C and sinapyl alcohol (S). Guaiacyl-syringyl-*p*-hydroxyphenyl lignins occur in grasses (monocotyledons). In the lignin molecule, the basic modules are linked with a variety of chemical bonds, ether and carbon-carbon linkages. The β -O-4-linkage is the most frequent interunit linkage. Lignin quantity and composition vary as with the tree age, xylem and bark, between rot and stem wood, heartwood and sapwood, earlywood and latewood, and in different wood cells and cell wall layers. Although lignin occurs in wood throughout the cell wall, its concentration is high in the tertiary wall and middle lamella primary wall region. Lignin is also the primary site for bonding of chromium in wood preservatives (Pizzi, 1990).

- Hemicelluloses of wood (15 to 35%) are a complex combination of relatively short polymers made of xylose (pentose), arabinose, galactose, mannose, and glucose with acetyl and uronic side-groups. The major hemicellulose of hardwoods is the *O*-acetyl-(4-*O*-methylglucurono)-xylan or briefly xylan. Hemicelluloses of conifers (glucomannans, galactoglucomannans) consist mainly of the hexose mannan.
- Extractives are deposited in wood without strongly bonding with other wood substances and are soluble in organic solvents.

1.3.2 Protection and preservation of wood

Wood has been a major construction material throughout history. Wood can be damaged by fungi, bacteria, insects and termites (e.g. Schmidt, 2006). Manifold protection and preservation measures have been experienced or are still in use. Wood protection in the broader sense comprises non-chemical methods like organizational measures and measures by design, use of naturally durable woods, application of antagonists, wood modifications, thermal modifications and wood hydrophobizations that do not affect the environment (Willeitner and Schwab, 1981; Militz and Krause, 2003; Rapp and Müller, 2005). Wood preservation has been associated predominantly with chemical modifications.

Simple, however, often less effective application methods of chemical preservatives to the wood are brushing, spraying and dipping. Pressure treatment of wood with biocidal products is the primary industrial method utilized for developing treatment chemicals into wood and has been proven to protect the wood effectively from biological attacks. The degree of protection depends on the preservative chemical used and its proper penetration. To preserve the wood, it is necessary for biocide substances to penetrate into the wood adequately. Several factors influence the degree of protection that can be achieved with biocides such as (Morris, 1996):

- method of wood treatment,
- quantitative ratio of heartwood to sapwood,
- permeability of wood,
- wood moisture content.

1.3.3 Chromium and copper

For decades chromated copper arsenate (CCA) was the major preservative for residential and industrial construction with soil contact because it is very effective, inexpensive and can be fixed very well after treatment. Three different types of CCA-formulations for treatment of wood have been developed over time. Type A contained more chromium, while Type B had more arsenic. Type C of CCA is comprised of 47.5% chromium trioxide, 18.5% copper oxide and 34.0% arsenic pentoxide. Type C has been the most common formulation because of its resistance to leaching and excellent field efficacy.

Water-borne preservative treatments must be applied by a vacuum-pressure treating process. Fixation is generally referred to as the conversion of water-soluble inorganic components into stabilized components, which resist depletion and provide longer service life of the treated wood. Lebow (1996) pointed out that the essence of CCA fixation is the reduction reaction of chromium from the hexavalent to the trivalent state, and the subsequent precipitation or adsorption of copper. Factors including temperature, relative humidity and treating solution pH-value are the main parameters affecting fixation reactions (Pizzi, 1983a,b; Peek and Willeitner, 1981, 1988). A study by Guo et al. (2002) on the fixation of earlywood, latewood, sapwood and heartwood of CCA-treated Douglas fir, southern pine and eastern larch indicated that wood density, extractives and species affected the fixation of CCA.

Chromium is the least mobile of CCA components and its mobility depends on its valency state. Trivalent chromium is very reactive with organics and fixes to soil and sediments quickly. Hexavalent chromium is more soluble but less absorbed and the rate of its movement through soil and groundwater is the same (Rouse and Pyrih, 1990). The valence state of chromium is a function of the oxygen content and redox potential, pH-value, suspended inorganics, and the presence of dissolved or particulate organic matter (Lebow, 1996). When there are no organic compounds in the media, hexavalent chromium is the most stable form in equilibrium with atmospheric oxygen (McGrath and Smith, 1990).

Copper has been known for having wood protection qualities since the eighteenth century (Freeman and McIntyre, 2008). Copper is a primary fungicide and because of its excellent fungicidal properties and low mammalian toxicity has been used in many wood preservative

formulations. The production of wood treated with copper based preservatives has advantages: it is easy to create waterborne formulations; it is easy to analyze and determine penetration in wood; and copper slows photodegradation by UV radiation (Freeman and McIntyre, 2008). Adsorption of copper is a very important factor in determining its mobility and is influenced by pH-value, amount and type of adsorbents (Lebow, 1996).

1.3.4 Laboratory and field studies on preservative leaching

Over the past years, considerable attention has been focused on the depletion of biocidal products from treated wood due to public and scientific awareness. The performance of preservative chemicals can be achieved either under service conditions or under laboratory tests. Both laboratory tests and field tests have advantage and disadvantages (see section 1.1). Until recently, most studies were conducted in the laboratory scale. Two laboratory procedures were proposed by a CEN working group to determine depletion from treated wood into the environment. The procedures are either based on constant immersion or short immersion cycles. Constant immersion tests are usually used to describe leaching of preservative-treated wood in contact with the ground or in contact with fresh or salt water. Short time immersions are intended to simulate intermittent wetting and drying events for wood held in storage after treatment and for wooden commodities that are not in ground or water contact.

Laboratory leaching tests are a fundamental approach to generate data from treated wood under controlled conditions. Their great advantage is their repeatability. Laboratory tests are rapid and inexpensive. However, The European Draft standard for laboratory leaching EN 1250:2 (1994) pointed out that results from these method tests cannot be applied to determine the depletion of preservative chemicals in real conditions since the results cannot be related to outdoor exposure of wood in service. There are a number of possible explanations for this. Wood exposed in laboratory leaching test is subjected to different conditions from those affecting wood under real service conditions. These include actual environmental conditions, physical stresses and metabolizing organisms. In addition, chemical retention, penetration and scale and size of the commercial treated wood are different than the treated wood in comparison to laboratory samples.

In recent years, there has been an increased focus on investigations of the performance of preservative in-service situations. Field exposure testing has the advantage that the treated wood is exposed to the actual environmental conditions, incorporates many variables present in the naturally occurring event and provides valuable information on the performance of the preservative chemical. As a disadvantage, field exposure can be more expensive, time-consuming and difficult to control. In addition, they are varying climatic, soil and other related conditions present different locations which can result in different exposure conditions between various field test sites (Lebow et al., 2004).

Environmental parameters are important for the preservative performance. The following section covers some important factors that impact on the chemical depletion from the treated wood during outdoor exposure.

Exposure time of the treated wood can determine the amount preservative leached from treated wood. Lebow (1996) stated that most of metal leaching from treated wood occurs during the first exposure to the leaching medium. This time-dependent depletion pattern is a function of the sample size, the amount and type of surface exposed and the amount of chemicals fixed to wood.

The climatic conditions also play an important role in the leaching process, particularly rainfall, temperature, and sunshine. Water is the key factor for depletion and mobility of preservatives in treated wood, regardless of exposure type. It has been demonstrated that leaching of CCA components is significantly increased due to a low pH-value of the leaching water (Murphy and Dickinson, 1990; Kim and Kim, 1993).

Temperature contributes on the drying and wetting of wood, solubility of the unfixed or poorly fixed preservative components and brings components to the wood surface (Choi et al., 2004). Increasing temperature increases the amount of leached CCA compounds (Van Eetvelde et al., 1994, 1995a,b). The amount of time directly exposed to sunlight can have an effect on the exposed surface of the wood and UV radiation leads to an attack on lignin (Choi et al., 2004) which is the primary bonding site of chromium (Pizzi, 1990).

The wood properties of the species are other factors affecting the amount of leaching. Low permeable species like spruce tend to be more resistance to leaching (Wilson, 1971). Wood species also affect the distribution of preservative within the wood (Lebow, 1996). CCA components fixation in latewood is much more than in earlywood due to more reacting substances and greater density.

An important factor in depletion of preservatives is the size and dimension of the wood sample (Lebow, 1996). Large surface area/volume ratio of small samples permits more surface area available for leaching and more rapid water penetration (Cooper, 1994). It may destroy a considerable amount of treated wood due to erosion and attack by organisms causing difficulty in interpretation of long-term leaching experiments (Lebow et al., 2008).

In a study of field tests, Evans and Edlund (1993) treated Scot pine sapwood (20×50×500 mm) stakes with CCA-B during 20 to 43 years in a Swedish test site and reported that 19% chromium, 23% copper and 25% arsenic leached based on the original retention data.

Wakeling (1996) established an outdoor test to evaluate the depletion of CCA components from 20×20×500 mm specimens after 4.5 and 5.5 years for pine in New Zealand and Australia. The amount of chromium, copper and arsenic leached from above ground section was 8, less than 1 and 15%, respectively. For below ground portion more than 9 and 30 and 22% chromium, copper and arsenic leached, respectively.

Melcher and Wegen (2000) investigated the remaining wood preservative components in EN 252 stakes exposed in ground contact at the DESOWAG GmbH, Rheinberg field test site. Stakes divided into 10 sections showed a remaining concentration of 90% for chromium and 40-70% for copper.

Osborne and Fox (1995) compared the above ground and below ground retentions of 5 CCA-C treated southern pine poles in service for over 6 years in Georgia, USA. There was no significant difference in the pole retentions in these two positions for any of the 12.5mm depth zones.

Jin et al. (1992) analyzed 19×19×450 mm Scot pine stakes treated with CCA-C after 44 months exposure in Hawaii and reported a loss of 8.9 chromium, 20.5 copper and 2% arsenic.

A study on the effect of fixation, sample size, wood species and leaching protocols on the leaching of copper in laboratory tests (Habicht et al., 2003) revealed that the most important factors determining copper depletion in the different tests are sample size and fixation conditions. Wood species and leaching protocols had little influence.

Lebow et al. (2008) tested three methods for evaluating ground-contact copper preservative depletion: field test (American Wood Protection Association (AWPA) method E7), laboratory soil exposure (AWPA method E20) and laboratory water immersion (AWPA method E11) and reported that average copper losses tended to be higher from the field samples than from the small method E20 laboratory samples. AWPA method E11 had lower copper depletion than both soil-contact leaching methods.

Yamamoto et al. (1999, 2000) compared the depletion of chromium, copper, arsenic and boron from CCA, ACQ and BAAC preservatives in a 10 day laboratory leaching test (2×2×1 cm) with a 6 months outdoor exposure (25×10×1 cm). Results indicated an overestimated chromium, copper, arsenic and boron release from laboratory leaching test. When different sample sizes were exposed to outdoor exposure, there was a positive correlation between the surface area to volume ratio and the leaching amount per wood volume.

Cooper et al. (2001) investigated CCA distribution and mass balance at above and below ground zones for CCA-treated red pine and jack pine after 1-50 years exterior environment. Total CCA retention and each of the three CCA components declined from the outer surface to the inner zones. No statistically significant metal retention and mass balance were observed between above and below ground portions. Copper leaching, however, was substantially higher in below ground section in comparison with above ground ones.

Lebow (1996) stated that laboratory standard protocols for small samples should not be used to predict the amount of leaching that occur from commercial sample sized products exposed to outdoor conditions. Development of laboratory tests to quickly provide comparable data to

outdoor exposure is an important part of any laboratory standard protocol. There is a considerable variability in loss of preservative over time from field tests (Lebow et al., 2009) which differs from laboratory testing results. This raises the necessity to compare laboratory and field studies and to find a correlation between field and laboratory test data.

2. Material and methods

The performance of wood preservative chemicals was evaluated using both field and laboratory experiments. During the field experiment, treated wood stakes were exposed to natural conditions and removed at different exposure times (4, 8, 12, 16, 20 and 24 months). Metal content in samples was determined according to the German standard DIN 52161-7:1985. The laboratory tests were accelerated by placing treated woods in deionized water followed by the determination of metal concentrations in wood stakes.

2.1 Sample preparation

The wood materials used are presented in Table 2.1.

Table 2.1: Wood material used

Standard/species	Dimensions (cm)	Sapwood/heart-wood
EN 252 (<i>Pinus sylvestris</i> L.)	50×5×2.5	sapwood
non-standard (<i>Pinus sylvestris</i> L.)	39×4×4	sapwood
EN 252 spruce (<i>Picea abies</i> L.)	50×5×2.5	“sapwood”+“heartwood”

Pine sapwood is the most common wood used for evaluating the performance of wood preservative and its efficacy in several European standards (EN 113, EN 252).

Spruce is one of the major commercially used wood species in the northern hemisphere and has many uses in a wide variety of industries.

In total for each species and dimension, 18 stakes were prepared for field exposure test. Four stakes were also prepared for laboratory leaching tests and 3 stakes of pine sapwood and 4 stakes of spruce were retained as references to determine actual retention and distribution of the metals in the wood.

2.2 Solution preparation

For all experiments, treating solutions with 1.5% commercial chromium-and copper-containing preservatives were used (Rütgers Organics GmbH Company, Germany). The treating solutions were made by diluting the chromium-and copper-containing preservatives with tap water.

2.3 Sample treatment and fixation

Prior to impregnation, the wood stakes were dried for 24 hours at 60°C to minimize cracking. Samples then were dried at 103°C for 24h and the dry weight was recorded. The stakes were treated by vacuum-pressure impregnation according to EN 252:1990. The duration of vacuum and pressure was held constant for all samples. The samples were placed in a pilot plant subjected to a vacuum of 100 KPa for 30 min followed by pressure 800 KPa for one hour in a treating cylinder (Figure 2.1). The samples were taken out after the pressure was released and then stored for two weeks in the conditioning room (20±2°C and 65±5% relative humidity) for fixation reactions. For all samples, the concentration of chromium and copper before and after impregnation was determined using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Perkin Elmer Optima 3000).



Figure 2.1: Pilot treating cylinder used for impregnation of wood samples

2.4 Determination of metal retention

2.4.1 Calculation of chromium and copper retention based on technical data sheet (“theoretical retention”)

The retention level of metals in the wood samples was calculated with the theoretic uptake of the chemicals determined from the uptake of treating solution and its concentration:

$$R_t = \left[\frac{W_2 - W_1}{V} \right] \times c \quad (1)$$

Where,

R_t -theoretical retention of salts-kg/m³

W_1 -weight of samples before impregnation-kg

W_2 -weight of samples after impregnation-kg

c-% of concentration of treating solution

V-volume of specimen-m³

$$X_{Cr/Cu}=R_t \times P_{Cr/Cu} \quad (2)$$

Where,

$X_{Cr/Cu}$ -theoretical retention of chromium/copper-kg/m³.

R_t -retention of salt-kg/m³.

P-% percent of chromium/copper in the treating solution.

Content of the copper in the original solution was 13.86%.

- 13.86% or 138.6 g/kg CuO
- $M_{Cr}=51.996$ g/mol
- $M_{Cu}=63.546$ g/mol
- $M_O=15.999$ g/mol
- $M_{CrO_3}=51.996$ g/mol+3(15.999 g/mol)=99.993 g/mol
- $M_{CuO}=63.546$ g/mol+15.999 g/mol=79.454 g/mol

M- Molar mass in g/mol

$$\% \text{ chromium} = M_{Cr} / M_{CrO_3} \times 35.01\% = 51.996 / 99.993 \times 35.01\% = 18.20\%$$

$$\% \text{ copper} = M_{Cu} / M_{CuO} \times 13.86\% = 63.546 / 79.454 \times 13.86\% = 11.07\%$$

As an example, the retention of chromium and copper was calculated for stake "1" EN 252 pine sapwood.

$$W_1 = 0.33867 \text{ kg}$$

$$W_2 = 0.76994 \text{ kg}$$

c=concentration of treating solution=1.5%

V=0.000625 m³

theoretical retention= $\left[\frac{(0.76994-0.33867)}{0.000625}\right] \times 1.5\%=10.35 \text{ kg/m}^3$

theoretical retention of Cr=10.35×18.20%=1.88 kg/m³

theoretical retention of Cu=10.35×11.07%=1.15 kg/m³

2.4.2 Calculation of chromium and copper retention based on analysis of impregnation solution

In addition to calculating the theoretical retention, the chromium and copper retention was determined by comparing the concentration of the treating solution before and after impregnation. Jüngel et al. (1998) reported that chromium is selectively adsorbed in the wood. Therefore, the concentration of the treating solution before and after impregnation has to be taken into account when making the evaluation of the metal retention. Concentration of chromium and copper in the treating solutions was measured using the ICP-OES, and retention level of metals in treated wood was calculated according to the following equations:

$$R_s = \left[\frac{(W_2 - W_1) \times C}{V} \right] \times 10^{-6} \quad (3)$$

Where,

R_s is the retention of metals in wood-kg/m³.

W=W₂-W₁ is the amount of treating solution absorbed by the stake (initial weight of stake subtracted from the initial weight plus the treating solution absorbed)-kg.

V is the stake volume-m³.

c_s is the concentration of the impregnation solution before (B) and after (A) impregnation-mg/kg.
That calculated by applying equation (4).

$$c = (c_{s(B)} - c_{s(A)}) + c_{s(B)} \quad (4)$$

Inductively-Coupled Plasma (ICP) analysis, as with all similar analyses, involves errors associated with the measurement, which should be considered when calculating the metal retention. The following formula was used to calculate the analytical error:

$$\text{Analytical Error}_{Cr/Cu} = \frac{\text{observed value}}{\text{expected value}} \quad (5)$$

As an example, the analytical error was calculated for copper (data in the parentheses obtained from Appendix 1).

$$\text{Analytical Error}_{Cu} = \frac{\text{observed value}}{\text{expected value}} = \left[\frac{(51.3 + 51.6/2)}{50} \right] = 1.03$$

Based on the equation (5), the analytical error for chromium was 0.97.

As an example, the retention of chromium and copper was calculated for stake “1” EN 252 pine sapwood.

$$W_1=0.33867 \text{ kg}$$

$$W_2=0.76994 \text{ kg}$$

$$V=0.000625 \text{ m}^3$$

c_{s(B)}-concentration of chromium before impregnation=2433.3 mg/kg

c_{s(A)}-concentration of chromium after impregnation=2093.3 mg/kg

$$c_{cr}=(2433.3-2093.3)+2433.3=2773.4 \text{ mg/kg}$$

$c_{s(B)}$ -concentration of copper before impregnation=1507 mg/kg

$c_{s(A)}$ -concentration of copper after impregnation=1307 mg/kg

$c_{cu}=(1507-1307)+1507=1707$ mg/kg

$$R_{Cr} = \left[\frac{(0.43127 \times 2773.4)}{0.000625} \right] = 1913734.74 \text{ mg/m}^3$$

$$R_{Cr} = \left(\frac{1913734.74}{0.97} \right) \times 10^{-6} = 1.97 \text{ kg/m}^3$$

$$R_{Cu} = \left[\frac{(0.43127 \times 1707)}{0,000625} \right] = 1177884.62 \text{ mg/m}^3$$

$$R_{Cu} = \left(\frac{1177884.62}{1.03} \right) \times 10^{-6} = 1.14 \text{ kg/m}^3$$

2.4.3 Chemical analysis for actual retention of metals in treated wood stakes

In order to obtain the actual retention of chromium and copper, three stakes of pine sapwood and four samples of spruce were kept as control and analyzed according to procedures described in the DIN 52161-7.

Before chemical analysis, the stakes were cut into 10 segments as illustrated in Figure 2.2.

Segment “A” refers to the top and segment “J” to the bottom.

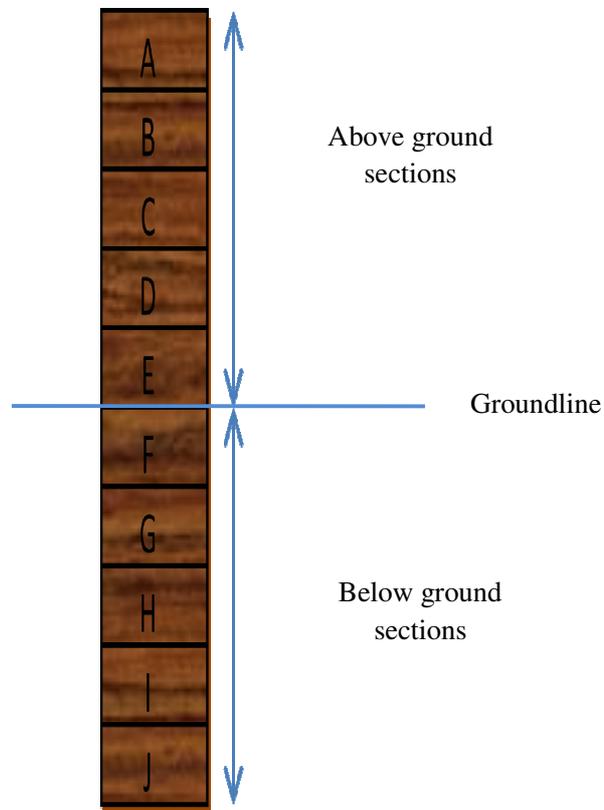


Figure 2.2. Sampling location used for analysis

Digestion according to DIN 52161-7 (1985)

After dividing the stakes into the segments, each segment was dried at 103°C to zero percent moisture content and their dimension were measured. These segments were crushed and were milled by using a grinder (IKA, MF 10 B, Germany). The ground samples were oven dried at 103°C to zero percent moisture content, followed by a cooling down period in a desiccator. Three oven dried wood samples (1.5g) were transferred into quartz crucibles and incinerated for 30 minutes with the Bunsen burner and then placed in a muffle oven (HERAEUS) for 90 minutes at a temperature of 560-580°C.

After a short cooling period the ashes were treated with 5 ml of 2 volumes 65% nitric acid and 5 volumes 95% sulfuric acid, and were heated on a heating plate until the ashes had completely dissolved. The solutions were then transferred into volumetric flasks, filled up to 100 ml with deionized water and analyzed to determine the amount of chromium and copper within the wood samples by means of the ICP-OES or Atomic Adsorption Spectrometry (AAS). The stages of sample preparation process, digestion according to DIN 52 161-7 and analysis are shown in Figure 2.3.

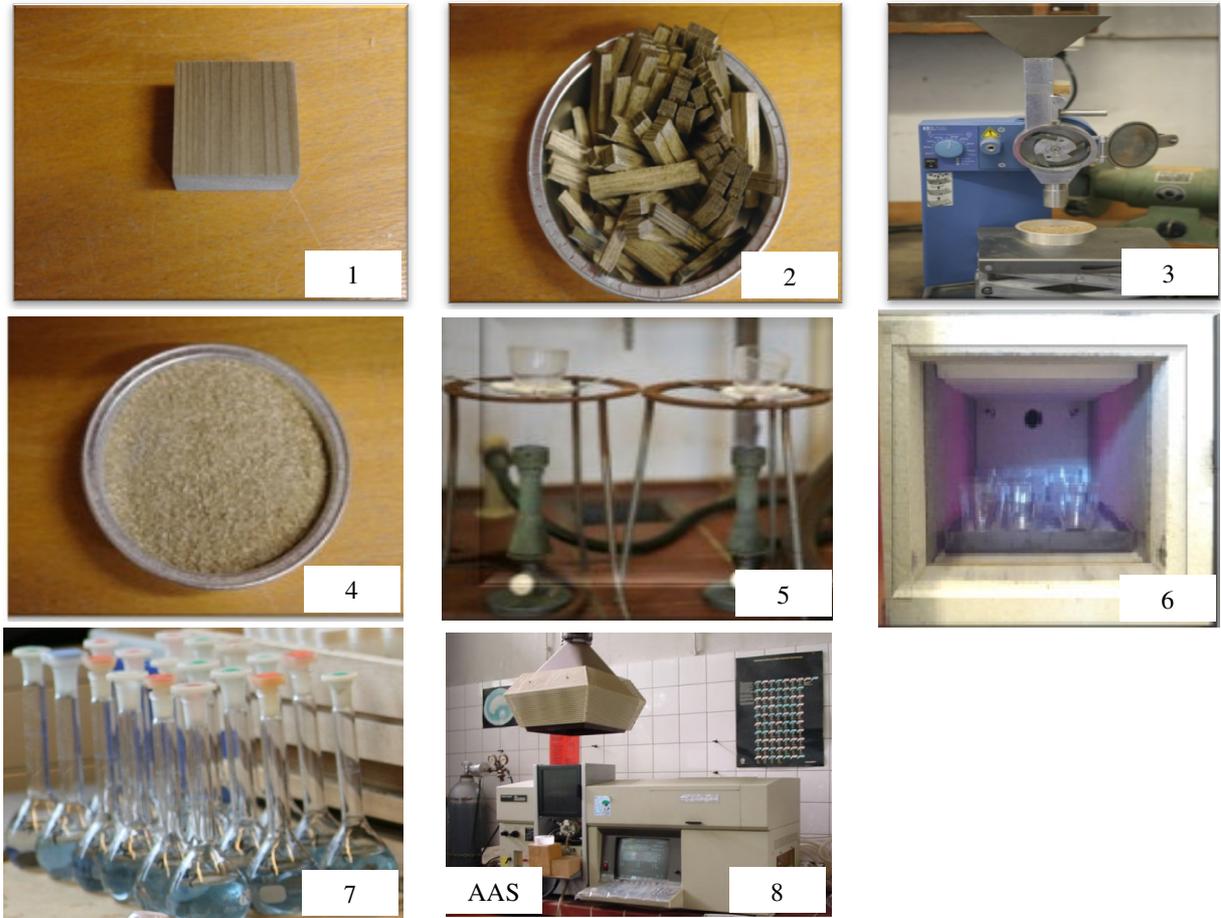


Figure 2.3: Stages of sample preparation and digestion for metal analysis

Since the AAS and ICP values are based on $\mu\text{g/ml}$, the values were converted to kg/m^3 according to the following equations:

$$m_{\text{Cr/Cu};100} = \alpha_{\text{Cr/Cu}} \times V \quad (6)$$

Where,

$m_{\text{Cr/Cu};100}$ -amount of chromium/copper in digested wood- μg .

$\alpha_{\text{Cr/Cu}}$ -content of chromium/copper in the digestion solution- $\mu\text{g/ml}$.

V -volume of produced digestion from a sample solution-ml.

$$Y_{\text{cr/cu}} = \frac{m_{\text{Cr/Cu};100} \times \rho_0}{m_{\text{wp}}} \times 10^6 \quad (7)$$

Where,

$Y_{Cr/Cu}$ -amount of chromium/copper in wood-kg/m³

$m_{Cr/Cu;100}$ -amount of chromium/copper in 100 ml digestion solution- μ g

ρ_o -density(dry)-kg/m³

m_{wp} -weight of wood powder-g

2.5 Field test exposure

Each of the eighteen pine stakes for the EN 252 standard and non-standard field stake test and the spruce test (EN 252) were randomly installed vertically with half their lengths in the ground at a field test site (Thünen-Institut site, Hamburg) (Figures 2.4 and 2.5). The stakes were placed in rows with a distance of approximately 30 cm between each stake. The climate of Hamburg is characterized by an average temperature of 9.4°C and precipitation of 793 mm per year (DWD.de). The soil at the test site is sandy loam. Three stakes were removed after 4, 8, 12, 16, 20 and 24 months for metal content determination and its distribution in the wood stakes.



Figure 2.4: DIN EN 252-stakes and non-standard stakes installed in ground on July 30, 2010



Figure 2.5: Samples of EN 252 pine sapwood (left), non-standard pine sapwood (center) and EN 252 spruce (right) to demonstrate the different sizes

2.6 Moisture content

After each sampling, the stakes were cut into two sections to separate above and below ground areas and these were dried at 103 °C to zero percent moisture content. Moisture content (%) was determined by the formula:

$$MC(\%) = \frac{W_1 - W_2}{W_2} \times 100 \quad (8)$$

Where,

MC-% moisture content

W₁-wet weight-g

W₂-oven-dried weight-g

2.7 Laboratory leaching tests

Two modified laboratory tests were used to perform leaching on the treated stakes. CEN/TS 15119-1:2008 as a discontinuous and CEN/TS 15119-2:2008 as a continuous procedure. Four stakes from each pine and spruce samples were set up for the leaching experiments. Before leaching, the EN 252 and non-standard stakes were cut into half of their length and end-sealed with silicon (Figure 2.6).

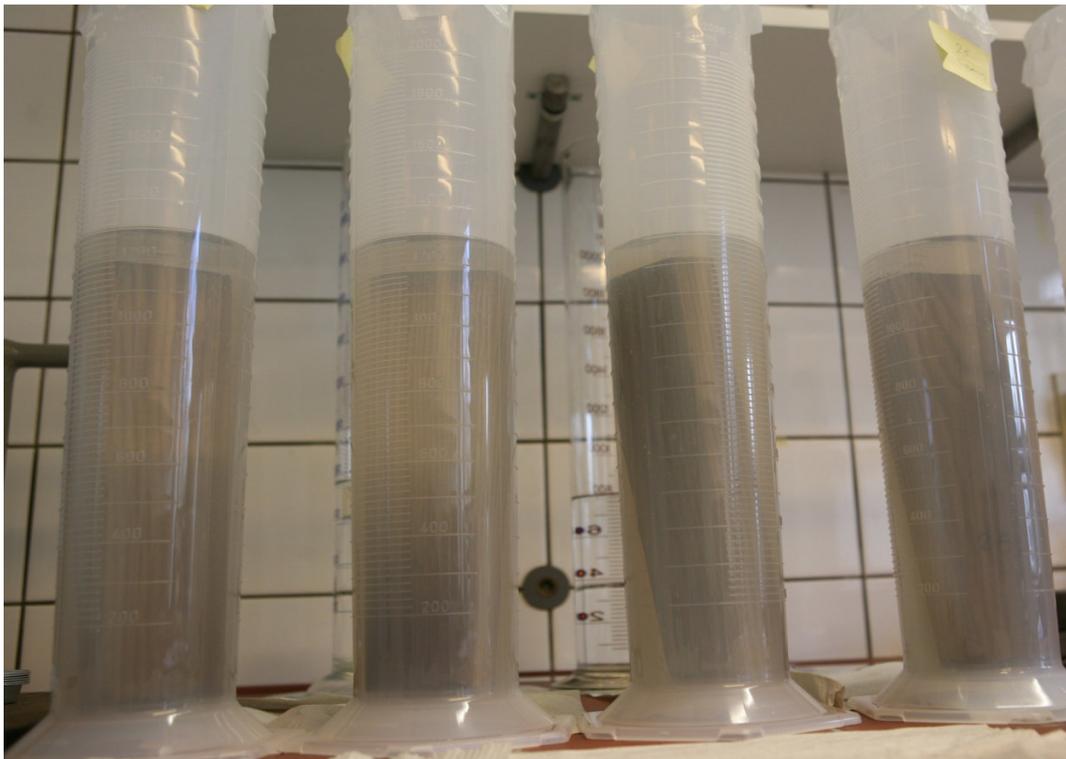


Figure 2.6: Test assembly for laboratory leaching to demonstrate CEN/TS 15119-1 and CEN/TS 15119-2 tests

2.7.1 Discontinuous water immersion of treated stakes

The leaching test was performed according to CEN/TS 15119-1 which is the standard method for the leaching of wood samples in which the emissions from preservative treated wood to the environment are measured. Wood held in the storage yard after treatment and wooden commodities were exposed in Use Class 3 (not covered, not in contact with the ground).

The detailed information on each material is shown in Table 2.2.

Table 2.2: Wood materials and significant factors in the leaching tests

Wood materials	Specimen size (cm)	Surface area in container (cm ²)	Wood volume (cm ³)	Water (mL)	Ratio of surface area to specimen volume	Ratio of wood volume to water volume
pine sapwood (EN 252)	25×5×2.5	375	313	937	1.20	0.33
pine sapwood (non-standard)	19.5×4×4	312	312	780	1.00	0.40
spruce (EN 252)	25×5×2.5	375	313	937	1.20	0.33

The volume of water required was calculated based on 2.5 cm³ per cm² of wood as mentioned in the standard. Each specimen was exposed in deionized water for 1 min and then removed and allowed to dry. This procedure was repeated three times during on immersion day (nine leaching

days during three weeks). Chromium and copper concentration in the leachate were determined by Graphite Furnace Atomic Absorption Spectrometry (GFAAS)¹.

Wood samples were also analyzed according to DIN 52161-7:1985 at the end of the leaching test to compare mass balance and total metal loss with initial retention values.

2.7.2 Continuous water immersion of treated stakes

The second laboratory leaching test was performed using the CEN/TS 15119-2 procedure which determines emissions from preservative treated wood to the environment, considering wooden commodities exposed in Use Class 4 or 5 (in contact with the ground, fresh or sea water). The volume of deionized water required was calculated similar as described in the discontinuous test. Each sample was placed into a container and the amount of deionized water per specimen was added. The water was replaced after 6 hours, 1, 2, 3, 4, 5 and 6 days during 21 days of leaching. Metal concentrations in the leachate were determined by GFAAS².

Similar to the discontinuous immersion, chemical analysis of the wood samples was conducted at the end of the leaching tests to compare mass balance and total metal loss with initial retention values.

^{1,2} The analysis of the water samples took place in the Institute of Inorganic and Chemistry, Department of Chemistry of Hamburg University.

2.8 Calibration of atomic absorption spectrometry (AAS) and inductively coupled plasma spectrometer-optical emission spectrometry (ICP-OES)

As described above, the concentration of chromium and copper in the treated wood stakes were determined by means of AAS and ICP-OES. For AAS calibration, standard chromium and copper solutions of 0, 0.5, 1, 2, 4 and 6 ppm were created using 1000 ppm chromium and copper concentrations (Merck, Germany).

For ICP-OES calibration, standard solutions of chromium and copper at levels of 0, 0.5, 1, 10, 50 and 100 ppm were prepared using 1000 ppm chromium and copper concentrations.

2.9 Statistical analysis

Analysis of variance (ANOVA) was used to analyze the effects of the variables (i.e., stake position, wood species, and exposure time) on the remaining content of chromium and copper in the treated wood. The Pearson's correlation test was used to indicate the correlation between the residual metal content in the laboratory and field tests. Data was processed by SPSS 18 (Statistical Package for the Social Sciences) statistics software.

3. Results and discussion

3.1 Retention of metal contents

The initial retention of metal contents in the EN 252 pine sapwood, non-standard pine sapwood and EN 252 spruce stakes are shown in Tables 3.1, 3.2 and 3.3. The tables contain the weight of stakes before and after impregnation as well as chromium and copper concentrations prior and after treatment.

Table 3.1: Weight of stakes, concentration of chromium and copper (before and after impregnation) and initial retention of metals in EN 252 pine sapwood stakes

Sample	Weight before impregnation (g)	Weight after impregnation (g)	Uptake (g)	Conc. Cr before impregnation (mg/kg)	Conc. Cu before impregnation (mg/kg)	Conc. Cr after impregnation (mg/kg)	Conc. Cu after impregnation (mg/kg)	Cr retention (kg/m ³)	Cu retention (kg/m ³)
1	338.67	769.94	431.27	2433.30	1507.00	2093.30	1307.00	1.97	1.14
2	313.29	765.24	451.95	2433.30	1507.00	2093.30	1307.00	2.07	1.20
3	327.77	772.90	445.13	2433.30	1507.00	2093.30	1307.00	2.04	1.18
4	345.87	757.56	411.69	2433.30	1507.00	2093.30	1307.00	1.88	1.09
5	326.79	773.55	446.76	2433.30	1507.00	2093.30	1307.00	2.04	1.18
6	338.48	769.26	430.78	2433.30	1507.00	2093.30	1307.00	1.97	1.14
7	324.36	765.34	440.98	2433.30	1507.00	2093.30	1307.00	2.02	1.17
8	322.14	757.59	435.45	2433.30	1507.00	2093.30	1307.00	1.99	1.15
9	325.00	760.90	435.90	2433.30	1507.00	2093.30	1307.00	1.99	1.16
10	309.30	761.89	452.59	2433.30	1507.00	2093.30	1307.00	2.07	1.20
11	320.16	772.30	452.14	2433.30	1507.00	2093.30	1307.00	2.07	1.20
12	341.52	769.39	427.87	2433.30	1507.00	2093.30	1307.00	1.96	1.13
13	331.86	771.93	440.07	2433.30	1507.00	2093.30	1307.00	2.01	1.17
14	328.69	764.38	435.69	2433.30	1507.00	2093.30	1307.00	1.99	1.16
15	318.04	757.49	439.45	2433.30	1507.00	2093.30	1307.00	2.01	1.17
16	318.82	769.54	450.72	2433.30	1507.00	2093.30	1307.00	2.06	1.20
17	311.26	764.06	452.80	2433.30	1507.00	2093.30	1307.00	2.07	1.20
18	314.52	756.07	441.55	2433.30	1507.00	2093.30	1307.00	2.02	1.17
19	337.19	778.85	441.66	2433.30	1507.00	2093.30	1307.00	2.02	1.17
20	326.01	764.66	438.65	2433.30	1507.00	2093.30	1307.00	2.01	1.16
21	331.21	758.40	427.19	2433.30	1507.00	2093.30	1307.00	1.95	1.13
22	328.73	761.24	432.51	2433.30	1507.00	2093.30	1307.00	1.98	1.15
23	344.32	765.18	420.86	2433.30	1507.00	2093.30	1307.00	1.93	1.12
24	328.16	761.66	433.50	2433.30	1507.00	2093.30	1307.00	1.98	1.15
25	345.53	779.64	434.11	2433.30	1507.00	2093.30	1307.00	1.99	1.15
26	336.59	758.64	422.05	2433.30	1507.00	2093.30	1307.00	1.93	1.12
27	333.96	775.82	441.86	2433.30	1507.00	2093.30	1307.00	2.02	1.17
28	334.17	763.93	435.76	2433.30	1507.00	2093.30	1307.00	1.99	1.16

Table 3.2: Weight of stakes, concentration of chromium and copper (before and after impregnation) and initial retention of metals in non-standard pine sapwood stakes

Sample	Weight before impregnation (g)	Weight after impregnation (g)	Uptake (g)	Conc. Cr before impregnation (mg/kg)	Conc. Cu before impregnation (mg/kg)	Conc. Cr after impregnation (mg/kg)	Conc. Cu after impregnation (mg/kg)	Cr retention (kg/m ³)	Cu retention (kg/m ³)
1	290.94	751.07	460.13	2406.60	1478.00	2073.30	1263.00	2.08	1.21
2	292.89	750.35	457.46	2406.60	1478.00	2073.30	1263.00	2.07	1.20
3	310.73	751.31	440.58	2406.60	1478.00	2073.30	1263.00	1.99	1.16
4	286.64	736.33	449.69	2406.60	1478.00	2073.30	1263.00	2.03	1.18
5	283.69	742.33	458.64	2406.60	1478.00	2073.30	1263.00	2.07	1.21
6	297.56	748.02	450.46	2406.60	1478.00	2073.30	1263.00	2.04	1.18
7	269.18	736.16	466.98	2406.60	1478.00	2073.30	1263.00	2.11	1.23
8	282.23	736.80	454.57	2406.60	1478.00	2073.30	1263.00	2.05	1.20
9	290.95	747.90	456.95	2406.60	1478.00	2073.30	1263.00	2.07	1.20
10	298.63	756.97	458.34	2406.60	1478.00	2073.30	1263.00	2.07	1.21
11	293.10	748.06	454.96	2406.60	1478.00	2073.30	1263.00	2.06	1.20
12	320.51	762.65	442.14	2406.60	1478.00	2073.30	1263.00	2.00	1.16
13	307.59	748.08	440.49	2406.60	1478.00	2073.30	1263.00	1.99	1.16
14	290.10	744.75	454.65	2406.60	1478.00	2073.30	1263.00	2.05	1.20
15	284.02	742.00	457.98	2406.60	1478.00	2073.30	1263.00	2.07	1.20
16	297.93	752.22	454.29	2406.60	1478.00	2073.30	1263.00	2.05	1.19
17	280.57	744.27	463.70	2406.60	1478.00	2073.30	1263.00	2.10	1.22
18	305.97	746.83	440.86	2406.60	1478.00	2073.30	1263.00	1.99	1.16
19	295.92	738.42	442.50	2406.60	1478.00	2073.30	1263.00	2.00	1.16
20	273.25	739.11	465.86	2406.60	1478.00	2073.30	1263.00	2.11	1.23
21	309.62	749.02	439.40	2406.60	1478.00	2073.30	1263.00	1.99	1.16
22	312.09	756.82	444.73	2406.60	1478.00	2073.30	1263.00	2.01	1.17
23	281.73	742.46	460.73	2406.60	1478.00	2073.30	1263.00	2.08	1.21
24	267.40	736.96	469.56	2406.60	1478.00	2073.30	1263.00	2.12	1.23
25	305.83	757.15	451.32	2406.60	1478.00	2073.30	1263.00	2.04	1.19
26	333.70	760.32	426.62	2406.60	1478.00	2073.30	1263.00	1.93	1.12
27	286.94	747.58	460.64	2406.60	1478.00	2073.30	1263.00	2.08	1.21
28	289.25	739.96	429.76	2406.60	1478.00	2073.30	1263.00	1.97	1.14

Table 3.3: Weight of stakes, concentration of chromium and copper (before and after impregnation) and initial retention of metals in spruce stakes

Sample	Weight before impregnation (g)	Weight after impregnation (g)	Uptake (g)	Conc. Cr before impregnation (mg/kg)	Conc. Cu before impregnation (mg/kg)	Conc. Cr after impregnation (mg/kg)	Conc. Cu after impregnation (mg/kg)	Cr retention (kg/m ³)	Cu retention (kg/m ³)
1	231.63	541.88	310.25	2360.00	1462.00	2073.30	1308.00	1.35	0.78
2	255.47	555.30	299.83	2360.00	1462.00	2073.30	1308.00	1.31	0.75
3	274.85	478.92	204.07	2360.00	1462.00	2073.30	1308.00	0.89	0.51
4	267.39	556.56	289.17	2360.00	1462.00	2073.30	1308.00	1.26	0.73
5	269.9	473.49	203.80	2360.00	1462.00	2073.30	1308.00	0.89	0.51
6	249.65	587.46	337.81	2360.00	1462.00	2073.30	1308.00	1.47	0.85
7	226.55	568.04	341.49	2360.00	1462.00	2073.30	1308.00	1.49	0.86
8	250.97	552.13	301.16	2360.00	1462.00	2073.30	1308.00	1.31	0.76
9	258.76	483.48	224.72	2360.00	1462.00	2073.30	1308.00	0.98	0.56
10	259.30	622.64	363.34	2360.00	1462.00	2073.30	1308.00	1.59	0.91
11	253.76	529.70	275.94	2360.00	1462.00	2073.30	1308.00	1.20	0.69
12	265.87	463.30	197.43	2360.00	1462.00	2073.30	1308.00	0.86	0.50
13	318.09	591.30	273.21	2360.00	1462.00	2073.30	1308.00	1.19	0.69
14	255.30	680.23	424.93	2360.00	1462.00	2073.30	1308.00	1.86	1.07
15	239.51	517.39	277.88	2360.00	1462.00	2073.30	1308.00	1.21	0.70
16	253.03	536.90	283.87	2360.00	1462.00	2073.30	1308.00	1.24	0.71
17	277.38	563.37	285.99	2360.00	1462.00	2073.30	1308.00	1.25	0.72
18	288.88	494.18	205.30	2360.00	1462.00	2073.30	1308.00	0.90	0.52
19	265.34	507.43	242.09	2360.00	1462.00	2073.30	1308.00	1.06	0.61
20	272.97	472.12	199.15	2360.00	1462.00	2073.30	1308.00	0.87	0.50
21	273.45	598.38	324.93	2360.00	1462.00	2073.30	1308.00	1.42	0.82
22	286.20	592.88	306.68	2360.00	1462.00	2073.30	1308.00	1.34	0.77
23	271.35	465.99	194.64	2360.00	1462.00	2073.30	1308.00	0.85	0.49
24	263.00	485.18	222.18	2360.00	1462.00	2073.30	1308.00	0.97	0.56
25	274.00	512.35	238.35	2360.00	1462.00	2073.30	1308.00	1.04	0.60
26	245.59	568.77	323.18	2360.00	1462.00	2073.30	1308.00	1.41	0.81
27	232.29	493.83	261.54	2360.00	1462.00	2073.30	1308.00	1.14	0.66
28	235.28	512.00	276.72	2360.00	1462.00	2073.30	1308.00	1.21	0.69

Figure 3.1 shows the average retention of metal contents in pine and spruce stakes before field and laboratory tests.

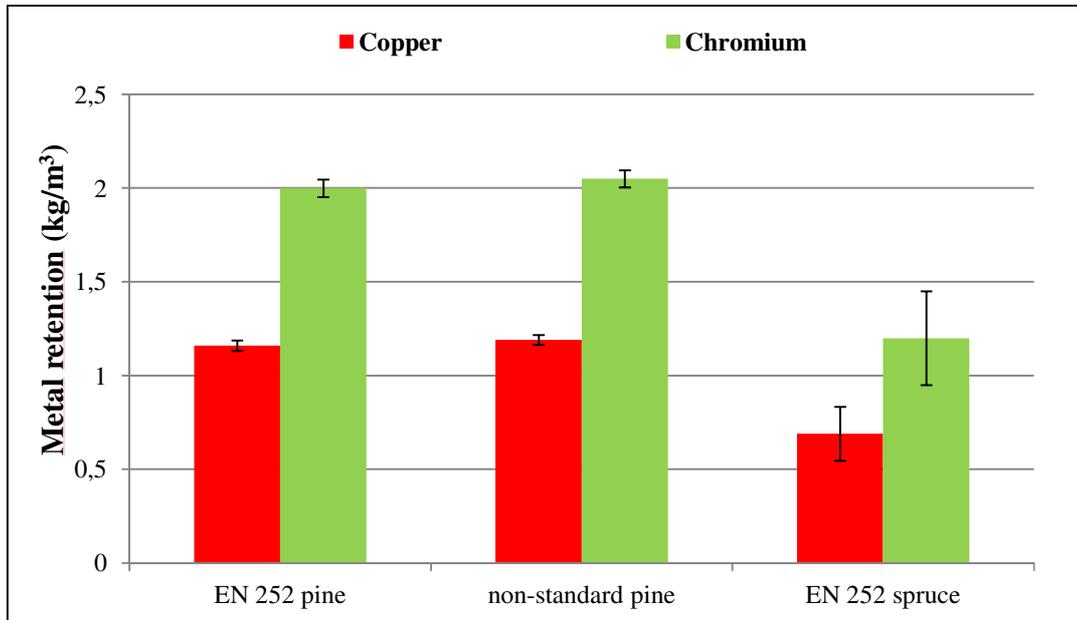


Figure 3.1: Average chromium and copper retention in EN 252 and non-standard pine sapwood as well as spruce treated stakes (n=28). Error bars=standard deviation.

There was a significant difference ($\alpha=0.05$) between retention of chromium and copper in pine and spruce stakes. The metal retention in the pine stakes was higher than that in spruce stakes. The reason for the observed differences can be explained by the anatomical structures of the wood species. It is known (Baines and Saur, 1985) that the sufficient penetration of preservatives in refractory wood species such as *Picea abies* is difficult, whilst the sapwood of *Pinus sylvestris* (as permeable species) has a more easily uptake of preservatives. Visual observation of the cross section showed that penetration of metal components was complete in most pine sapwood stakes, while in spruce stakes the metal components mainly concentrated in the outer layers (Figure 3.2).

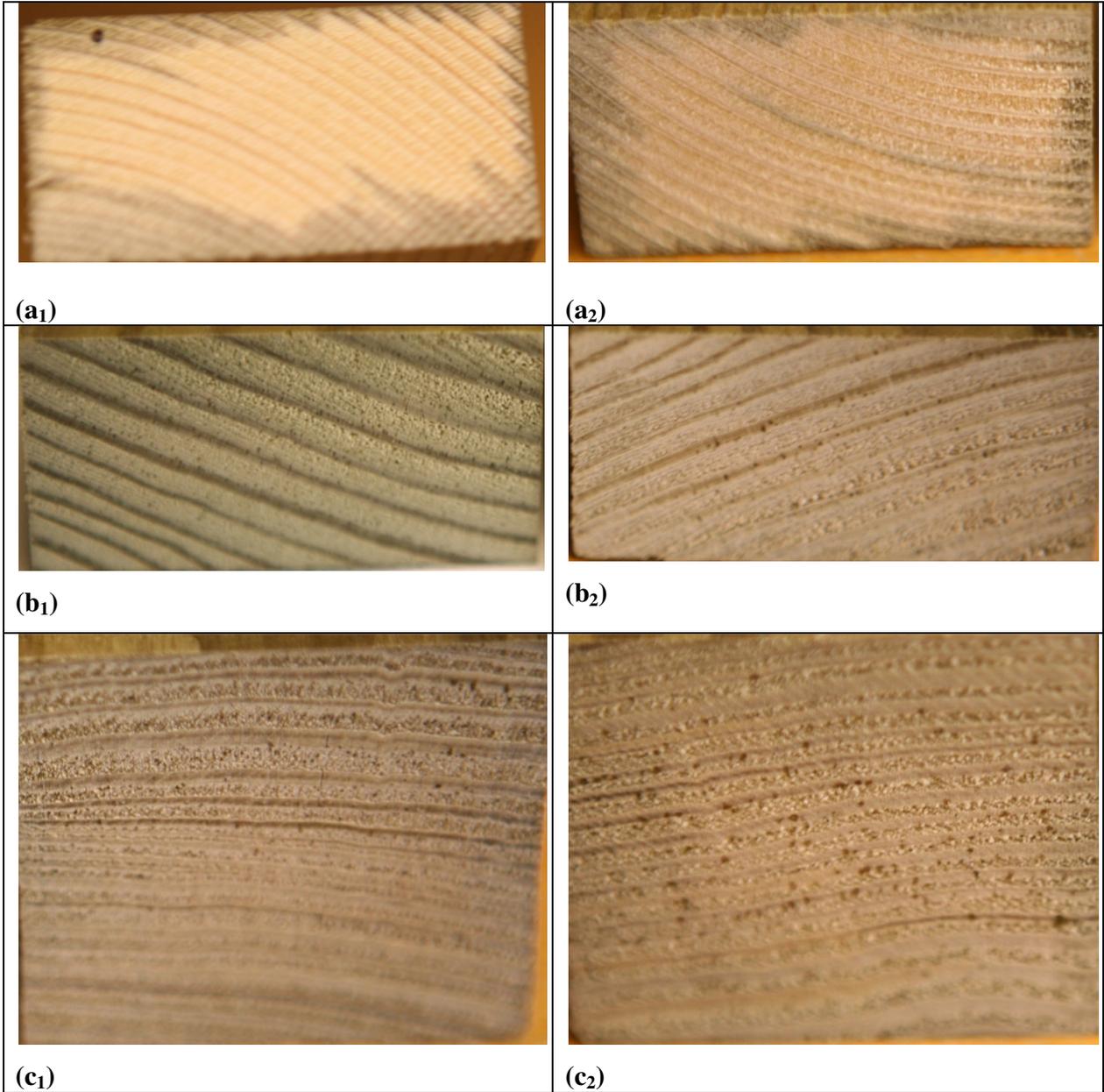


Figure 3.2: Treated cross section of unexposed stakes [EN 252 spruce (a_{1,2}), EN 252 pine sapwood (b_{1,2}), non-standard pine sapwood (c_{1,2})]

3.2 Chromium and copper content in treated stakes in relation to the basis of calculation

Chromium and copper retentions determined by theoretical and analytical values are given in Table 3.4.

Table 3.4: Average chromium and copper content in unexposed treated stakes

Materials	Theoretical content (kg/m ³)		Content based on analytical data (kg/m ³)	
	Chromium	Copper	Chromium	Copper
EN 252 pine	1.86	1.13	1.95 (treatment)	1.13 (treatment)
			1.94 (3 stakes)	1.12 (3 stakes)
Cr-Cu ratio	1.65		1.73	
non-standard pine	1.95	1.19	2.01 (treatment)	1.18 (treatment)
			2.00 (3 stakes)	1.19 (3 stakes)
Cr-Cu ratio	1.64		1.68	
EN 252 spruce	1.13	0.69	1.13 (treatment)	0.65 (treatment)
			1.13(4 stakes)	0.65 (4 stakes)
Cr-Cu ratio	1.64		1.74	

The table shows a strong correlation between treatment and actual content when the retention was calculated based on the analytical data which were achieved from the treating solution. Jüngel et al. (1998) however indicated that the theoretical retention is different from analytical retention.

3.3 Distribution of chromium and copper in unexposed stakes

3.3.1 EN 252 pine sapwood

The relative distribution of chromium and copper in unexposed EN 252 pine stakes is shown in Figure 3.3.

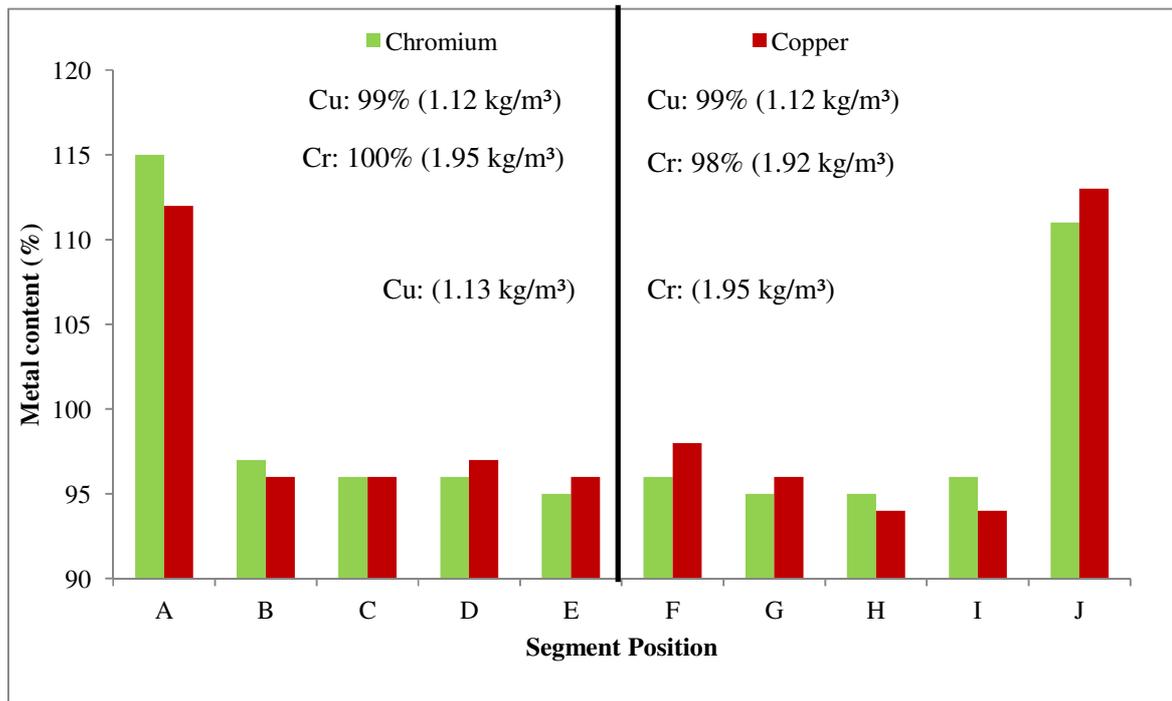


Figure 3.3: Distribution of chromium and copper in unexposed EN 252 pine sapwood stakes

The chromium and copper content in the eight middle segments (segments B to I) ranged from 95 to 97% and averaged to almost 95%. This relatively uniform distribution of metals between stake segments could be due to the applied vacuum pressure impregnation. In the end segments (segments A and J) the chromium and copper uptake was the highest compared to the interior segments as also indicated by Evans and Edlund. (1993). The relatively high metal retention at both end grain of the treated stakes during impregnation is due to the fact that longitudinal flow is much greater than radial and tangential (Hudson and Shelton, 1969). It can be concluded that the recovery rate for chromium with 100% and for copper with 99% was high. The single data are shown in Appendix 2.

3.3.2 Non-standard pine sapwood

The results of the relative distribution of chromium and copper in unexposed non-standard format pine stakes are summarized in Figure 3.4.

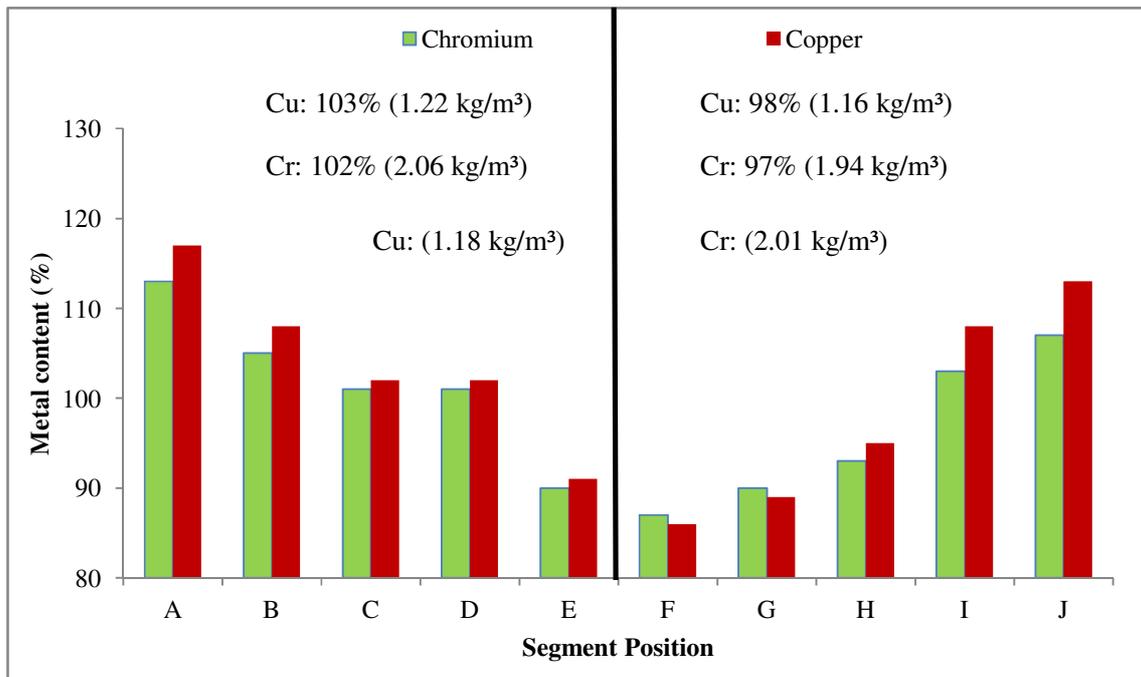


Figure 3.4: Distribution of chromium and copper in unexposed non-standard pine sapwood stakes

In contrast to the EN 252 pine stakes, the distribution of chromium and copper in the non-standard stakes format was not so uniform. The reason could be due to a worse tangential-radial-ratio, which was 1:1 in non-standard and 2:1 in EN252 stakes. However, it should be noted that the greatest chromium and copper content was found in the end grain segments whereby the recovery rate corresponded to 100%.

3.3.3 EN 252 spruce

Figure 3.5 shows the relative distribution of chromium and copper in unexposed EN 252 spruce stakes.

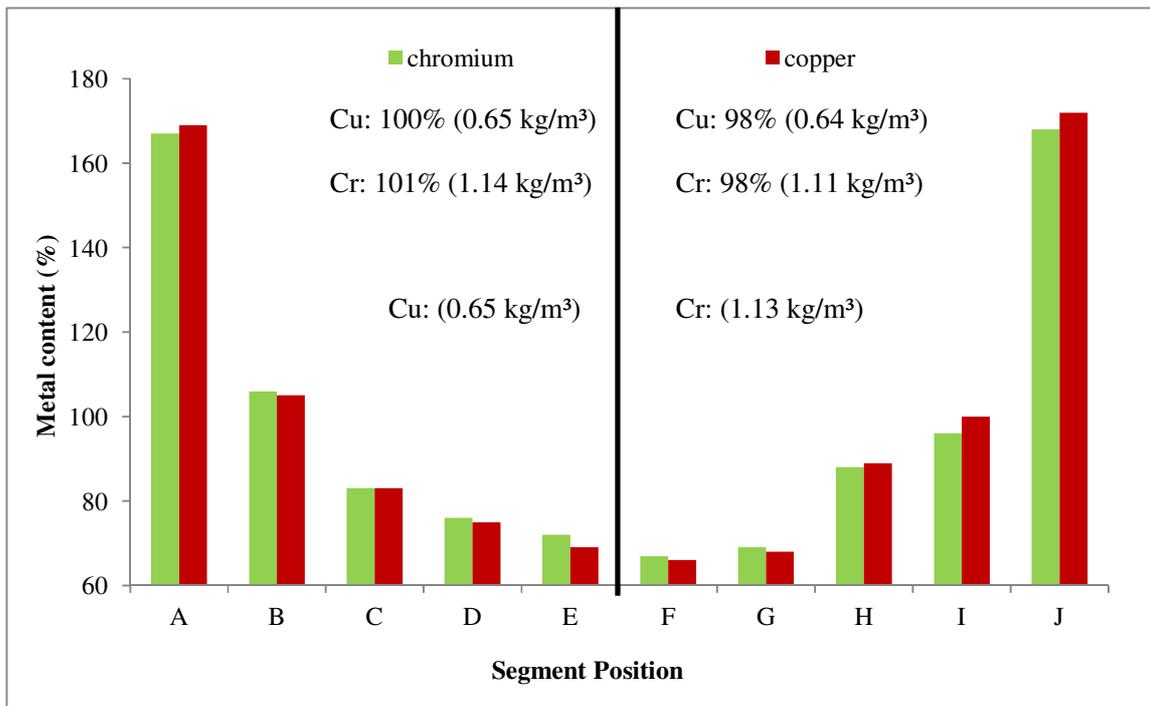


Figure 3.5: Distribution of chromium and copper in unexposed EN 252 spruce stakes

The distribution of chromium and copper showed a considerable variation with a high uptake in the end grain segments (A and J) in comparison with the middle segments (B up to I). For example, whereas more than 160% of chromium and copper was found in the end grain segments less than 80% were observed in the middle segments D, E, F and G. Thus, the average percentage of chromium and copper in the end grains was two times higher than of the eight middle segments. In comparison with standard and non-standard pine stakes, there is a steeper gradient through the length of the spruce stakes. This may be due to the anatomical structure of spruce wood. The open or closed pits in the walls of tracheids play an important role in permeability of softwood species (Siau, 1984, 1995). The low treatability of spruce wood is due to the fact that the pits in the tracheids usually become aspirated during heartwood formation (Liese and Bauch, 1967) or during the initial drying phase before treatment (Banks, 1970).

It can be inferred that the recovery rate for both chromium and copper is 99%. The single data are shown in Appendix 4.

3.4 Laboratory leaching tests

Laboratory leaching tests were conducted according to CEN/TS 15119-1 (discontinuous procedure) and CEN/TS 15119-2 (continuous procedure).

3.4.1 Analyses of leachate for chromium and copper

Tables 3.5 show the amounts of chromium and copper released from the treated stakes in the discontinuous procedure according to CEN/TS 15119-1 for pine and spruce specimens. The amount of metals leached after the test, expressed as a percentage of the initial amount retained in wood, also are given in Table 3.6.

Table 3.5: Average amount of chromium and copper leached from CC-treated samples according to CEN/TS 1511-1

Days of leaching	Chromium (mg)	Copper (mg)
EN 252 pine		
1	0.004	0.021
3	0.004	0.021
5	0.004	0.020
8	0.003	0.022
10	0.003	0.022
12	0.003	0.024
15	0.002	0.028
17	0.002	0.026
19	0.002	0.027
non-standard pine		
1	0.008	0.023
3	0.007	0.023
5	0.006	0.017
8	0.005	0.022
10	0.004	0.021
12	0.004	0.020
15	0.006	0.027
17	0.003	0.029
19	0.004	0.030
EN 252 spruce		
1	0.005	0.010
3	0.005	0.012
5	0.005	0.013
8	0.004	0.013
10	0.004	0.013
12	0.004	0.013
15	0.002	0.016
17	0.002	0.018
19	0.002	0.023

Table 3.6: Total metal content leached from wood treated with chromium and copper after discontinuous water immersion

	EN 252 pine		non-standard pine		EN 252 spruce	
	Chromium	Copper	Chromium	Copper	Chromium	Copper
Initial amount (mg)	1225.00	712.50	1281.25	743.75	781.25	450.00
Total cumulative leached (mg)	0.03	0.21	0.05	0.21	0.03	0.13
% Leaching	0.002	0.029	0.004	0.028	0.004	0.03

The results show that after three weeks of leaching (27 minute total submersion), the amount of leached metals was rather low. This could be due to the short contact time with water. Since water is a dominant factor for leaching of water-soluble preservatives, it seems that a one-minute contact with water was too short for penetration and for a concentration gradient of metals from the inner to the outer layers. As a result, only slight quantities of metals that deposited on the wood surface were probably leached during the leaching process.

The amount of chromium and copper leached from the treated stakes in the continuous approach for pine and spruce samples are given in Table 3.7. The amount of metals leached after the test, expressed as a percentage of the initial amount retained in wood, is also shown in Table 3.8.

Table 3.7: Average amount of chromium and copper leached from CC-treated samples according to CEN/TS 1511-2

Leaching cycles	Chromium (mg)	Copper (mg)
EN 252 pine		
6 hour	0.21	0.56
1day	0.25	1.55
2d	0.27	2.94
3d	0.28	3.82
4d	0.32	5.46
5d	0.33	5.38
6d	0.38	6.03
non-standard pine		
6 h	0.16	0.51
1d	0.18	1.26
2d	0.20	2.40
3d	0.29	3.35
4d	0.31	4.31
5d	0.39	4.57
6d	0.43	5.28
EN 252 spruce		
6 h	0.10	0.33
1d	0.13	0.90
2d	0.12	1.53
3d	0.17	2.16
4d	0.25	2.38
5d	0.30	2.34
6d	0.30	2.44

The cumulative amount of leached metals from all specimens showed that copper leaching was higher than that of chromium (Table 3.8). The resistance of chromium to leaching should be due to fixation properties of chromium in wood. It is known that during fixation reactions with wood, chromium reacts strongly with lignin (Eadi and Wallace, 1962) while copper binds with cellulose materials (Flomina, 1967; Dahlgren et al., 1972). The low amount of chromium depletion was observed in numerous laboratory and field studies (Archer et al., 1994; Evans et al., 1994; Lebow, 1996; Cooper and Ung, 1997; Melcher and Wegen., 2000; Garcia-Valcarcel et al., 2004).

The cumulative copper losses in the leachate from the EN 252 pine were 3.61% and were high in comparison to the leachate from the non-standard and EN 252 spruce specimens (2.91% and 1.55%, respectively). The higher copper leaching in EN 252 pine samples compared to non-standard was likely related to their greater surface area in contact with water (see Table 2.2). The cumulative chromium losses in the leachate from all specimens were below 1% (Table 3.8).

Table 3.8: Total metal leached from wood treated with chromium and copper after continuous water immersion

	EN 252 pine		non-standard pine		EN 252 spruce	
	Chromium	Copper	Chromium	Copper	Chromium	Copper
Initial amount (mg)	1225.00	712.50	1281.25	743.75	781.25	450.00
Total cumulative leaching amount (mg)	2.05	25.74	1.96	21.68	1.36	2.68
% Leaching	0.17	3.61	0.15	2.91	0.17	1.55

Moreover, the determination of chromium and copper mass in the leachate and the mass balance of the two metals were checked by comparing the amount of metals detected in the leachate and the amount of remaining after laboratory leaching. The recovery rate of the two elements ranged from 95 to 99% for continuous and discontinuous approaches (Table 3.9).

Table 3.9: Recovery rate of chromium and copper in CC-treated wood after laboratory leaching tests

	Water immersion type	Initial amount (mg)	Final amount (mg)	Recovery rate (%)
EN 252 pine				
Chromium	discontinuous	1225.00	1200.00	98
	continuous		1187.50	97
Copper	discontinuous	712.50	693.75	97
	continuous		675.00	95
non-standard pine				
Chromium	discontinuous	1281.25	1231.25	96
	continuous		1231.25	96
Copper	discontinuous	743.75	731.25	98
	continuous		712.50	96
EN 252 spruce				
Chromium	discontinuous	718.25	775.00	99
	continuous		768.75	98
Copper	discontinuous	450.00	443.75	99
	continuous		437.50	97

When the mass balance was taken into account, for example in the EN 252 pine samples, it was found that less than 1% and almost 4% copper leached from the samples in the discontinuous and continuous tests. Chemical mass balance metals of the wood specimens at the end of leaching period revealed 97 and 95% copper remaining in the wood in the discontinuous and continuous tests, respectively, illustrating the accurate results of chromium and copper determined by chemical analysis. However, it appears there are some deviations between metal remaining in the wood and metals in the leachate (mass balance) especially for chromium. This variation could be

associated with the error of this procedure since the individual analytical data of the stakes showed an error of about $\pm 5\%$ for pine stakes and $\pm 3\%$ for spruce stakes (Appendices 2, 3 and 4).

3.4.2 Analysis of wood specimens for chromium and copper content after laboratory leaching tests

At the end of both leaching tests (continuous and discontinuous) specimens was analyzed according to DIN 52161-7 for residual content of chromium and copper. For all cases, remaining metal was expressed as a percentage of initial retention.

3.4.2.1 EN 252 pine

The distribution pattern of chromium and copper after laboratory leaching tests is shown in Figures 3.6 and 3.7. In all cases, segments A to E refers to CEN/TS 15119-1 and segments F to J refer to CEN/TS 15119-2. The graphs also contain the initial distribution of metal components in the unexposed stakes.

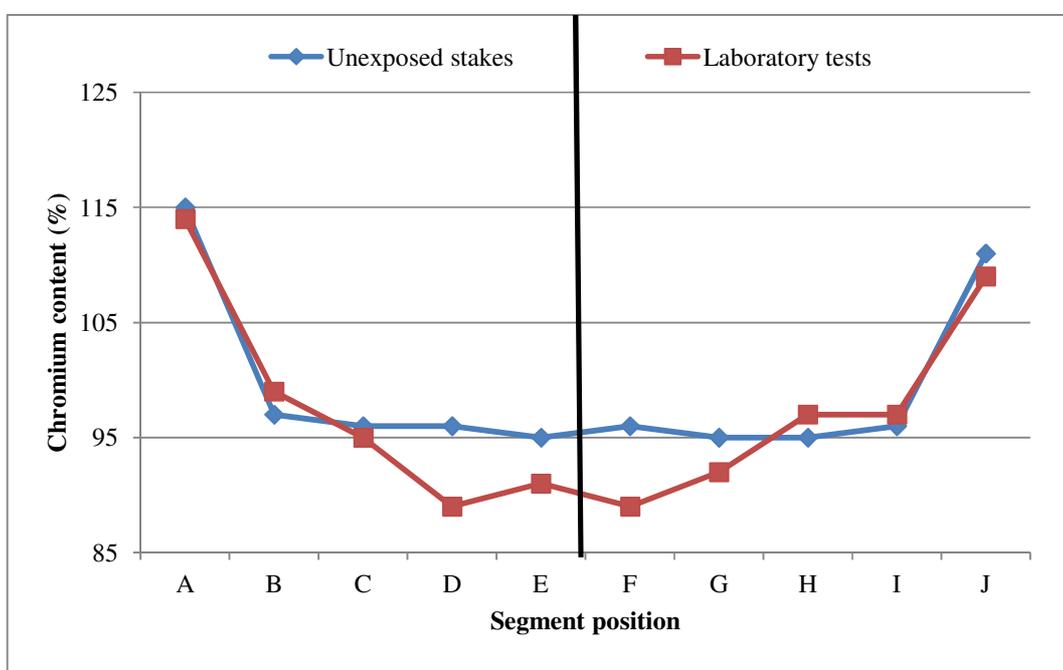


Figure 3.6: Distribution of chromium in EN 252 pine stakes before and after laboratory experiments

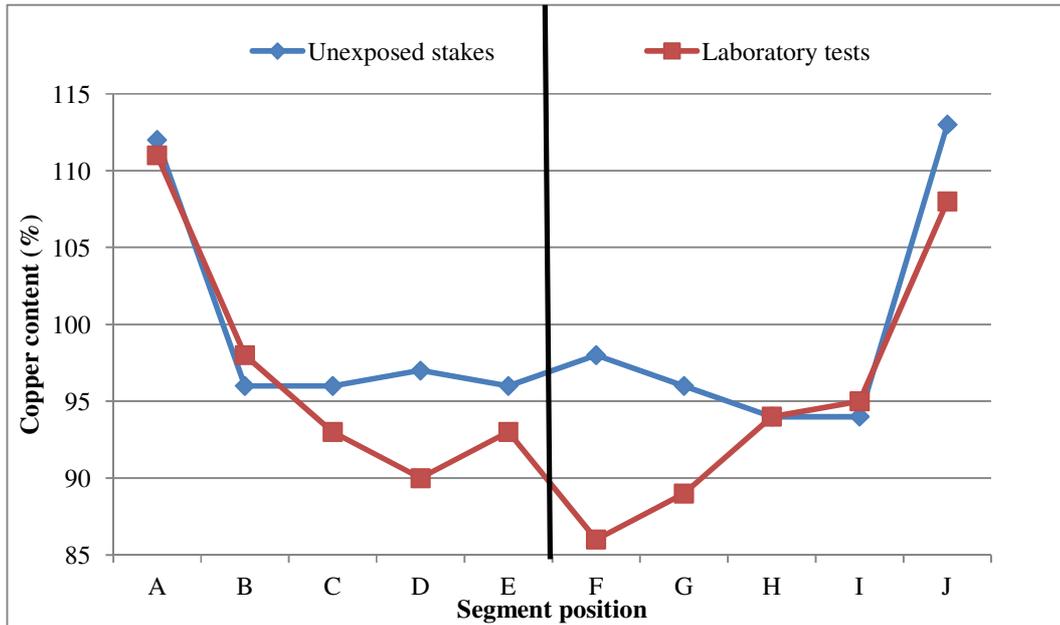


Figure 3.7: Distribution of copper in EN 252 pine stakes before and after laboratory experiments

It is evident from Figure 3.7 that copper distribution was affected by continuous water immersion with some depletion of copper whereas the distribution pattern in the discontinuous water immersion less substantially changed. It appears that the short duration of each water immersion event may not sufficiently wet specimens and leach the chemical preservatives as demonstrated by considerable low metal concentrations in the leachate (see section 3.4.1). As a result, no significant change in the distribution pattern in discontinuous immersion was observed. It should be noted that in some segments (e.g. segments B, H and I) metal concentration was slightly higher than in the unleached ones. These deviations should be related to the variations between the samples and not to the metal migration/redistribution. However, the consideration of the copper concentration in the segments F and G reveals a significant difference as compared to the unleached ones, illustrating copper leaching from these segments into the water.

It is interesting to note the differences in mass balance of the metals between specimens subjected to the continuous and discontinuous water immersion. In unexposed stakes the ratio of chromium to copper was 1.73 (Table 3.4). After laboratory test the ratio of Cr to Cu was calculated at 1.76 in the continuous immersion, suggesting a greater loss of copper than chromium.

At continuous immersion, residual copper, as a percentage of initial retention, ranged from 86 to 108% and averaged 95%; in the discontinuous immersion residual copper ranged from 90-111% and averaged 98%. This indicates that almost two percent more copper remained at discontinuous immersion as compared to the continuous one.

3.4.2.2 Non-standard pine

The distribution pattern of chromium and copper in non-standard pine samples before and after laboratory leaching tests is presented in Figures 3.8 and 3.9.

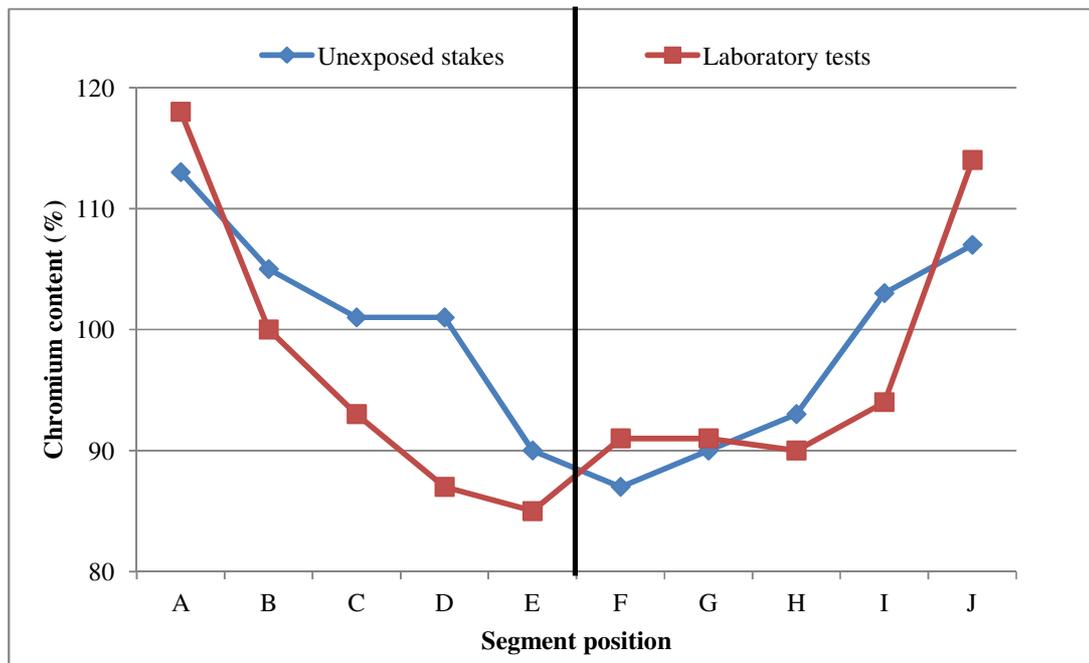


Figure 3.8: Distribution of chromium in non-standard pine sapwood stakes before and after laboratory experiments

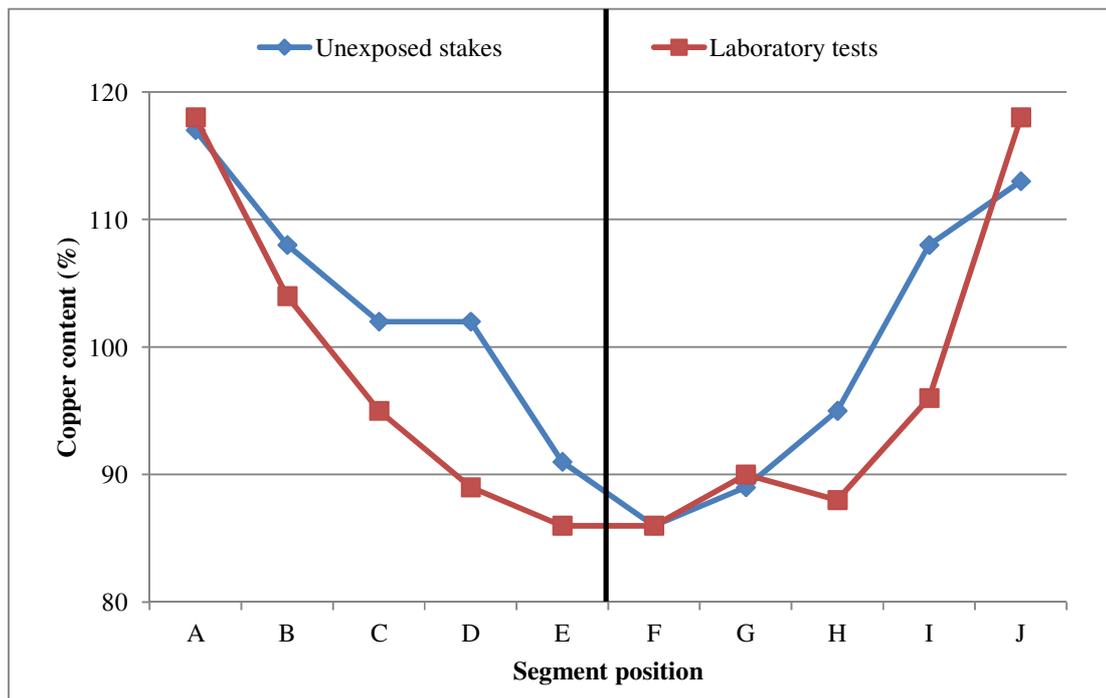


Figure 3.9: Distribution of copper in non-standard pine sapwood stakes before and after laboratory experiments

The metal distribution curves in both continuous and discontinuous experiments are similar to the unleached ones, although metal concentration in some segments is relatively higher than in unexposed ones which were related to variations between samples and not the metal migration. However, metal leaching was observed in the segments C, D, H for chromium and in C, D, H and I for copper significant differences in metal concentration between unexposed and exposed segments were found.

In unexposed stakes the chromium to copper ratio was 1.68 (Table 3.4). After laboratory test the ratio of Cr to Cu was calculated 1.73 in the continuous immersion, suggesting that a higher loss of copper than of chromium.

Residual copper, as a percentage of initial retention from 86 to 118% and averaged 96% were obtained in accordance with the continuous water immersion, in the discontinuous immersion residual copper ranged from 86-118% and averaged 98%. Thus higher copper leaching occurred in the continuous test as compared to the discontinuous test.

3.4.2.3 EN 252 spruce

Figures 3.10 and 3.11 show the distribution pattern of chromium and copper in EN 252 spruce stakes prior and after laboratory leaching tests.

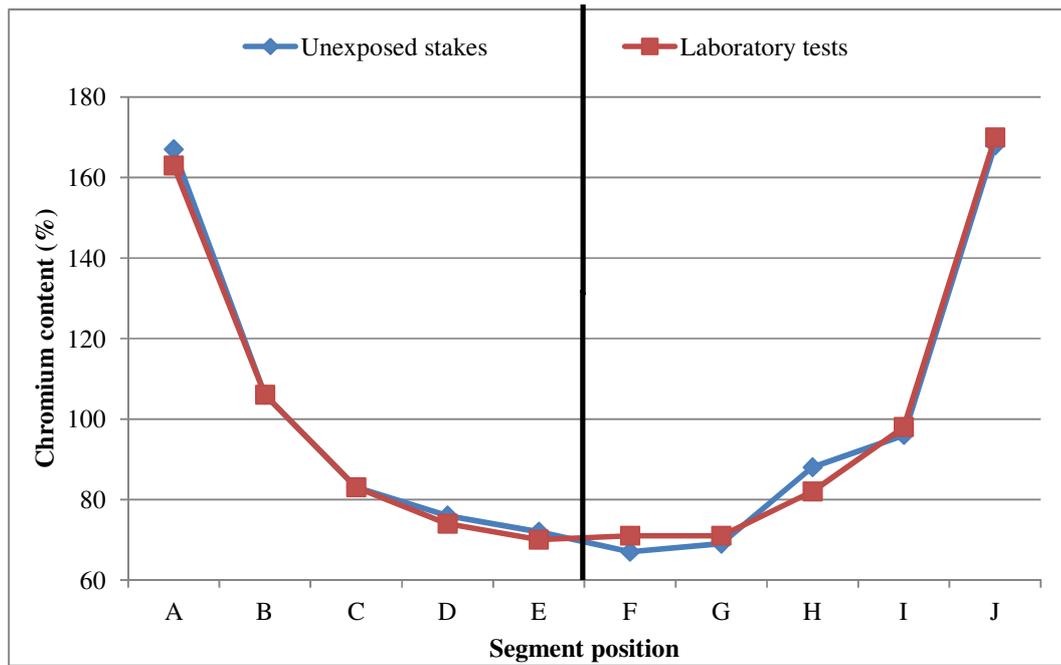


Figure 3.10: Distribution of chromium in EN 252 spruce stakes before and after laboratory experiments

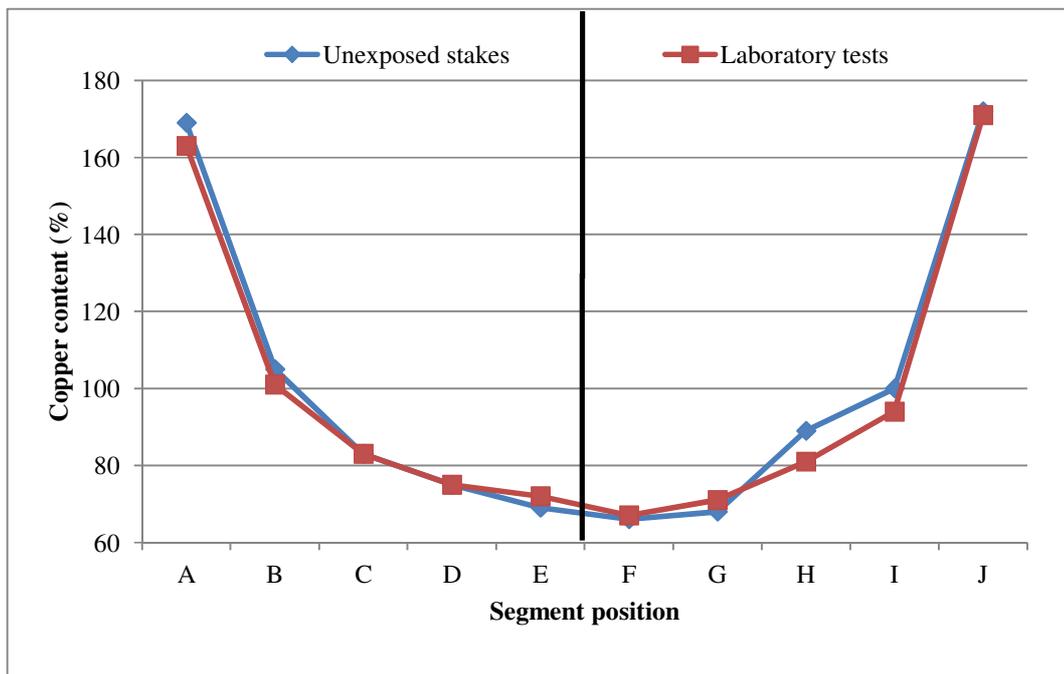


Figure 3.11: Distribution of copper in EN 252 spruce stakes before and after laboratory experiments

The distribution pattern of chromium and copper are very similar before and after discontinuous water immersion. This could be a result of a combination of resistance of spruce wood to water penetration and to the short contact interval of one minute per immersion with water and the establishment of a concentration gradient of metals from the inner to the outer treated layers. It shall be also noted that there were some differences in metal content of unleached and leached stake segments, suggesting initial variations in metal content among the segment stakes rather than the effects of leaching. Nevertheless, a decrease in the copper concentration in continuous water immersion was observed whereby copper loss was higher than chromium loss.

The chromium to copper ratio in the unexposed spruce was 1.74 while after laboratory test the ratio was 1.76 in the continuous immersion.

Results indicated that at the continuous water immersion, residual copper ranged from 67 to 171% and averaged 97%; in the discontinuous immersion residual copper ranged from 72 to 163% and averaged 99%. This indicates higher copper depletion in the continuous test in comparison with the discontinuous test as confirmed by the greater amount of copper in the leachate produced in the continuous test.

3.5 Field test exposure

3.5.1 Moisture content

The results of the moisture content of EN 252 pine, non-standard format pine and EN 252 spruce stakes during outdoor exposure are shown in Figures 3.12, 3.13 and 3.14. There were significant differences ($\alpha=0.05$) over time in the percent of moisture content between above and below ground sections. This was expected, because below-ground sections are continually exposed to contact with soil and moisture.

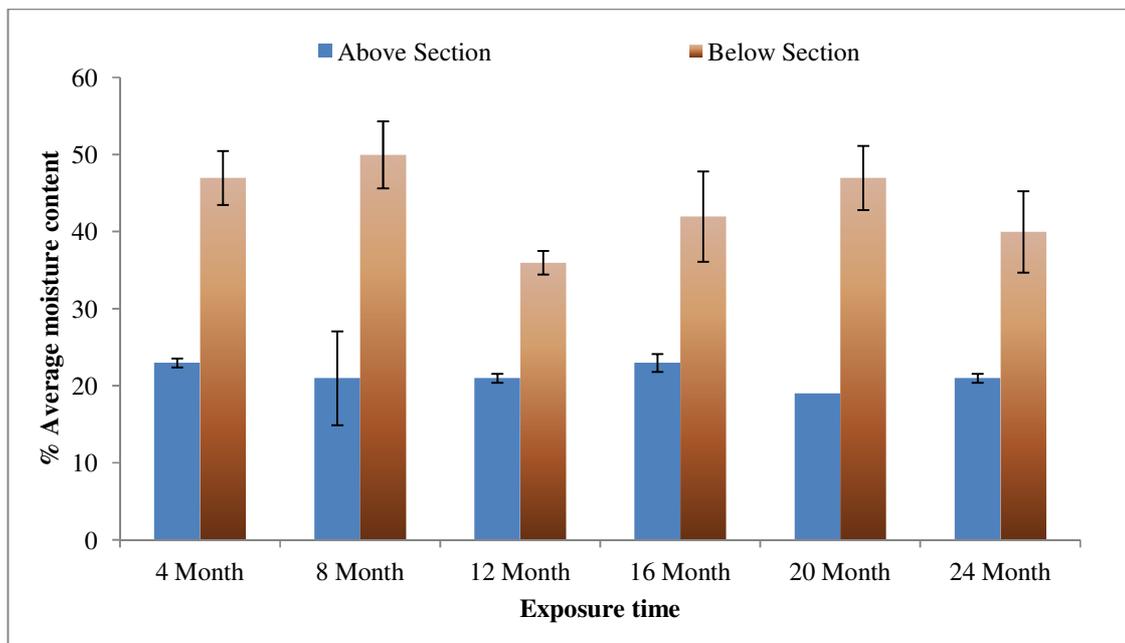


Figure 3.12: Average moisture content in EN 252 pine sapwood stakes during outdoor exposure. Error bars=standard deviation.

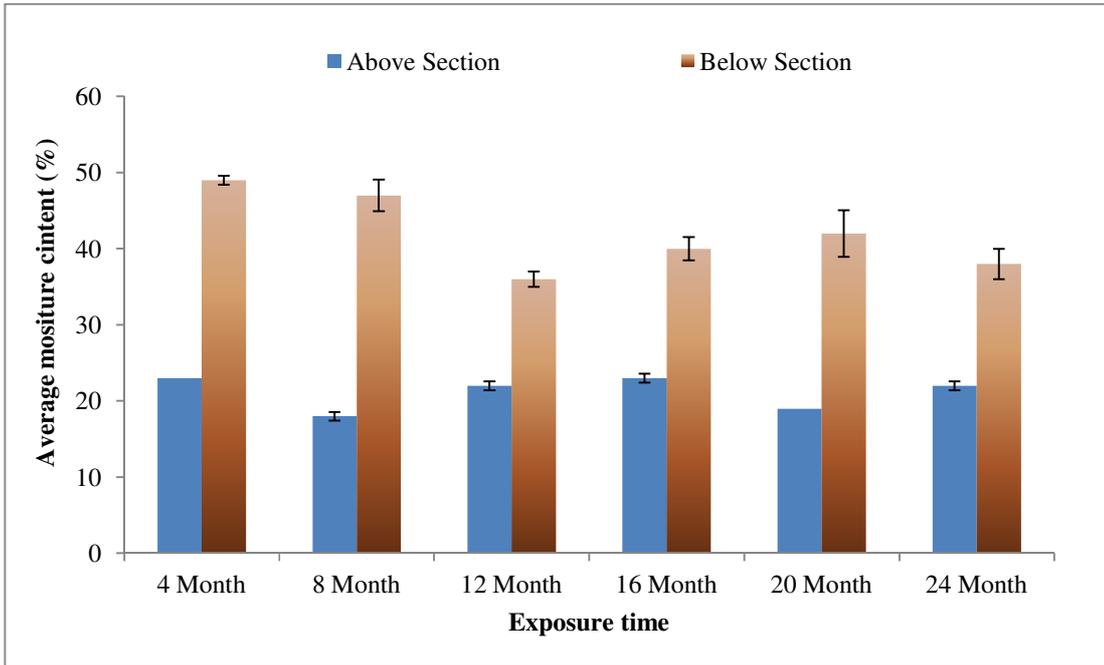


Figure 3.13: Average moisture content in non-standard pine sapwood stakes during outdoor exposure. Error bars=standard deviation.

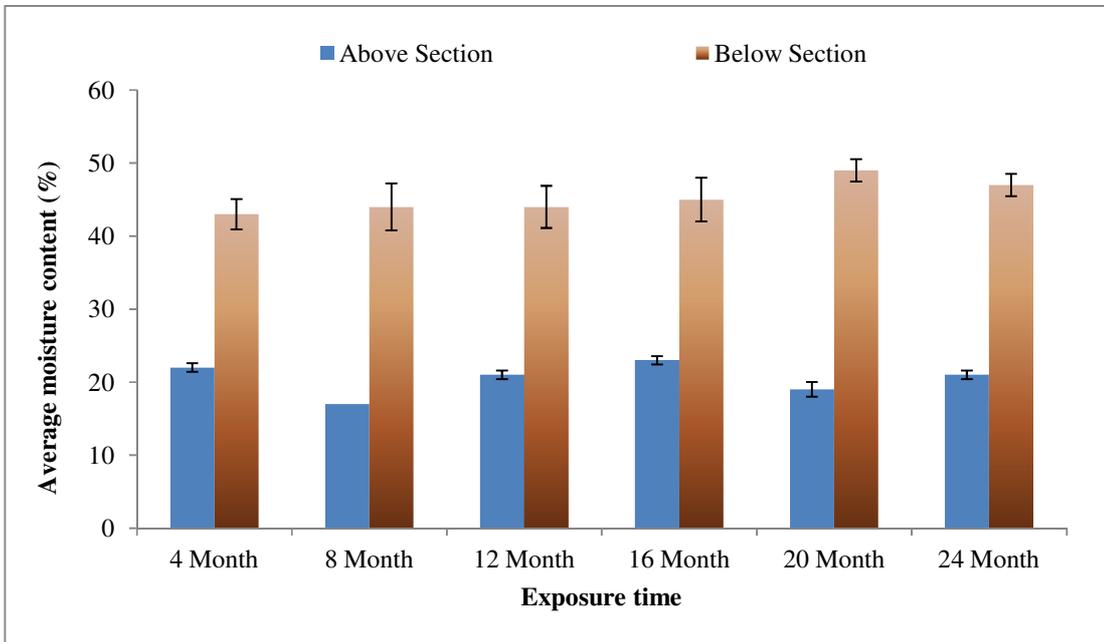


Figure 3.14: Average moisture content in EN 252 spruce stakes during outdoor exposure. Error bars=standard deviation.

3.5.2 Distribution of chromium and copper in wood stakes during natural exposure

The remaining chromium and copper contents which were analyzed by digestion of three replicate stakes in different intervals were expressed as percentage of the initial retention.

3.5.2.1 EN 252 pine sapwood

Figures 3.15 and 3.16 show the results of the distribution of chromium and copper before and after 4 months, Figures 3.17 and 3.18 after 8 months and Figures 3.19 and 3.20 after 12 months of exposure. These graphs also contain the initial distribution of metal components in the unexposed stakes.

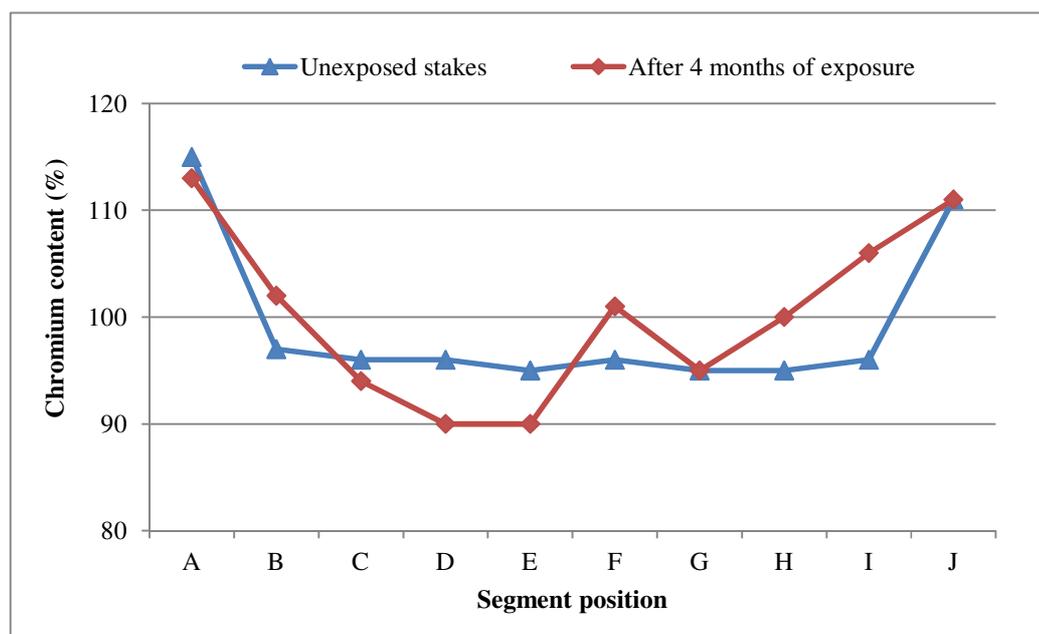


Figure 3.15: Distribution of chromium in EN 252 stakes before and after 4 months of exposure

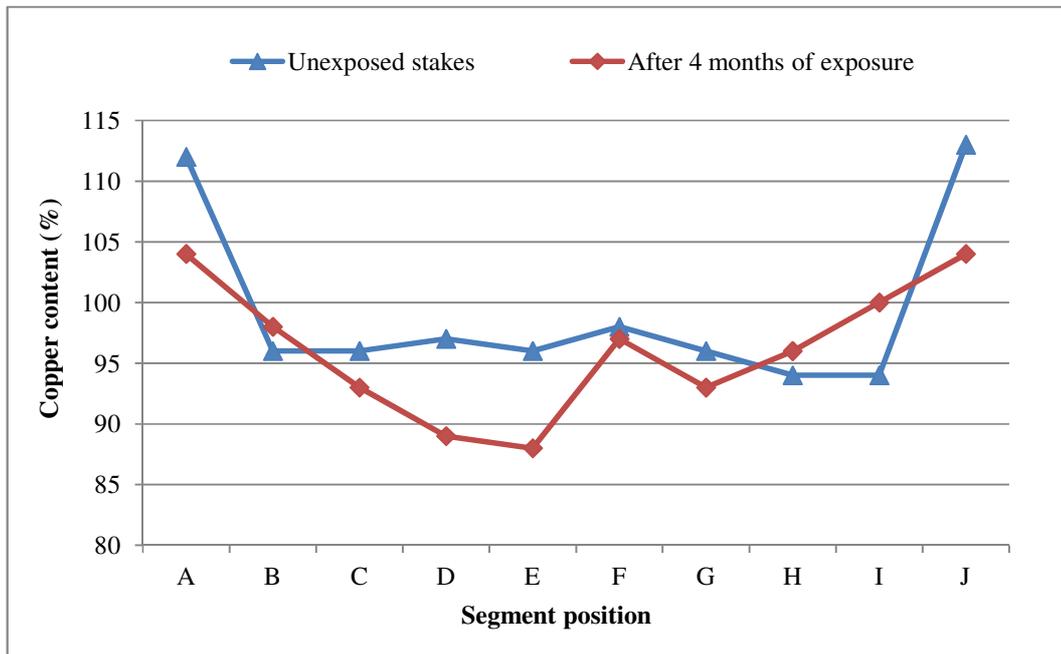


Figure 3.16: Distribution of copper in EN 252 stakes before and after 4 months of exposure

Although unexposed stakes had a fairly uniform copper distribution in the middle segments (B to D), after 4 months of field exposure, the copper distribution was not uniform (Figure 3.16). This non-uniform distribution after exposure could be explained by the migration and loss of copper within the stakes as discussed below. Copper content decreased from segment A to E, increased slightly from E to F, decreased again and then increased for the remaining length of the stake segments. The distribution of chromium was similar to the distribution of copper (Figure 3.15).

It is obvious that the amount of chromium and copper in some segments (e.g. B, H, F and I for chromium and B, H and I for copper) was slightly higher than in the unexposed ones. The higher content in these segments after four months exposure could be due to migration of deposited chromium and copper on the surface of wood and movement from the upper to the lower segments. Generally, redistribution of chemicals in wood usually refers to changes in chemical content of treated wood. It has been demonstrated that preservative components leach from treated wood during outdoor exposure (Lebow, 1996; Hingston et al., 2001). It is likely that a fraction of the metal compounds migrate/redistribute throughout the treated wood during exterior application due to water flow from sample top to bottom and its penetration into the inside of the stake through formation of checks and cracks. Besides water penetration, metal migration/redistribution within treated wood may be also influenced by sample size, exposure

time, wood density (sapwood and heartwood), pit aspiration, preservative retention and weathering situation.

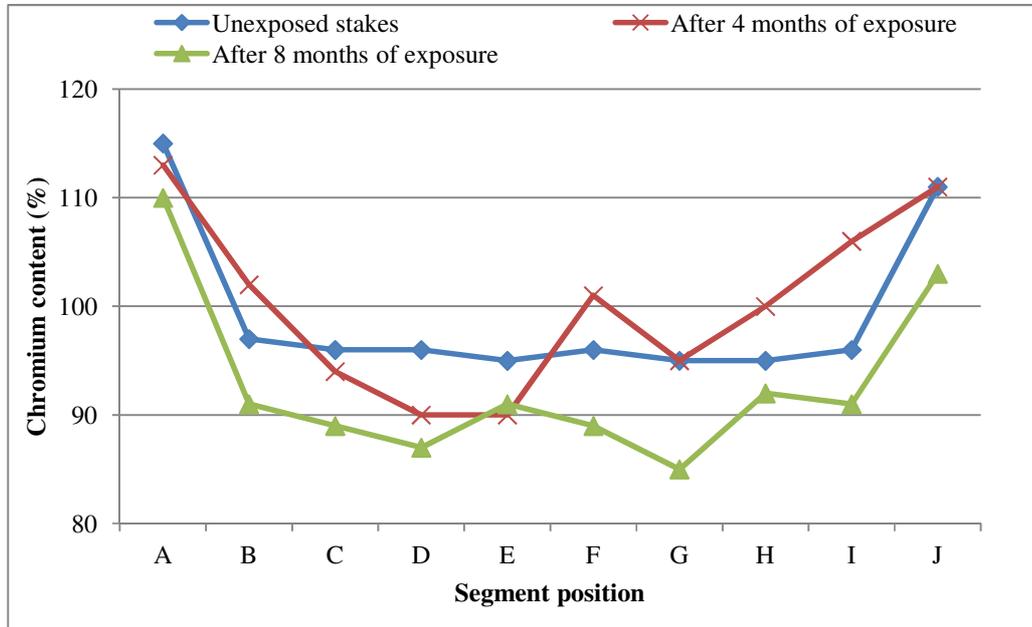


Figure 3.17: Distribution of chromium in EN 252 stakes before and after 4 and 8 months of exposure

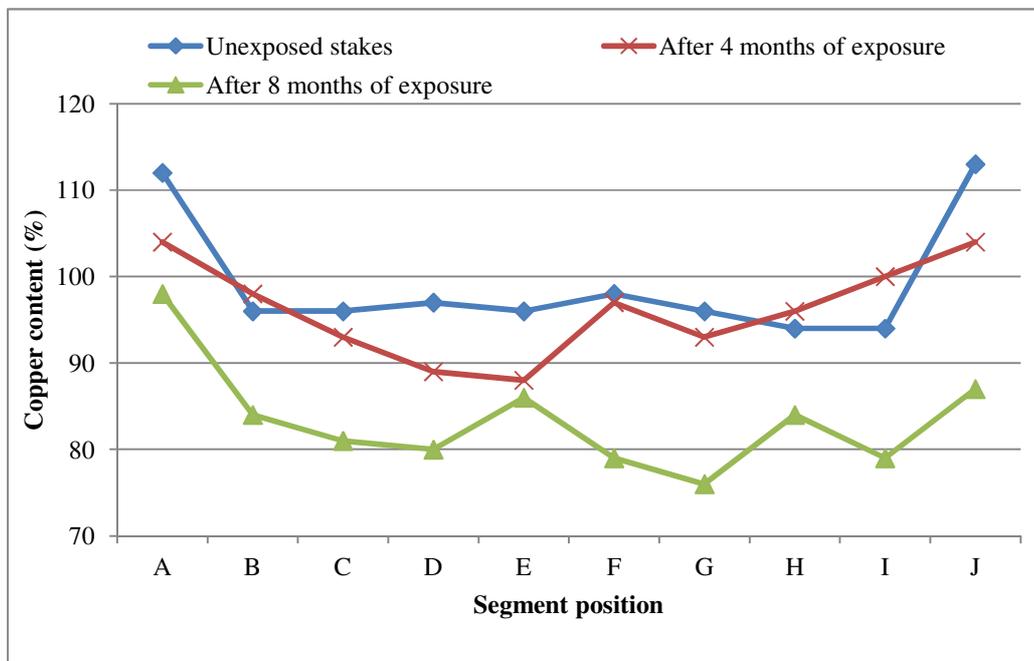


Figure 3.18: Distribution of copper in EN 252 stakes before and after 4 and 8 months of exposure

Figure 3.18 shows that after 8 months exposure the amount of copper in the treated stakes was decreased significantly compared to unexposed stakes. It appears that a significant amount of unfixed or poorly fixed copper that previously migrated at 8-months exposure were released from the wood surface, particularly in the below ground sections. It has been indicated that CCA-treated components are released through leaching and migration of mobile compounds in the ground through diffusion (Arsenault, 1975). Change in the chromium content was also observed in the segments as compared to unexposed segments although this was not statistically different (Figure 3.17). This can be attributed to better fixation or lower leaching of chromium.

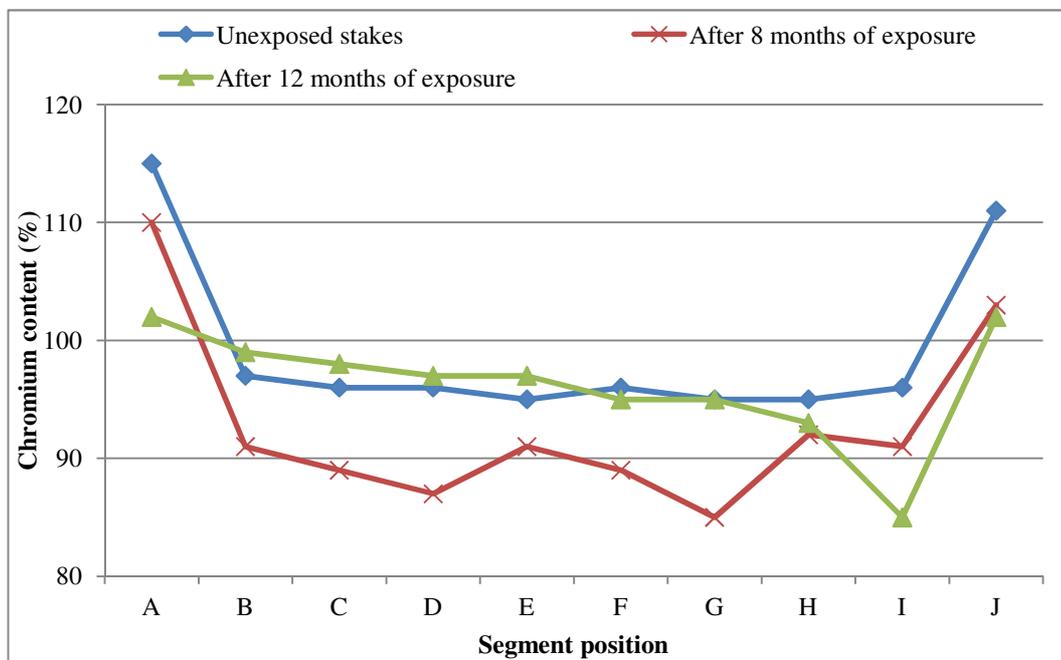


Figure 3.19: Distribution of chromium in EN 252 stakes before and after 8 and 12 months of exposure

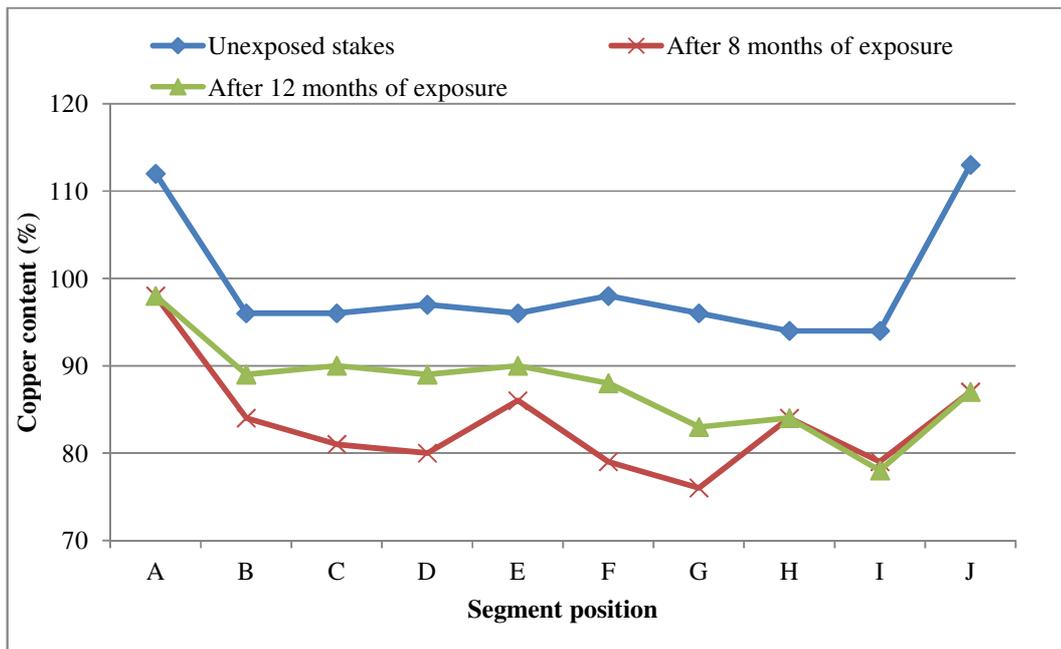


Figure 3.20: Distribution of copper in EN 252 stakes before and after 8 and 12 months of exposure

Once the unfixed metals were removed from the surface of wood, a concentration gradient generated between the surface (lower concentration) and the inner layers (higher concentration) and metal components were transported through diffusion to the wood surface. When the water flow starts again, the diffused metals can be migrated from upper sections to the lower sections. The phenomenon of metal diffusion and migration becomes obvious in the metal content at the 12-month sampling. Figures 3.19 and 3.20 show that the metal content from segment B to H is greater than of the 8-month exposure. This increase of the metal content could be related to metal diffusion from inner to the outer layers.

The highest change in metal content in above ground segments was observed at segment A as compared to unexposed segments, with about 11% decrease in chromium and about 13% decrease in copper. This may be related to the formation of cracks on the top surface and migration of metals from the upper segments to the lower parts. This was proven by increased metal content in segments B to H. The highest depletion of metals was observed in the segments I and J at the below portion section in comparison with unexposed segments.

The residual chromium from 85 to 102% of initial retention at the below ground and from 97 to 102% in the above ground section were obtained. Also, at the below ground section, residual copper was from 78 to 88% and averaged 84%; in the above ground section, residual copper was between 89 to 98% and averaged 92% one year after exposure. This shows that nearly 10% more copper remained at the above ground sections compared to below ground portions.

During one year exposure, it appears that the change in the chromium and copper concentration can be characterized by removal of surface deposits on treated wood and the redistribution of metals from the inner layers to surface layers by diffusion.

Figures 3.21 to 3.26 show the chromium and copper changes during the second year of exposure at 16, 20 and 24 months in comparison with the initial distribution of metal components in unexposed stakes as well as exposed stakes.

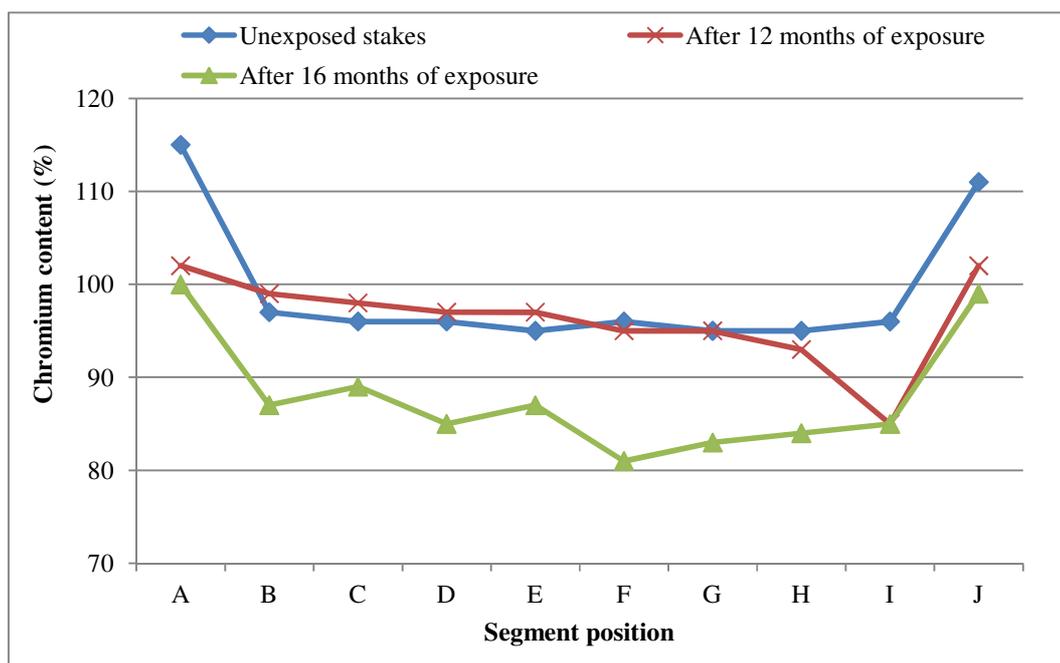


Figure 3.21: Distribution of chromium in EN 252 stakes before and after 12 and 16 months of exposure

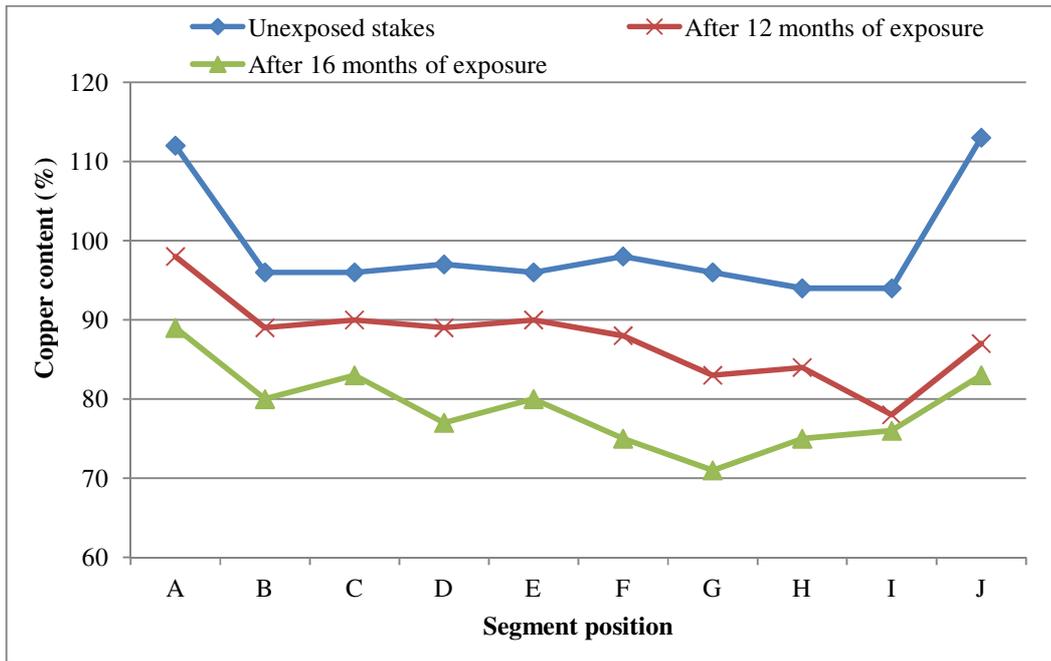


Figure 3.22: Distribution of copper in EN 252 stakes before and after 12 and 16 months of exposure

The chromium concentration in segments B to H at 12 months sampling was greater than at the 8 months sampling. A complete reversal of the chromium behavior can be seen in these segments from 12 months through to 16 months. At these sampling times, the chromium concentration is lower than at the 12 months sampling suggesting that chromium was leached or displaced from the end grain segment stakes. The behavior of copper shows the same trend during the exposure time. Statistical analysis illustrated a significant difference in the copper concentration in all segments in comparison with the unexposed ones confirming the depletion of copper from these sections (Figures 3.21 and 3.22).

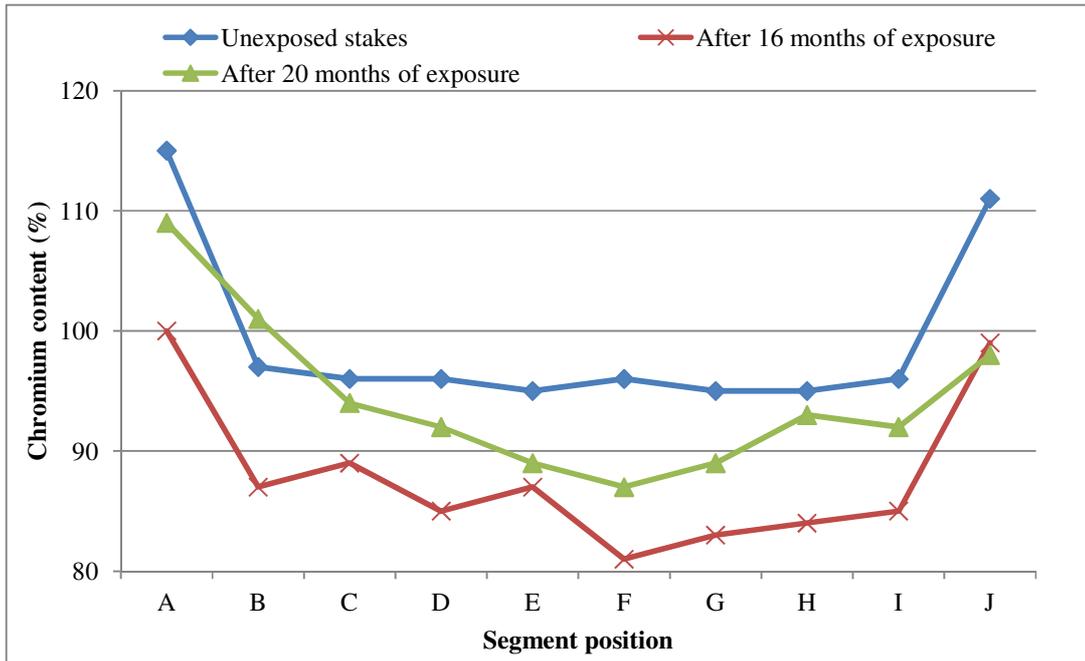


Figure 3.23: Distribution of chromium in EN 252 stakes before and after 16 and 20 months of exposure

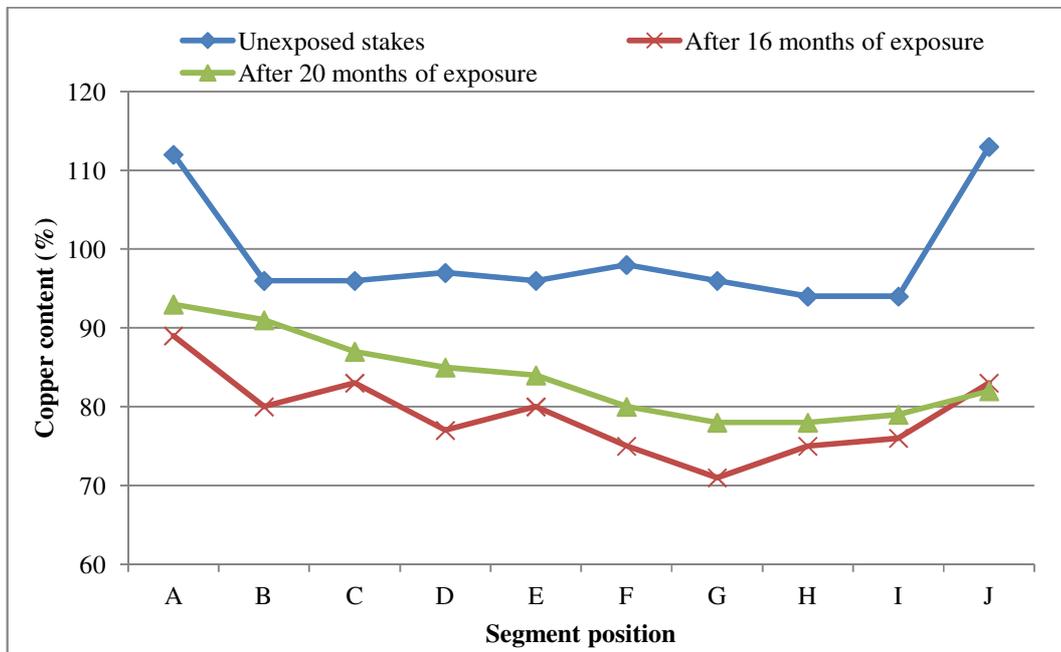


Figure 3.24: Distribution of copper in EN 252 stakes before and after 16 and 20 months of exposure

Figure 3.24 shows a slightly steady decrease in copper content from segment A up to G and a slight increase from segment H up to J after 20 months whereas a nearly homogenous copper distribution was found in the segments B to I in the unexposed stakes. In all segments, a higher chromium and copper content was found compared to the segment sampled 4 months earlier. This shows again the diffusion of chromium and copper from the inner to the outer zones and movement toward the lower parts. Statistical analysis did not show a statistically difference between the metal content from 16 to 20 months suggesting that migration and diffusion metals. The chromium concentration in the segment B shows higher chromium in the exposed segment compared to unexposed one after 20 months. This increase in concentration in segment B could be related to chromium migration from segment A. As a result, change in the chromium content of segment A is mainly related to migration and not to the leaching.

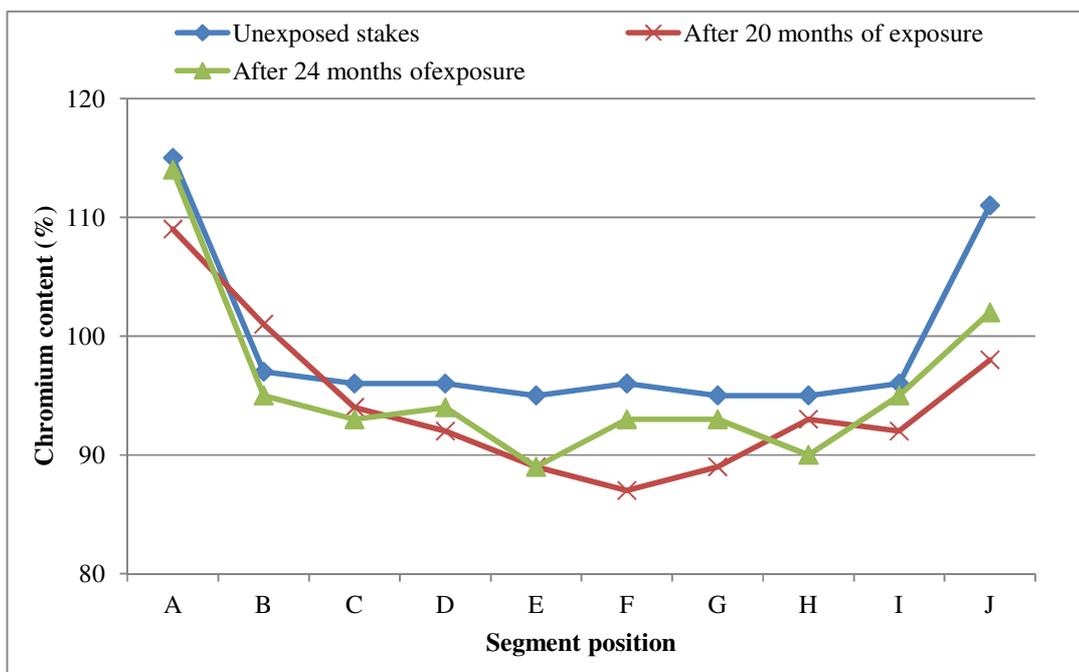


Figure 3.25: Distribution of chromium in EN 252 stakes before and after 20 and 24 months of exposure

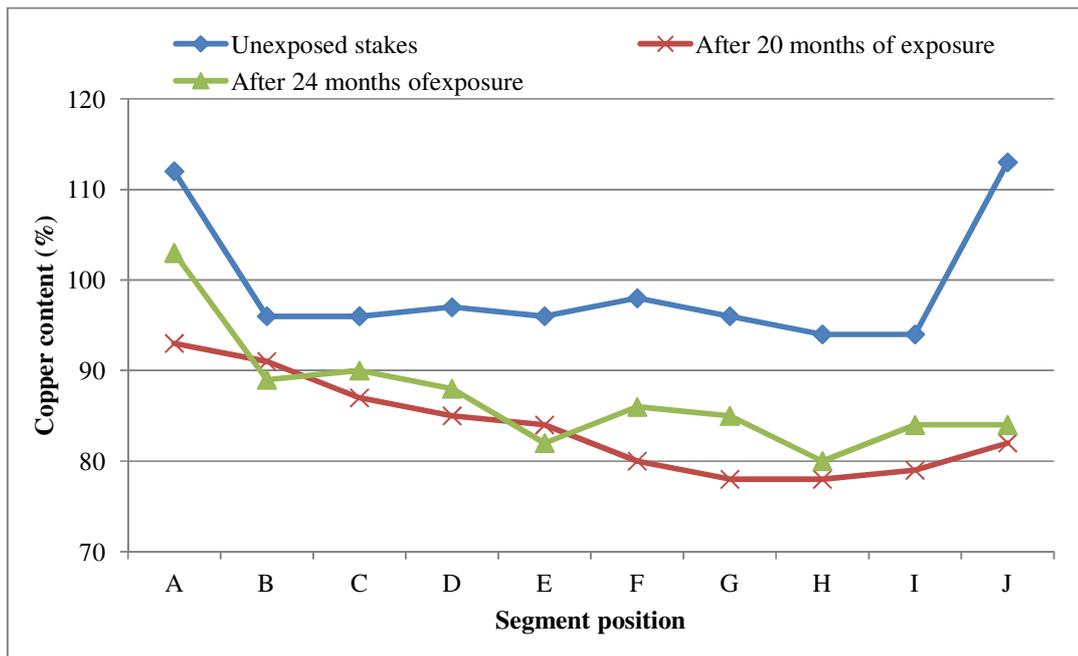


Figure 3.26: Distribution of copper in EN 252 stakes before and after 20 and 24 months of exposure

Results of 24 months of exposure indicate that the diffusion and metal mobility is still occurring as confirmed by increased metal concentration in the middle segment compared to the results of the 20 months as well as insignificant differences between metal content from 20 to 24 months (Figures 3.25 and 3.26). It was therefore deduced that the major change in the metal content had been related to migration and diffusion during the exposure time. Two years after exposure, the highest metal content was found in the end grain stakes. This can be attributed to the greater initial content compared to the inner segments. It was also found that the concentration of copper in segment A was higher than in segment J which is the end grain of wood stakes in the soil. This was expected, since wood in ground contact has greater potential for biodegradation and metal losses than above ground contact.

The lowest metal concentration was observed in the area around the soil-air zone (Figures 3.25 and 3.26). It could be explained by the presence of organic acids such as humic acid as well as much water flow in this section to increase the loss of the metals from this section. Cooper et al. (2000) stated that humic acids can increase the leaching of chromium and copper with higher effect on copper. Since the soil-air area (groundline) of the treated wood has the most water flow, it appears that this region has the lowest metal concentration and would be vulnerable to

biological degradation by decay fungi years after exposure. This becomes obvious in Figure 3.27. The figure shows mycelium on the wood surface near the groundline area. It is obvious signs of the fungal growth (mycelium) on the wood surface near the groundline area. To judge by appearances, fungi may belong to the basidiomycetes. Schmidt (unpublished) identified from coniferous stakes of the same test field the white-rot species *Hypholoma fasciculare* and *Gymnopus erythropus* whose rot-type is unknown.

To prolong the useful service life of wood needs a use of hydrophobic substances or application of compatible coating on the treated wood particularly on the soil-air zone. Overall, these findings agree with the results by Melcher and Wegen (2000).

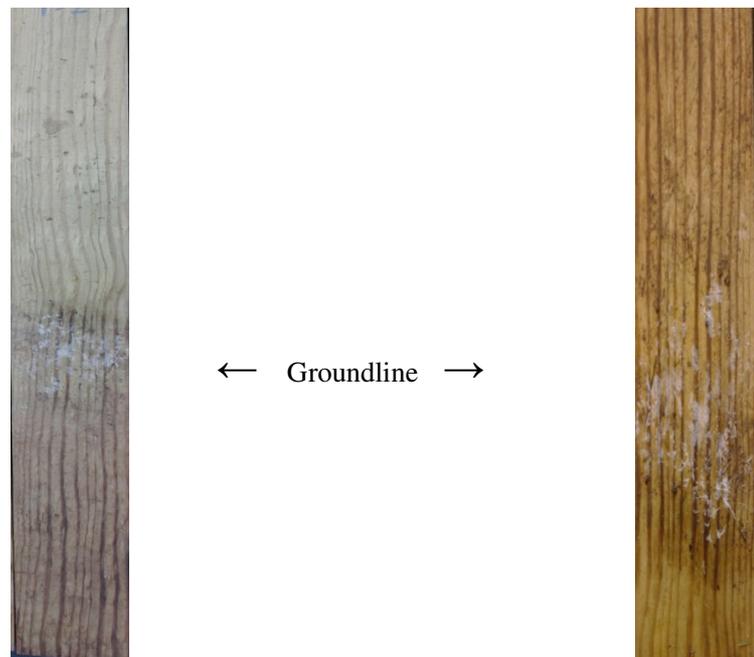


Figure 3.27: Fungal mycelium on the surface of treated wood stakes

After 24 months of field exposure, Chromium remaining ranged from 90 to 102% and averaged 95% at the below ground portion; in the above ground section, residual chromium ranged from 89 to 114% and averaged 97%. Residual copper ranged from 80 to 86% and averaged 84% of initial retention at the below ground and from 82 to 103% and averaged 90% in the above ground

portion. This indicates that 7% more copper remained at the above ground sections compared to below ground section.

It is proposed that different processes are involved in the change of metal concentration. These include the initial migration of unfixed or poorly fixed metals on the wood surface and their loss from the treated wood and then diffusion of metals from the inner layers to outer layers. These phenomena were observed during the first year of exposure. During the second year, the diffusion process continued along with the depletion of metals, especially copper, from the treated wood.

3.5.2.2 Non-standard pine sapwood

The distribution pattern of chromium and copper during one year (4, 8 and 12 months) exposure is shown in Figures 3.28 to 3.33. These graphs also contain the initial distribution of metal components in the unexposed stakes.

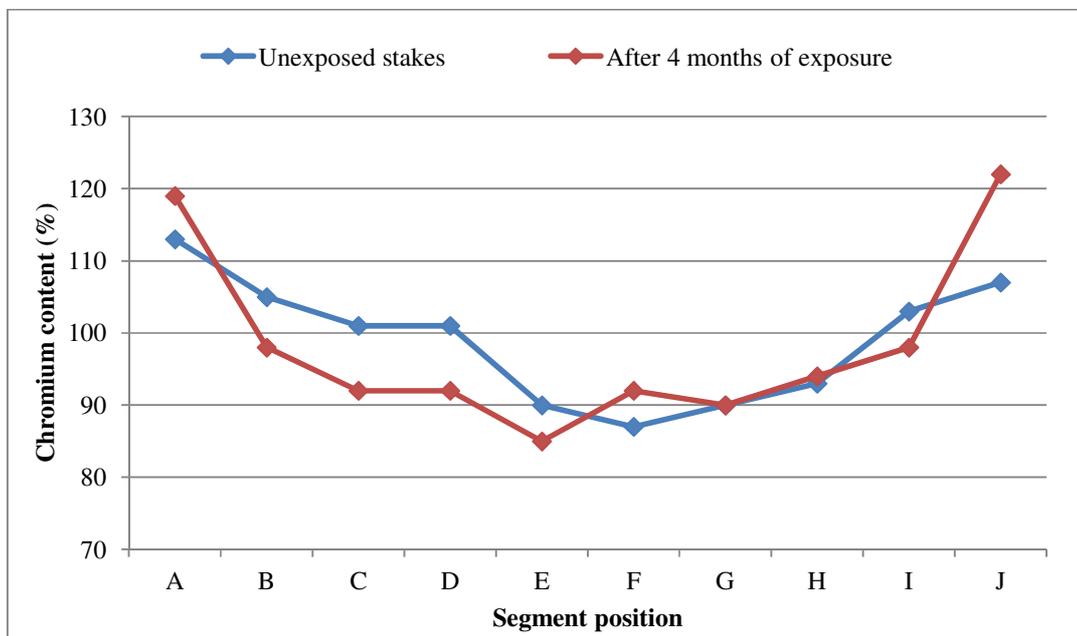


Figure 3.28: Distribution of chromium in non-standard format stakes before and after 4 months of exposure

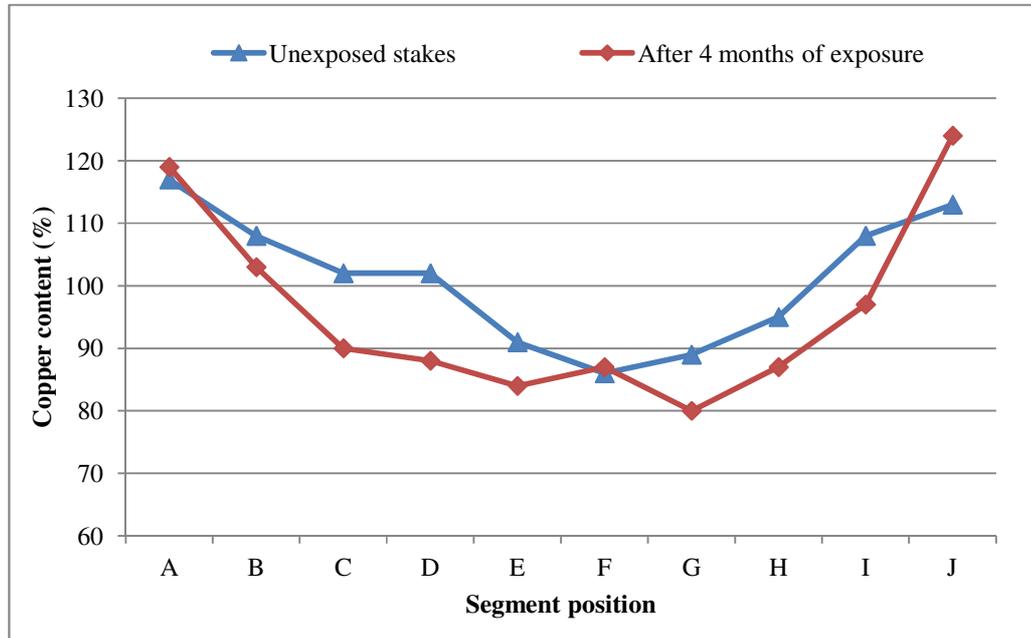


Figure 3.29: Distribution of copper in non-standard stakes before and after 4 months of exposure

As it can be seen from Figures 3.28 and 3.29 that metal content declined from segment A to E, increased slightly from E to F, decreases again at segment G and finally increased toward the bottom of stakes after four months of field exposure. The results show that copper concentration significantly declined in the segments C, D, E, G, H and I and conversely however copper content in the segment J significantly increased compared to the unexposed ones. The decreased copper content in these segments could be due to copper migration. It appears that the deposited metals on the surface of wood migrated from the upper section to the lower portions.

Also it is evident that the chromium and copper content in segment A is higher than of the unexposed segments. The reason could be related to variations between samples (individual analytical data of the stakes revealed that the error of the procedure was about $\pm 5\%$ (Appendix 3) as well as to short-term exposure. Consequently, in order to see change in metal content in the end grain segments, a large amount of metal components needs to migrate to deeper segments or leach into the environment.

There were more variations in the copper distribution after 8 months of exposure in the above ground segments in comparison with the four-month exposure (Figure 3.31). This could be a result of the copper mobility in these segments during service as proven by the decrease of copper concentration in all above ground segments compared to unexposed segments and the significantly increase in segment E. Results also indicate a significant difference between the copper content in all below ground segments compared with those unexposed ones suggesting a depletion of unfixed or poorly fixed copper from these segments into the environment.

Considering chromium content in segments B and E reveals a migration of chromium from upper segments to the lower segments particularly from segment A due to the formation of cracks since it was observed that metal concentration decreased in this segment and increased in the segment B when comparing metal concentration from 4 to 8 months. Statistical analysis showed a significant decrease in chromium content in segments D, F, G and H compared to the 4 months sampling reflecting the chromium depletion into the environment.

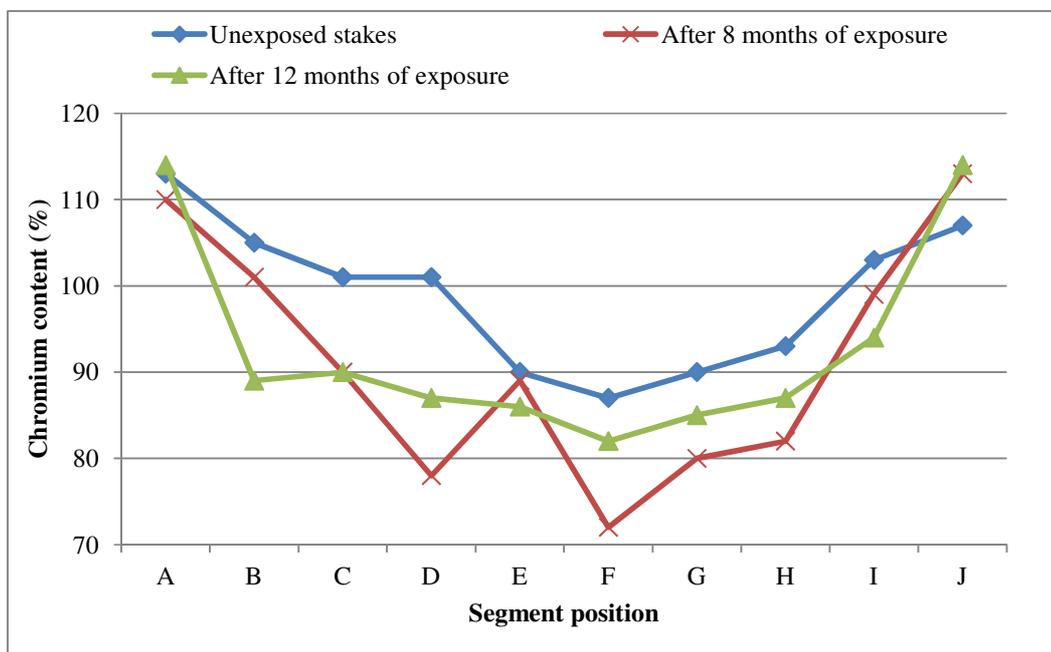


Figure 3.30: Distribution of chromium in non-standard stakes before and after 8 and 12 months of exposure

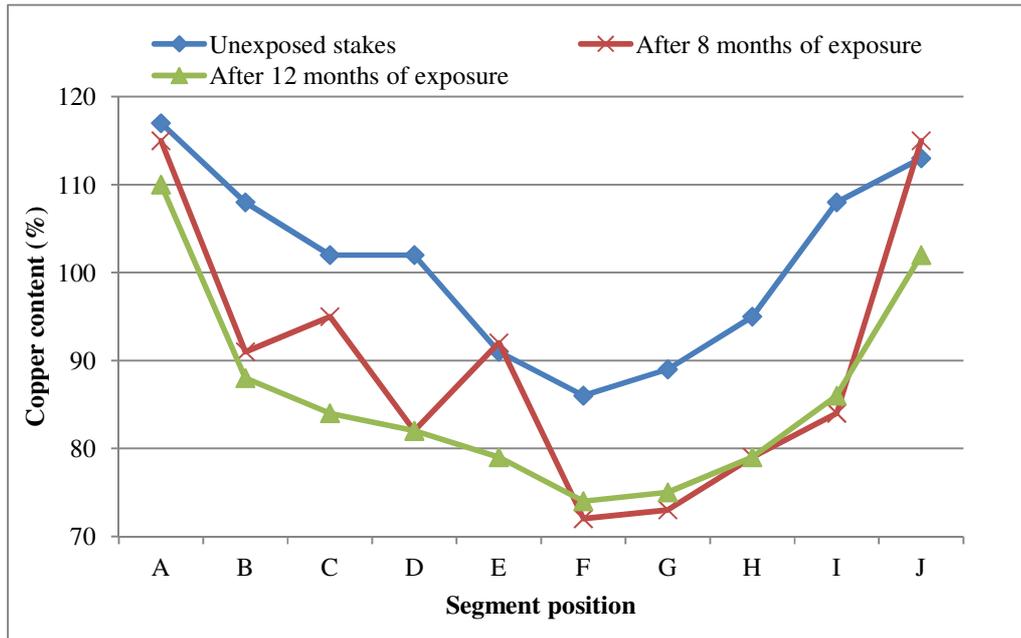


Figure 3.31: Distribution of copper in non-standard stakes before and after 8 and 12 months of exposure

After one year of field exposure, results show that the chromium mobility is still occurring, as the chromium concentration in some segments decreased in comparison with unexposed segments and increased relative to the 8 months exposure. For instance, chromium concentration in segments D, F, and G was higher than in the 8 months exposure (Figure 3.30). The increased chromium concentration could be related to movement from the upper segments. As a result, changes in the chromium content of these sections were associated with migration and not with leaching. There was an insignificant difference between copper concentration in most stake segments exposed out of ground and in ground after 8 and 12 months exposure, indicating the diffusion process and copper migration in the segments toward the lower parts due to gravity movement and water leaching. Results also show that the amount of copper in segment J which was in contact with soil was declined significantly (Figure 3.31).

It can be concluded that during the first year of exposure, the change in the metal concentration was mainly due to diffusion and migration/redistribution of metals within the treated wood.

Residual chromium was between 82 and 114% and averaged 92% in the below ground portion; in the above ground section, residual chromium was between 82 and 114% and averaged 94% of initial retention after 12 months of field exposure. Copper remaining ranged from 74 to 102% and

averaged 83% of initial retention at the below ground and from 79 to 110% and averaged 89% in the above ground portion. This shows 7% more copper remained at the above ground sections as compare to below ground section.

The distribution pattern of and chromium and copper during the second year (16, 20 and 24 month) of exposure is shown in Figures 3.32 to 3.37. These graphs also contain the initial distribution of metal components in the unexposed stakes.

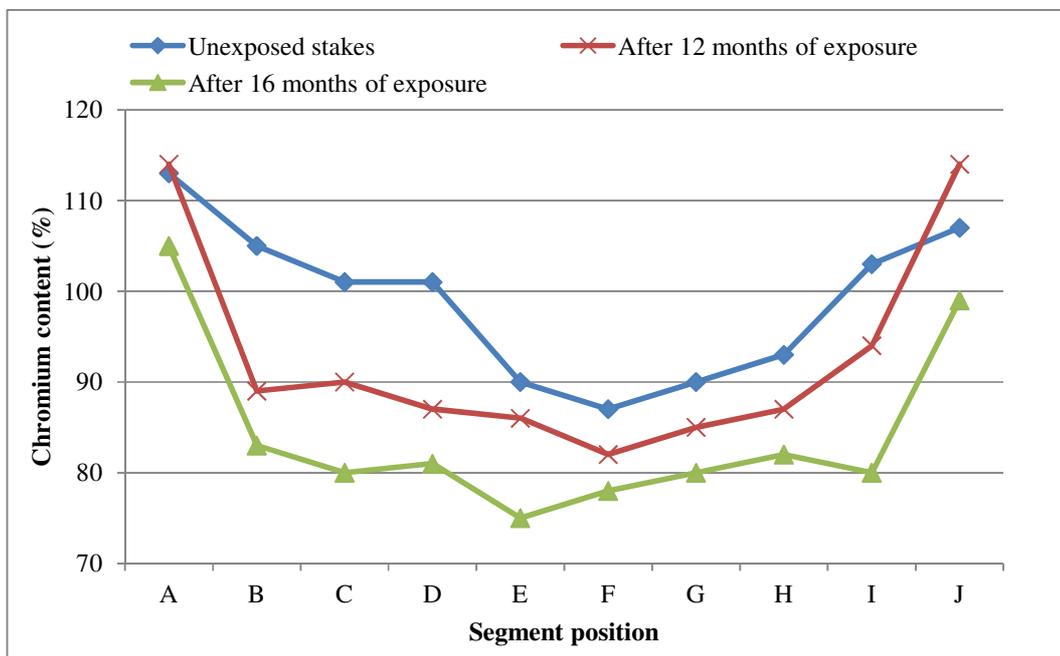


Figure 3.32: Distribution of chromium in non-standard stakes before and after 12 and 16 months of exposure

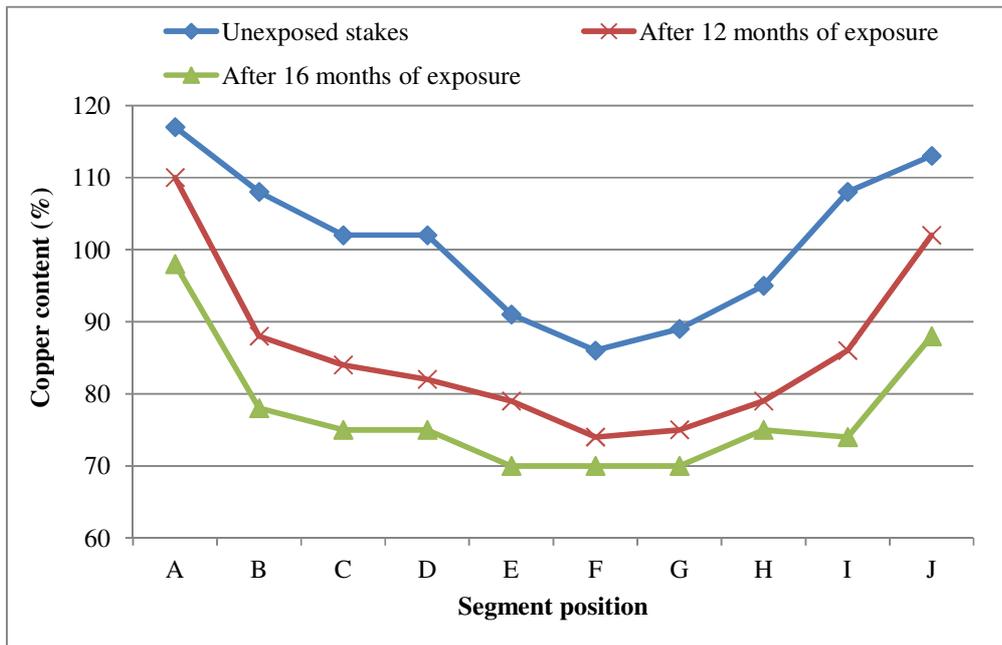


Figure 3.33: Distribution of copper in non-standard stakes before and after 12 and 16 months of exposure

Chromium and copper have migrated from the upper to the lower parts at the end of one year exposure; therefore considerable metal amounts became located at the surface of treated wood which easily can be removed by rainfall and soil water. It appears that this process happened between 12 and 16 months because of substantial metal lost during that time of exposure particularly from the below-ground segments. It can be stated that the changes in the metal concentration were largely related to the leaching of chromium and copper between 12 and 16 months.

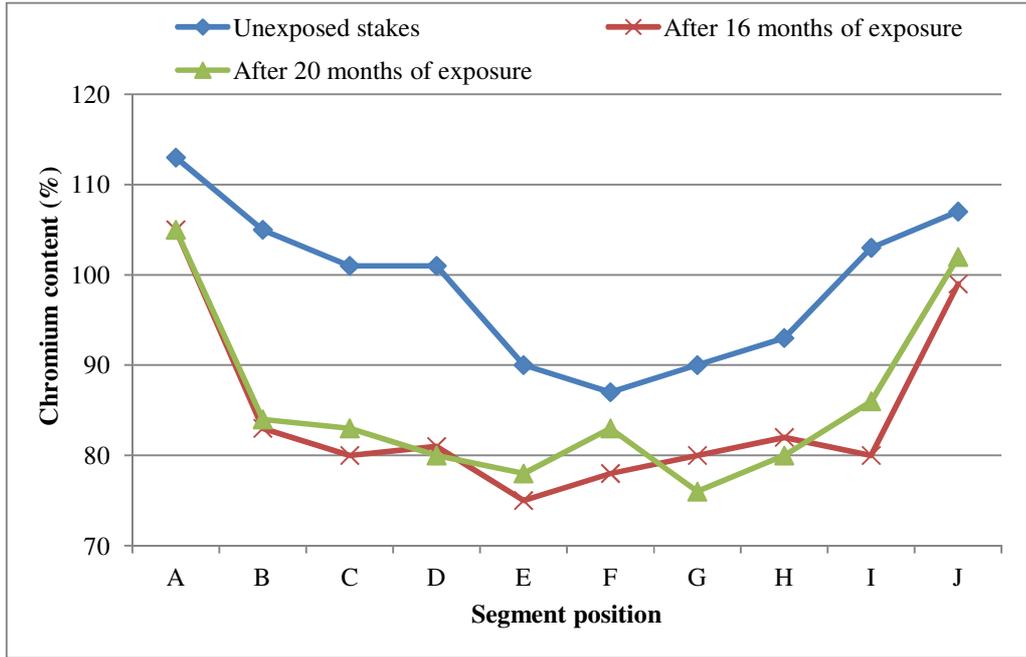


Figure 3.34: Distribution of chromium in non-standard stakes before and after 16 and 20 months of exposure

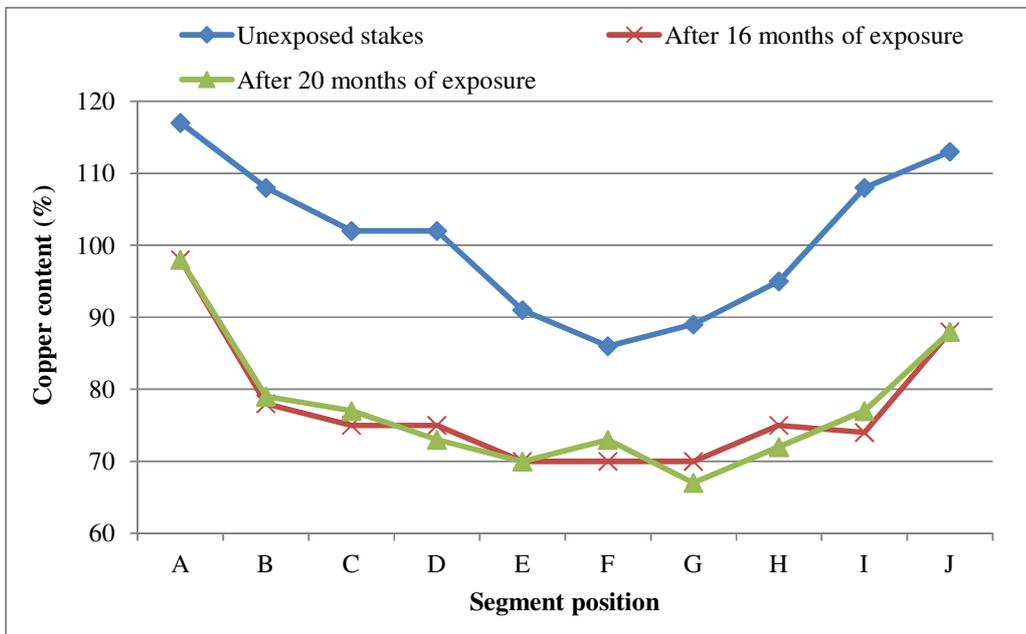


Figure 3.35: Distribution of copper in non-standard stakes before and after 16 and 20 months of exposure

Changes in the metal content within the treated wood after 20 months of exposure are shown in Figure 3.34 and 3.35. Once the unfixed metals were removed from the wood surface, a difference in metal concentration occurred between the surface and the inner layers of wood. After this process, the changes in the metal concentration could be due to a combination of the transportation of metals by diffusion as well as motion due to gravity toward the lower parts. Since the difference between the total chromium and copper of the whole stake was insignificant after 16 and 20 months, it can be concluded that the changes in the metal concentration were mainly related to diffusion.

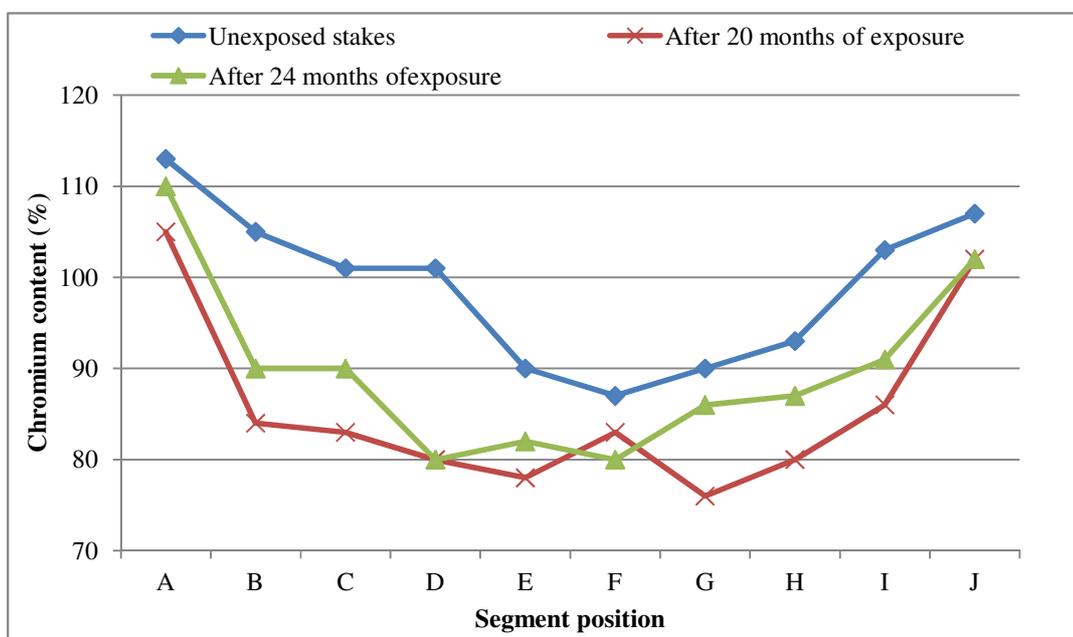


Figure 3.36: Distribution of chromium in non-standard stakes before and after 20 and 24 months of exposure

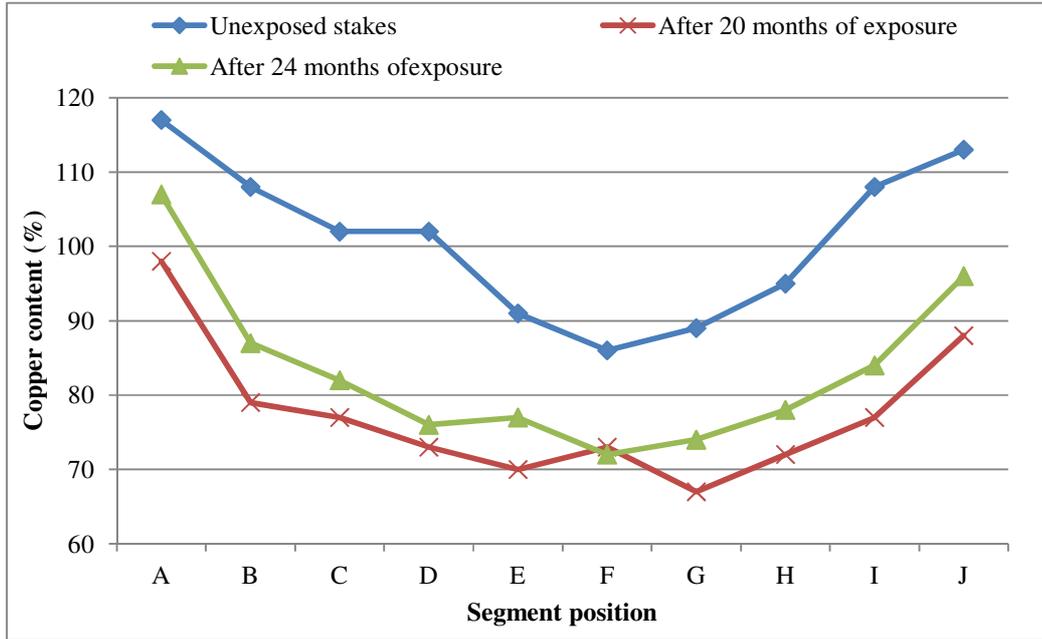


Figure 3.37: Distribution of copper in non-standard stakes before and after 20 and 24 months of exposure

Figures 3.36 and 3.37 show the results for chromium and copper after 2 years of exposure. The metal concentration increased compared to the stake segments sampled 4 months earlier. This indicates an ongoing diffusion process. Therefore it can be stated that the changes in metal concentration from 20 to 24 months is mainly associated with diffusion as it was also observed between 16 and 20 months. Similar to the results of EN 252 pine sapwood, the highest metal content was found in the end grain stakes. As already described, this could be result from a higher initial content compared to the inner segments. Segment J was characterized by a high initial concentration of copper in the end grain but a lower content than in segments exposed above ground. Results also illustrated the lowest concentration of chromium and copper in the area around the soil-air-zone as was also observed in standard pine stakes.

At the end of 2 years of outdoor exposure, residual chromium ranged from 80 to 102% of initial retention at the below ground and from 80 to 110 % in the above ground section. At the below ground section, residual copper, ranged from 72 to 96% and averaged 81%; in the above ground section, residual copper ranged from 77 to 107% and averaged 86 %. This shows 6% more copper remaining in the above ground sections compare to below ground section.

3.5.2.3 EN 252 spruce

The distribution pattern of chromium and copper during one year (4, 8 and 12 months) exposure is shown in Figures 3.38 to 3.43. These graphs also contain the initial distribution of metal components in the unexposed stakes.

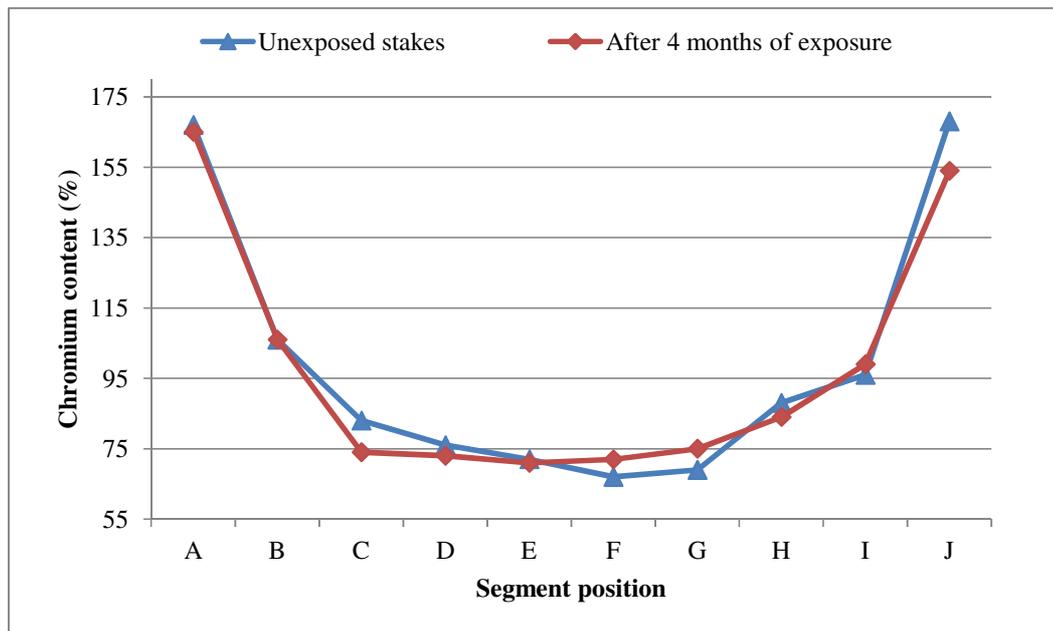


Figure 3.38: Distribution of chromium in EN 252 spruce stakes before and after 4 months of exposure

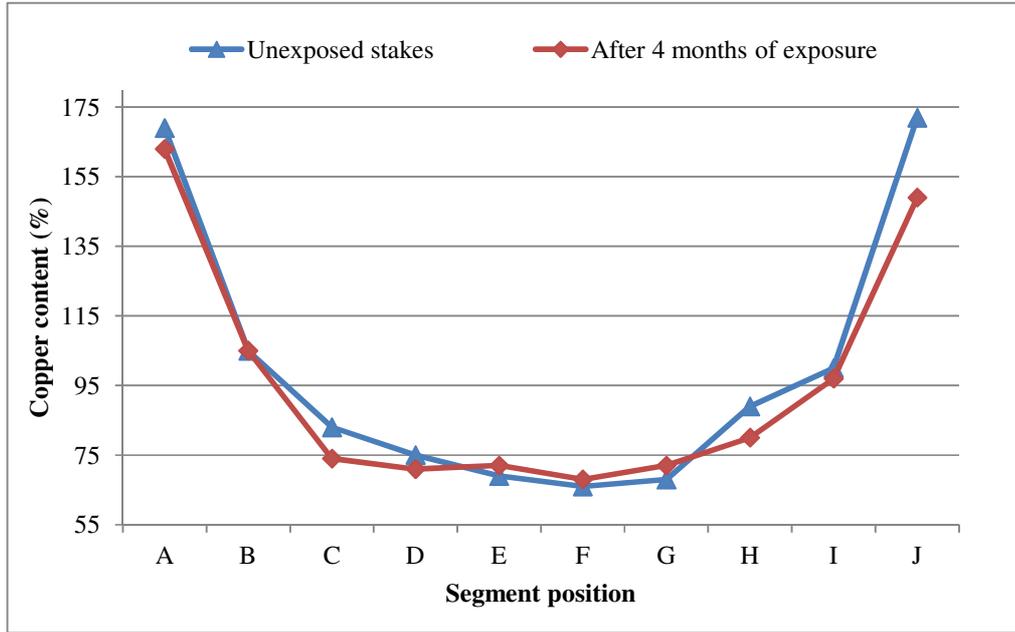


Figure 3.39: Distribution of copper in EN 252 spruce stakes before and after 4 months of exposure

Four months after exposure, the chromium and copper distribution changed slightly as compared to the exposed stakes. As can be seen in Figures 3.38 and 3.39 there is deviations in metal concentration between exposed and unexposed stake segments that were mainly related to the variations between stake segments and not to the metal migration or leaching. Significant difference occurred in copper content in the segments A, C, H and J and in the segments C and J in chromium content compared to the unexposed ones illustrating metal migration and their loss.

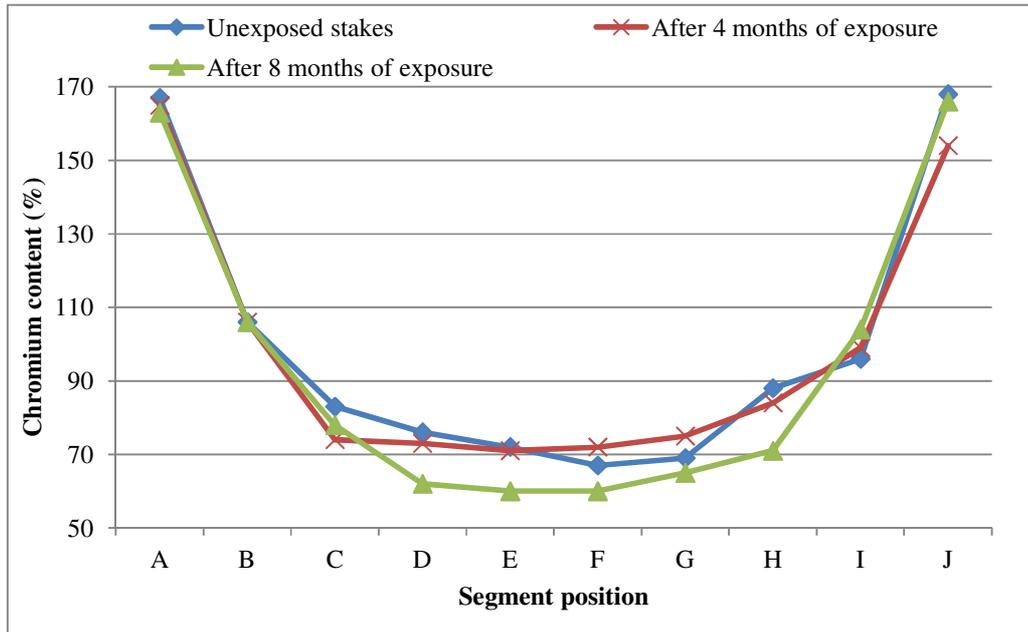


Figure 3.40: Distribution of chromium in EN 252 spruce stakes before and after 4 and 8 months of exposure

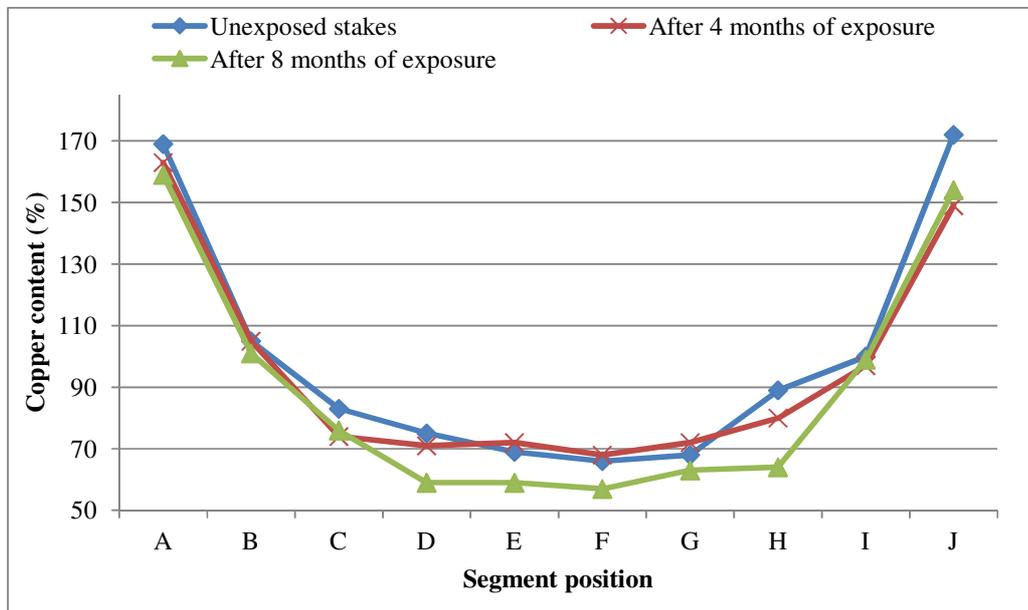


Figure 3.41: Distribution of copper in EN 252 spruce stakes before and after 4 and 8 months of exposure

Figure 3.41 shows that the copper concentration increased in segment C in comparison with the segment sampled 4 months earlier, suggesting copper mobility from the A and B segments. This was confirmed by the decreased copper concentration of these segments compared to the earlier sampling (4 months). This behavior was also observed for chromium. There is a significant difference decline in copper content in the segments D to H and conversely it was increased in segments I and J, suggesting copper depletion as well as its migration from upper to the lower stake segments.

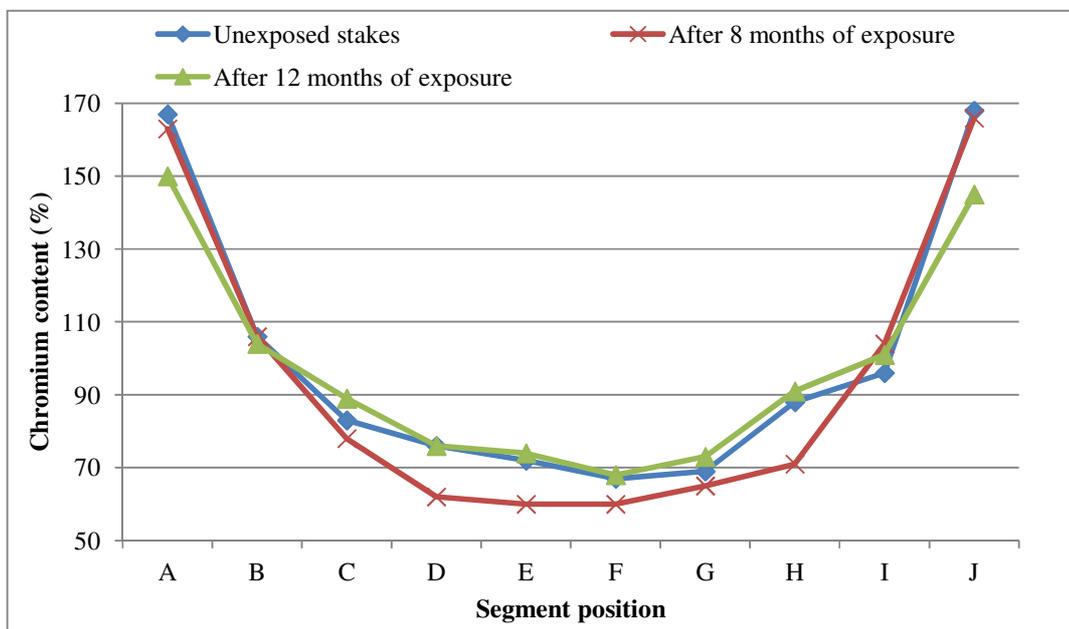


Figure 3.42: Distribution of chromium in EN 252 spruce stakes before and after 8 and 12 months of exposure

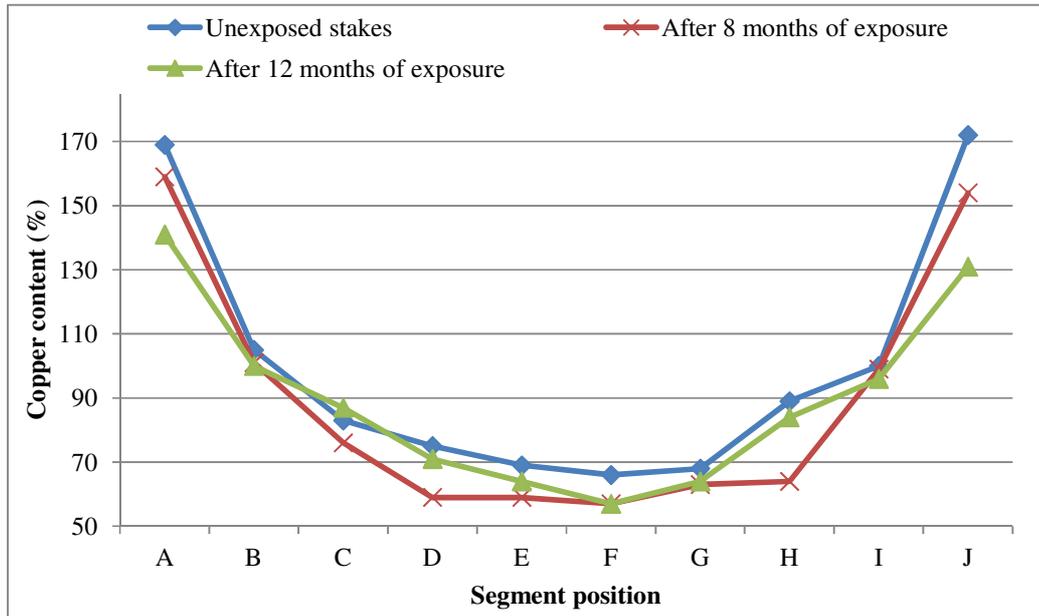


Figure 3.43: Distribution of copper in EN 252 spruce stakes before and after 8 and 12 months of exposure

Although copper distribution followed in principle the progression curve of unexposed stakes after one year, chromium and copper mobility was still occurring (Figures 3.42 and 3.43). Obviously, the chromium and copper concentration in the segments C to E and C to H is higher than that of the 8-month exposure, respectively. This resulted from a metal migration due to the movement of water from the upper segments to the lower segments. It can be concluded that the major change in the metal concentration during that time frame was related to the migration of metals on the wood surface. Chromium remaining ranged from 68 to 145% of initial retention at the below ground and from 74 to 150% in the above ground section one year after exposure. At the below ground section residual copper ranged from 57 to 131% and averaged 86%; in the above ground section, residual copper ranged from 64 to 141% and averaged 93% after one year of examination. This express 8% more copper remaining at the above sections compared to below ground sections.

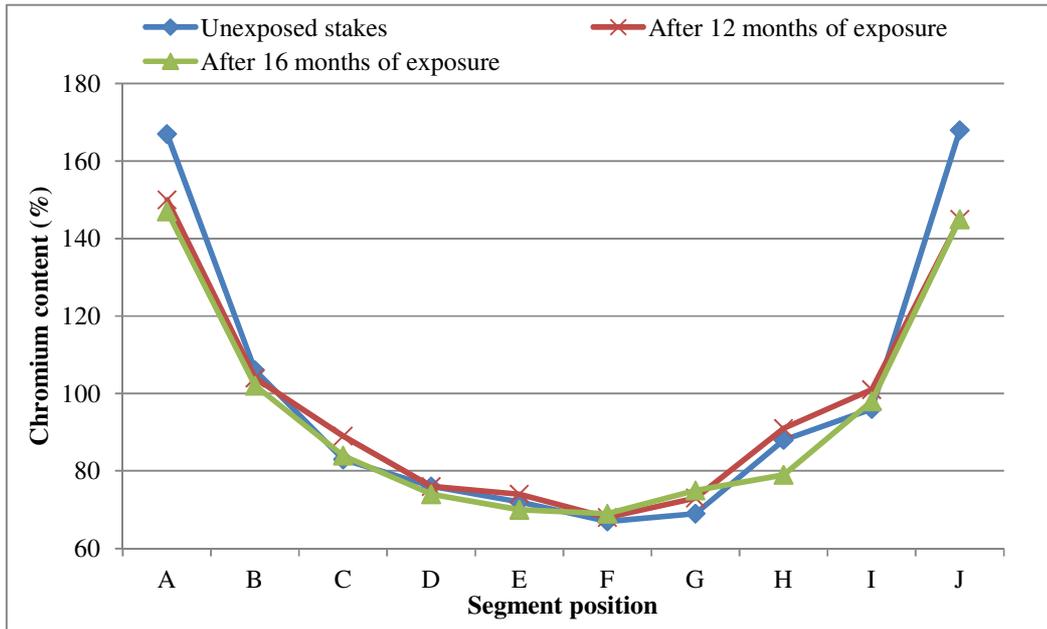


Figure 3.44: Distribution of chromium in EN 252 spruce stakes before and after 12 and 16 months of exposure

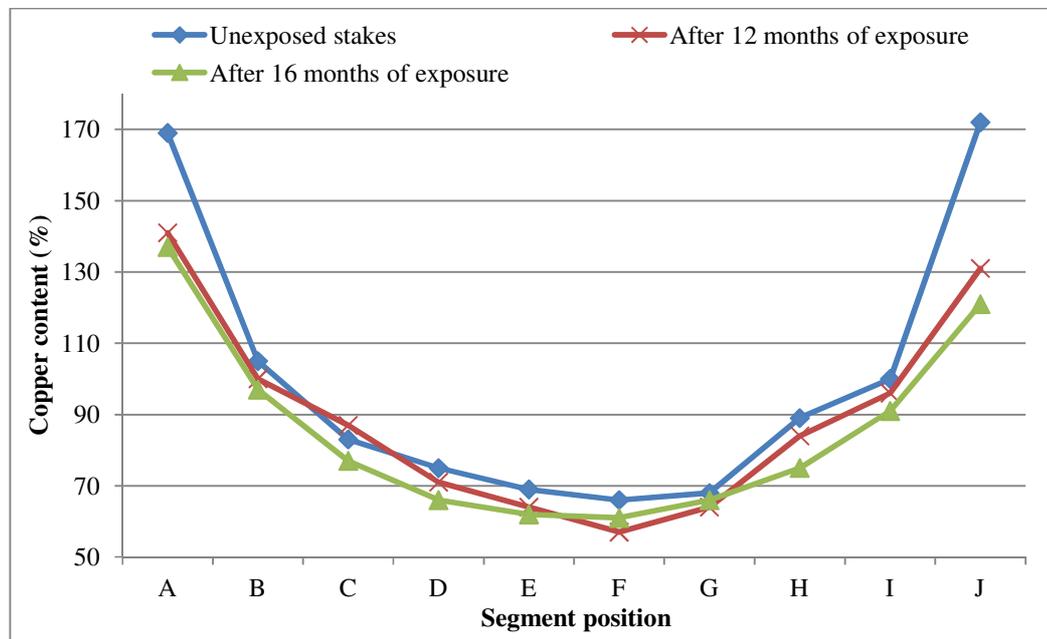


Figure 3.45: Distribution of copper in EN 252 spruce stakes before and after 12 and 16 months of exposure

There was a significant decrease in copper content in most stake segments compared to those unexposed and exposed after one year, illustrating the depletion of copper from these segments (Figure 3.45). It can be stated that the major change in copper content from 12 to 16 months was mainly due to a depletion process. It was an insignificant difference was found between chromium content in most stake segments from 12 to 16 months indicating the chromium change in the stake segments was likely related to migration and diffusion (Figure 3.44).

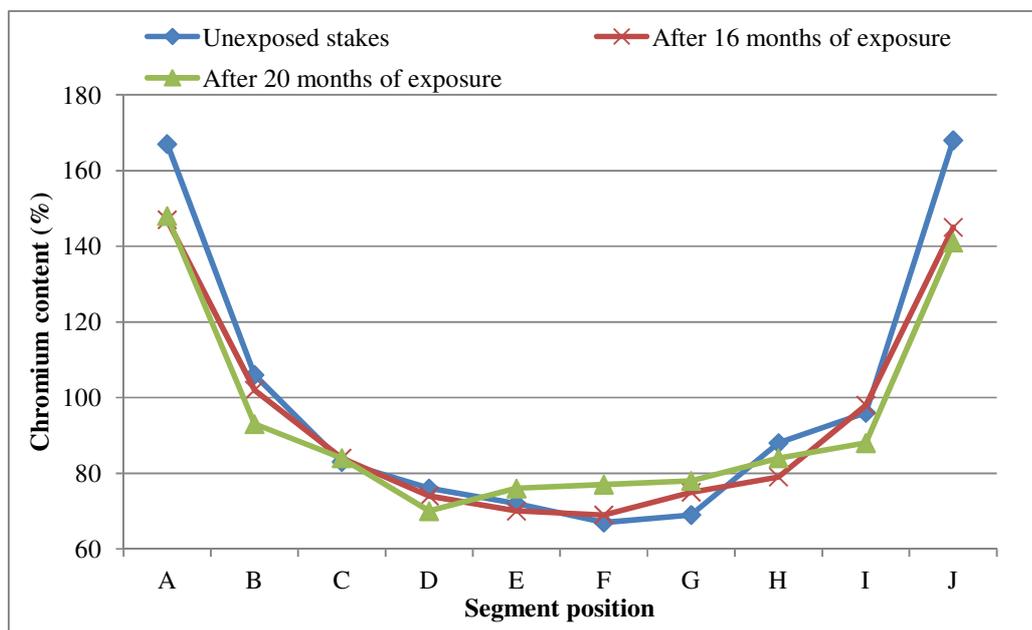


Figure 3.46: Distribution of chromium in EN 252 spruce stakes before and after 16 and 20 months of exposure

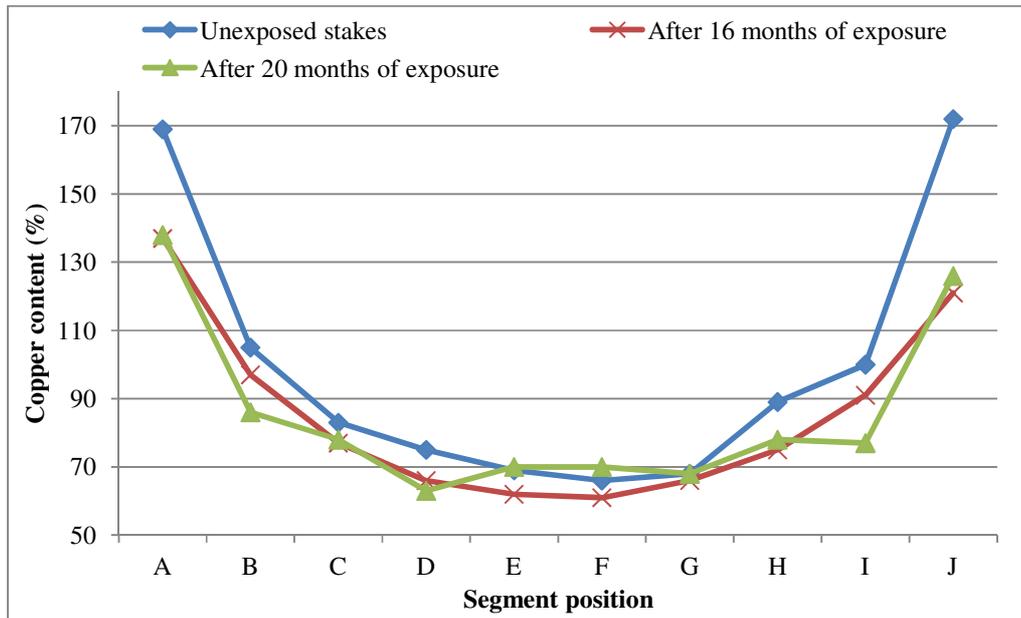


Figure 3.47: Distribution of copper in EN 252 spruce stakes before and after 16 and 20 months of exposure

A combination of diffusion and migration of chromium and copper took place after 20 months of exposure. Figures 3.46 and 3.47 show that the chromium and copper content declined steadily from stake top, reaching the minimum in the middle of the stakes and then the contents rises again to the bottom. Statistical analysis showed an insignificant difference between copper content in the segments as compared to the earlier sampling (16 months), reflecting a copper migration during that time. This becomes obvious in the increased copper content in the segments G and H compared with those obtained from segments samples 4 months earlier. It is interesting to note that the metal content in the end grains where chromium and copper content was significantly higher than at the 20 months sampling. This could be related to metal diffusion from inner to outer layers in the segment A and metal mobility from upper segments to lower segments and then their accumulations in the segment J.

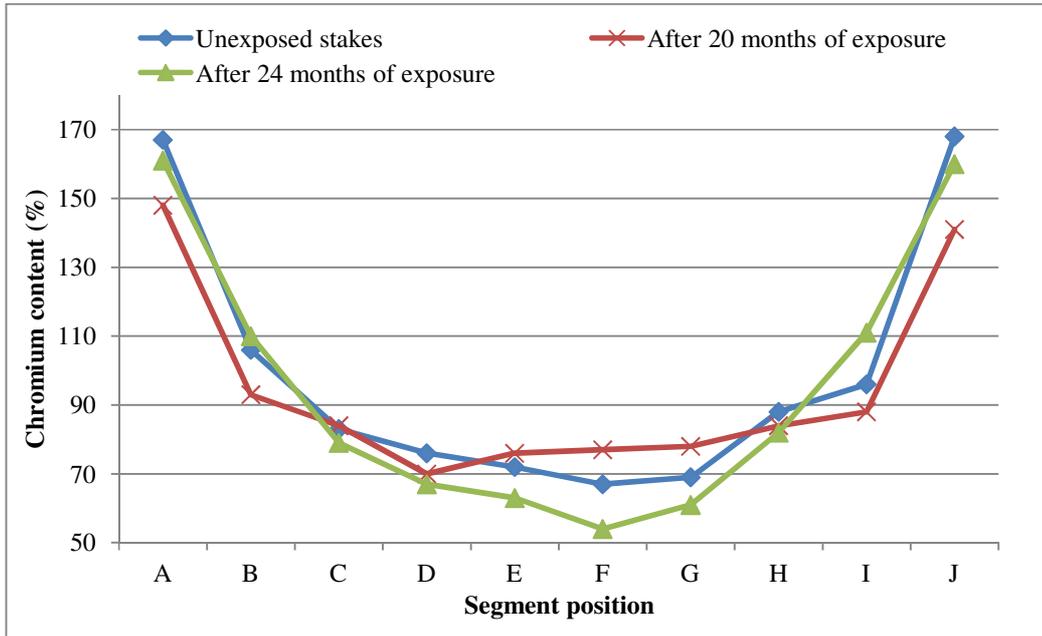


Figure 3.48: Distribution of chromium in EN 252 spruce stakes before and after 20 and 24 months of exposure

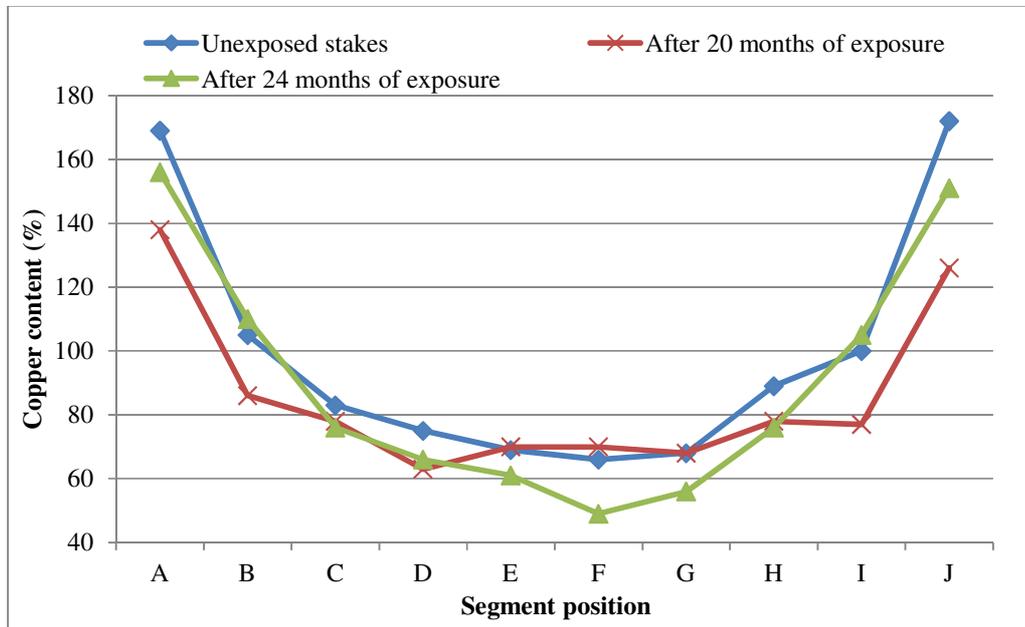


Figure 3.49: Distribution of copper in EN 252 spruce stakes before and after 20 and 24 months of exposure

Comparing the results of 24 months exposure with those obtained after 20 months indicate that the chromium and copper concentration increased in some segments (e.g. B, I and J), indicating metal migration and conversely the metal content decreased significantly in the below ground segments (e.g. E, F and J) indicating metal leaching (Figures 3.48 and 3.49). Therefore, it can be deduced that a combination of migration and diffusion as well as leaching of metals occurred at the 24-months sampling. Chromium remaining, ranged from 54 to 160% and averaged 93% at the below ground portion; in the above ground section, residual chromium ranged from 63 to 161% and averaged 96% after 2 years exposure. Copper remaining ranged from 49 to 151% and averaged 88% of initial retention at the below ground and from 61 to 156% and averaged 93% in the above ground portion. This shows approximately 6% more copper remaining at the above sections in comparison to the below ground sections.

The lowest chromium and copper concentration was found in the area around the soil-air-zone, both in the standard and non-standard pine stakes. As described earlier, this could be associated to water flow in the groundline of the stakes and to presence of humic acid.

Chromium and copper distribution did not change substantially during outdoor exposure as compared to standard and non-standard format pine sapwood. This could be due to water penetration into the spruce wood and then metal transportation is more difficult than pine sapwood stakes. Also, the standard and non-standard pine stakes had higher metal uptake with a complete metal penetration in the cross section (Figure 3.2) whereas metals mainly concentrated in the outer zones of spruce stakes. The above ground sections were subjected to irregular wetting and drying cycles that create cracks. It appears that in spruce stakes, some metals migrated to the inner layers due to crack formation and subsequently diffusion due to the difference in concentration between treated and untreated zones. Thus, metals would not be available to migrate to the wood surface as much as in pine stakes.

3.6 Factors affecting the remaining or leaching rates of metal components from preservative-treated during outdoor exposure

3.6.1 Impact of stake position and exposure time

3.6.1.1 EN 252 pine sapwood

The residual content of chromium and copper in EN 252 pine stakes is shown in Figures 3.50 and 3.51.

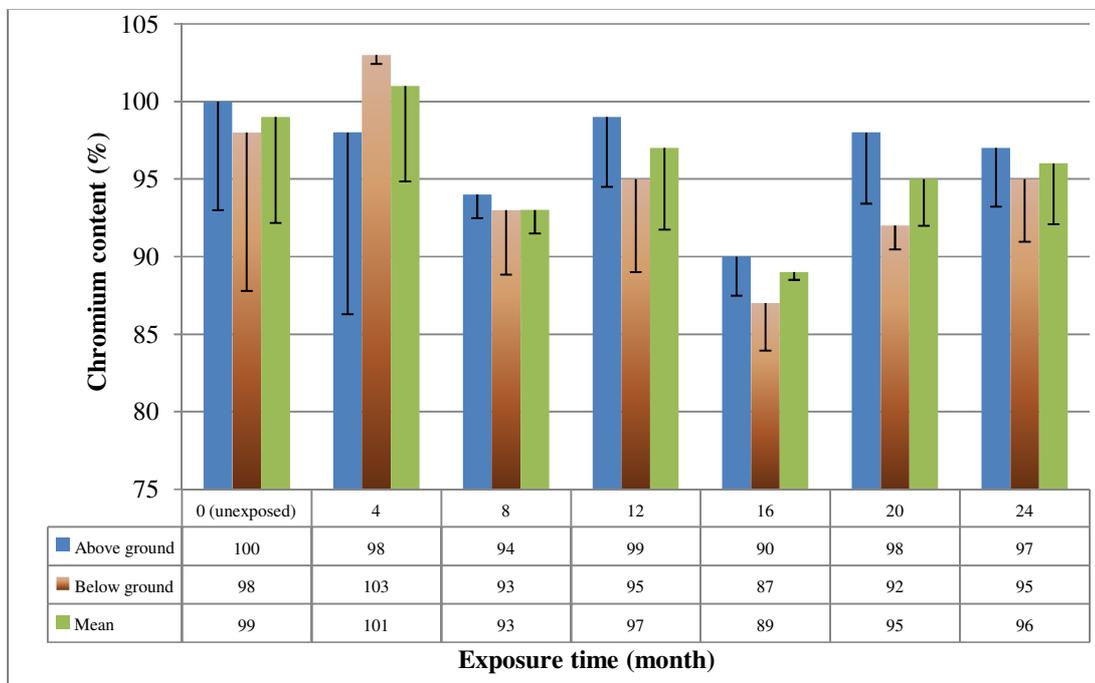


Figure 3.50: Average percentage of chromium content in EN 252 pine stake sections in relation to position and exposure time. Error bars=standard deviation

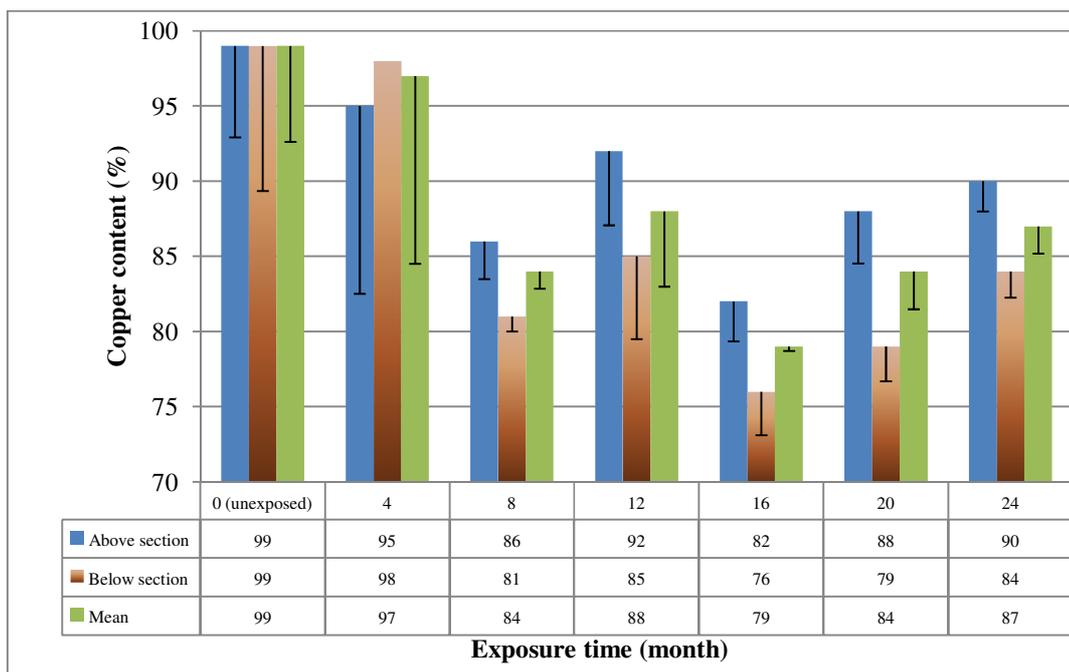


Figure 3.51: Average percentage of copper content in EN 252 pine sapwood stake sections in relation to position and exposure time. Error bars=standard deviation

Figure 3.50 shows that after 4 months of exposure there was no reduction in chromium content because total recovery rate was 101%. Considering that the loss of copper corresponds approximately to 4%. within the initial 8 months of outdoor exposure, the copper content decreased clearly from 100 to approximately 85%, whereby the remaining copper content in the above ground section was higher than in the below ground section. During the subsequent exposure the remaining copper content fluctuated between 79 and 88% which means that the variation/decline in concentration was predominantly characterized by leaching and diffusion² (Figure 3.51). An identical behavior was found for chromium however on a higher level. The chromium content ranged from 89 to 97% during that time frame. Finally it can be mentioned that in total 96% chromium and 87% copper remained in the treated material after 24 months of field exposure.

Metal losses exhibited a considerable variability during different exposure time. The fluctuation of metal depletion could have resulted from inherent natural variability of wood and the distribution of preservatives as well as their migration within the wood. A comparison of

² The paragraph was already published in IRG/WP 13-50291.

depletion from treated wood during the first and second years of exposure did not show significant difference in overall mean chromium and copper depletion.

At the beginning of the experiment, the chromium to copper ratio in unexposed stakes was 1.73 (Table 3.4). After 24 months of field exposure, the ratio of Cr to Cu was 1.85 and 1.94 at the above ground and below ground sections, respectively, suggesting a high relative loss of copper from treated wood in contact with water and ground.

In view of the effect of stake position on the metal remaining, the results showed that residual copper was significantly affected by stake position over the course of the experiment. After 2 years exposure, copper depletion in the below-ground section was higher than in the above-ground section. This was expected since below-ground sections were continually exposed to contact with water and soil constituents leaching solubilizing biocide components such as copper (Lebow et al., 2009). However, stake position did not have a noticeable effect on chromium losses. The resistance of chromium to leaching was observed in numerous laboratory and field test studies (e.g. Evans et al., 1994; Breslin and Adler-Ivanbrook, 1998; Melcher et al., 2000). The low depletion of chromium may be due to the strong fixation with wood components (Pizzi, 1981, 1982a,b). Nevertheless, pine stakes (20×20×500 mm) treated with a CCA preservative were reported that their chromium was more susceptible to depletion than their copper in above ground compared to below ground portion after 4.5 and 5.5 years in New Zealand and Australia (Wakeling, 2006). The author pointed out that the reason could be due to lignin degradation by ultraviolet radiation leading to preferential chromium depletion.

3.6.1.2 Non-standard pine sapwood

The average remaining chromium and copper in non-standard stakes is illustrated in Figures 3.52 and 3.53.

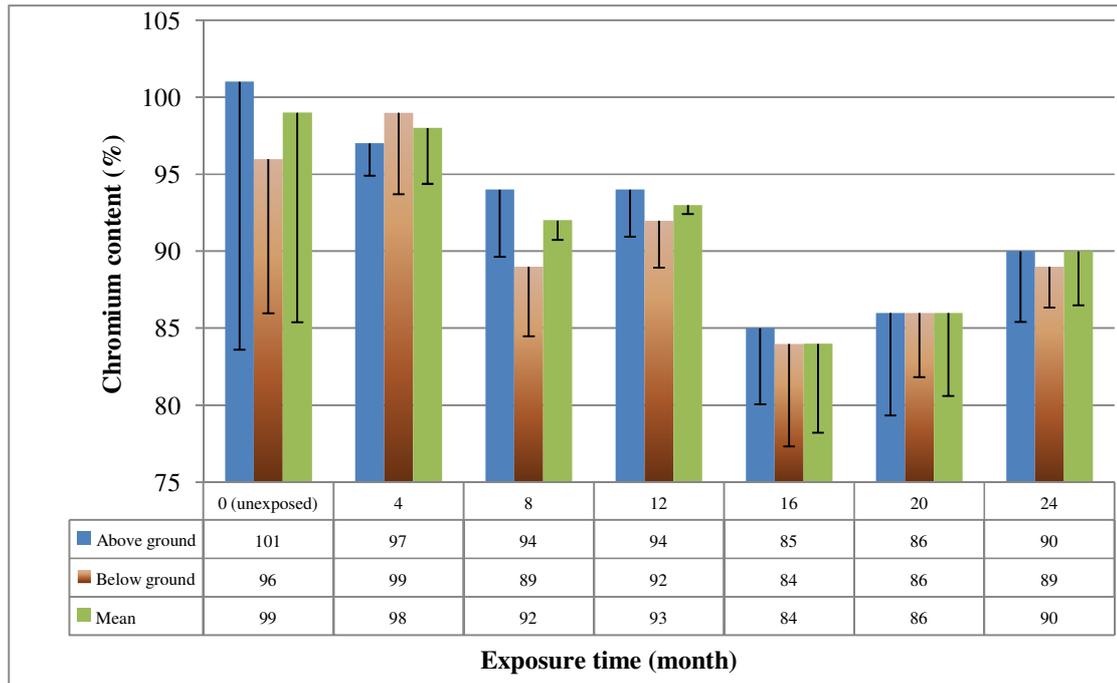


Figure 3.52: Average percentage of chromium content in non-standard stake sections in relation to position and exposure time. Error bars=standard deviation

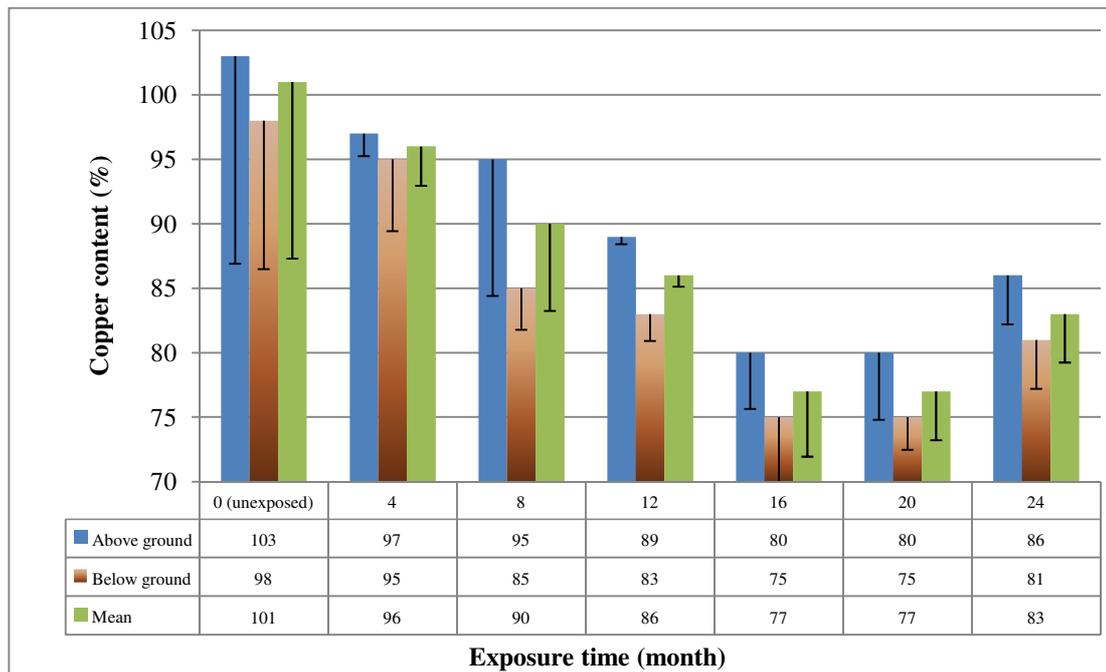


Figure 3.53: Average percentage of copper content in non-standard stake sections in relation to position and exposure time. Error bars=standard deviation

Figure 3.52 shows that the mean remaining content of chromium of the whole stake was 84% after 16 months exposure. Since a similar content was determined after 20 months it is to assume that between 12 and 16 months a change in the mode of depletion took place from washing up and migration to leaching (see section 3.2). This becomes obvious in Figure 3.53. In both sections, a steady decrease of copper content was to observe within the first 12 months of exposure whereby the loss in the above ground section was lower than in the below ground part³. The analyses of chromium and copper content did not indicate statistically significant differences in overall mean metal loss between the first and second years of field exposure. In total a loss of 11% chromium and 17% copper was found after 24 months exposure for non-standard stakes, which was a slightly higher than in case of EN 252 stakes.

³ The paragraph was already published in IRG/WP 13-50291.

3.6.1.3 EN 252 spruce

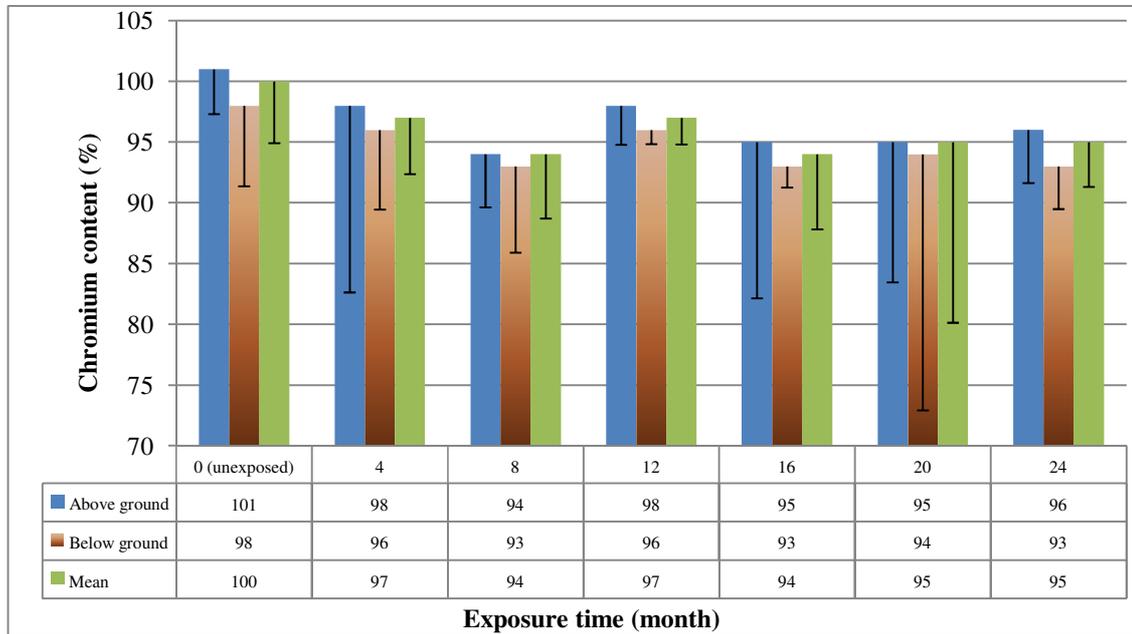


Figure 3.54: Average percentage of chromium content in EN 252 spruce stake sections in relation to exposure and exposure time. Error bars=standard deviation

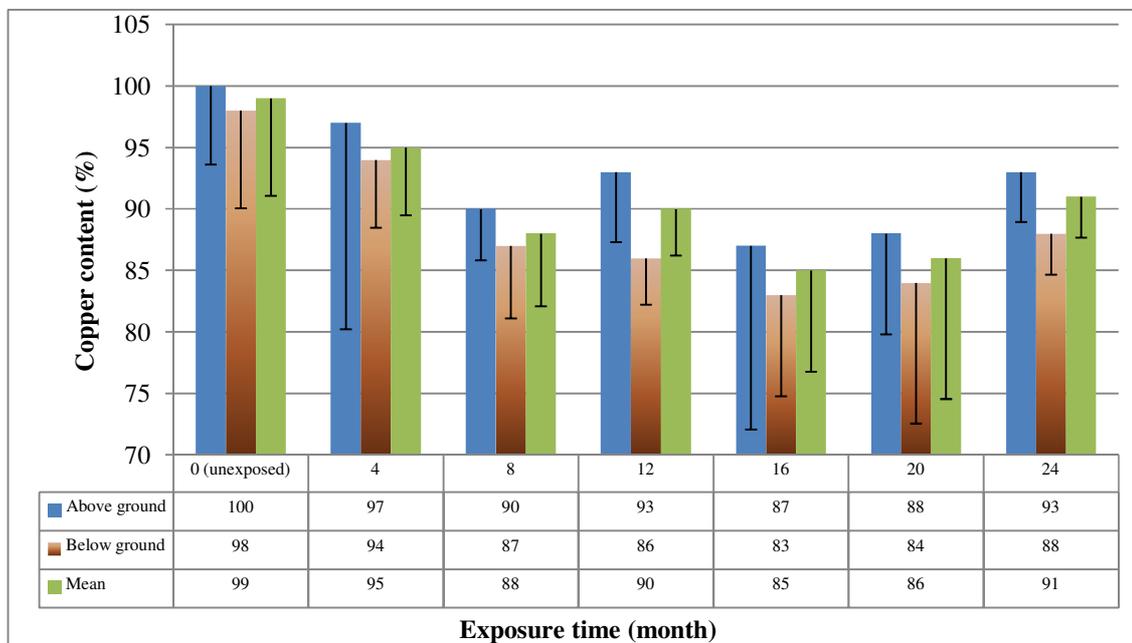


Figure 3.55: Average percentage of copper content in EN 252 spruce stake sections in relation to exposure and exposure time. Error bars=standard deviation

Figures 3.54 and 3.55 show that the chromium and copper content decreased gradually in both sections within the 8-months exposure which metal residual in the below ground section was lower than in the above ground portion. The average residual chromium level of the whole stake is 94% after 16 months. With respect to a similar content found after 24 months exposure, there may have been a decline/variation in concentration characterized by diffusion and migration. The loss of chromium and copper from treated wood after 24 months was 5 and 9%, respectively, which was lower than that of EN 252 pine stakes. There was no statistical difference in overall mean metal content when comparing residual content between the first and second years of exposure.

3.6.2 Impact of sample size

An important factor in determining the leaching of preservative chemicals is the size of wood sample. Laboratory studies on small samples have shown the leaching rate or leaching amount of preservatives decreased significantly with increasing sample size (Cooper, 1994; Hayes et al., 1994). Small sample sizes should not be employed to estimate the amount of loss from larger wood commodities in-service conditions because the leaching of preservative would be overestimated (Lebow, 1996).

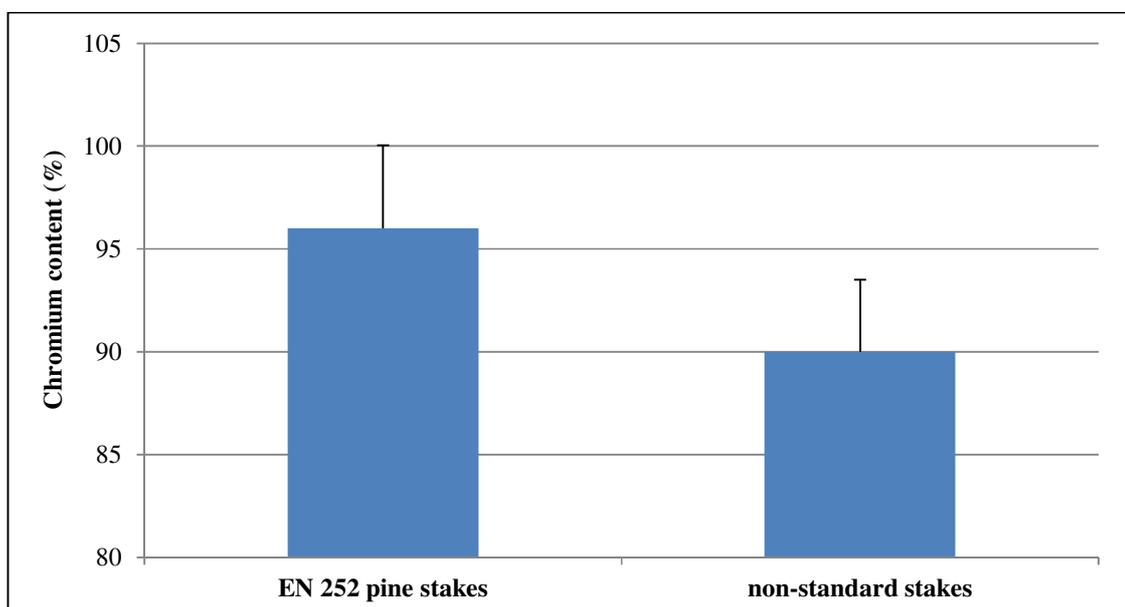
Larger specimens (EN 252) for better understanding the amount of preservative chemicals release into the environment and also metal leaching behavior are required.

In this research project, in addition to standard stakes according to EN 252 (50×5×2.5 cm), non-standard (39×4×4 cm) have been used for determining the leaching of metals from treated wood samples. With respect to EN 252, designated basically relative protective effectiveness of a wood preservative in ground contact, the consideration of different sample size can be helpful for developing a laboratory test method to estimate the depletion of metals from treated wood in natural exposure.

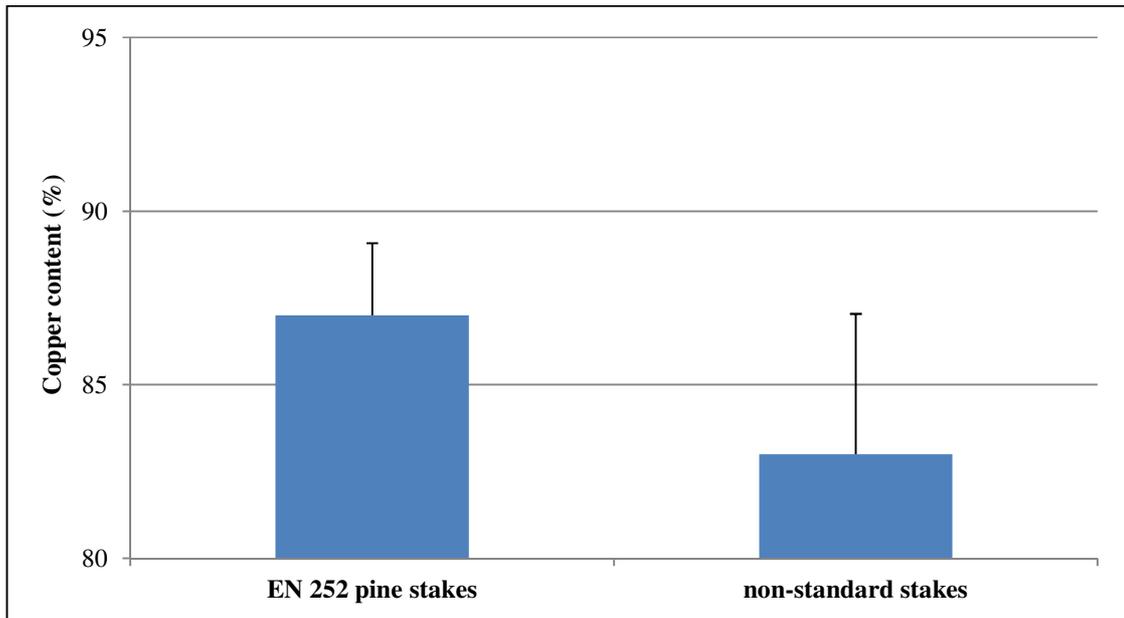
Figures 3.56 and 3.57 indicate the effect of the sample size on residual content of chromium and copper after 24 months of exposure. The mean percentage of metal content in EN 252 pine stakes was slightly higher than in non-standard pine format two years after field exposure. The average percentage chromium and copper remained in EN 252 pine stakes was 97 and 87% in comparison to 90% chromium and 85% copper in non-standard pine stakes. These results could be related to

the greater cross section of the non-standard format compared to EN 252 pine samples (16 cm² compared to 12.5 cm²). Statistical analysis indicated that there is no significant difference ($\alpha=0.05$) in residual metal content between EN 252 and non-standard pine format. The insignificant differences in metal depletion between the two sizes of stakes were possibly due to the differences in the surface area to volume ratio which did not differ enough. Based on these findings, field stake samples of 4×4×39 cm³ can be considered as alternative to EN 252 stakes of 50×5×2.5 cm³, in comparative field leaching tests.

As described above, change in the surface area to volume ratio in small sample size evaluations can have a major influence on the leaching of preservative components while results of this study indicated that this change in the larger sample (i.e. EN 252 and non-standard) is not the same as those of the small specimens probably due to a smaller surface area to volume ratio of the larger samples. Yamamoto et al. (2000) studied preservative depletion of three dimensions (10×10×25 cm³, 5×10×25 cm³, 2×10×25 cm³) treated with CCB after exterior exposure for 6 months. They pointed out differences between laboratory experiments using 2×2×1 cm³ and outdoor exposure due to differences in the surface area to volume ratio of samples.



3.56: Average percentage chromium remaining in wood stakes 2 years after exposure. Error bars=standard deviation



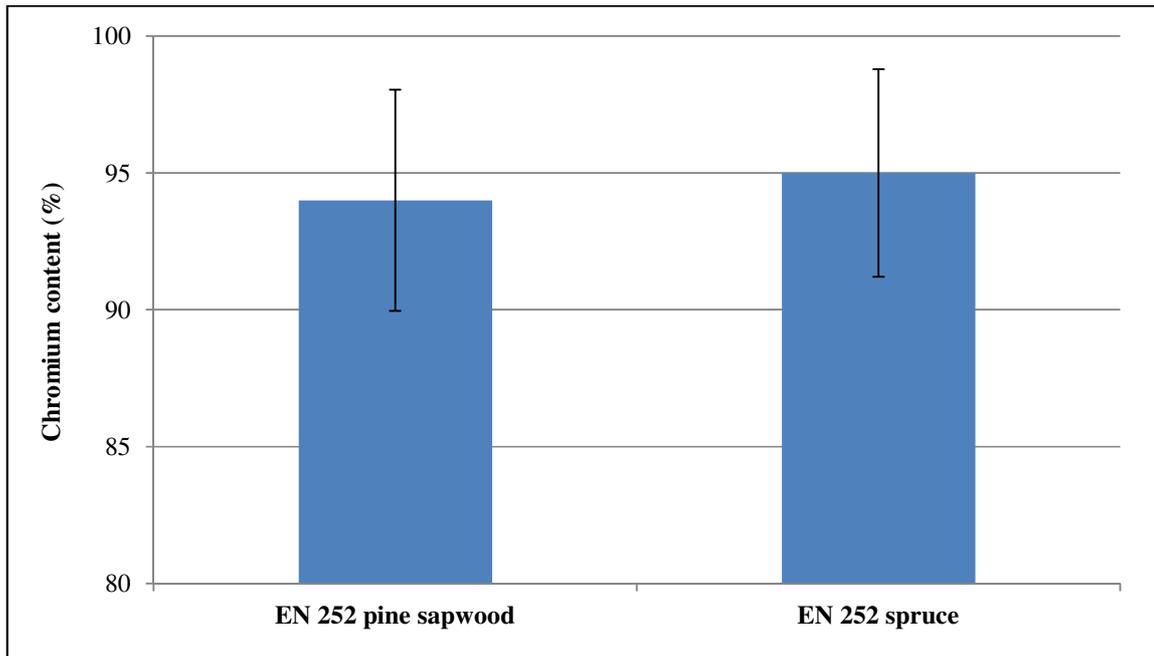
3.57: Average percentage copper remaining in wood stakes 2 years after exposure. Error bars = standard deviation

3.6.3 Impact of wood species

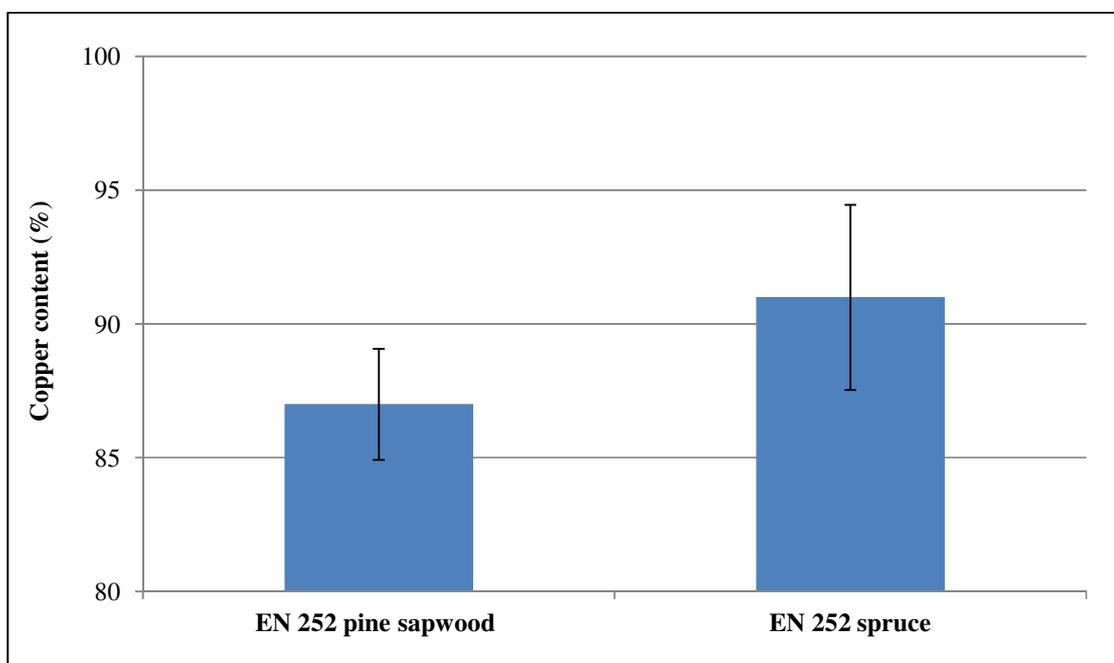
The wood species can influence the depletion of wood preservatives, since the chemical composition (e.g. cell wall components) and anatomical/physical characteristics (e.g. cell wall structure and permeability) of wood differs between species (Cooper, 1990; Lebow, 1996). Most studies investigated the influence of wood species on leaching in a controlled laboratory scale where the situation is completely different from the real conditions. In addition, in most previous studies on leaching of preservative components in outdoor exposure, experiments were conducted on samples with a single wood species (Evans and Edlund, 1993; Melcher, 1998; Melcher and Wegen, 2000). From the point of view of applications, it would be of interest to compare the depletion of preservative components in samples made of various wood species.

Figures 3.58 and 3.59 illustrate the average remaining of chromium and copper in whole stakes of EN 252 pine sapwood and EN 252 spruce after 24 months outdoor exposure. When copper content is compared between wood species, the loss of copper in the EN 252 pine is higher than that of spruce stakes (13 compared to 9%). Previous studies indicated (Lebow, 1996; Cockcroft and Laidlow, 1978; Wilson, 1971) that the loss of preservative was more in permeable wood

since the penetration of water through those wood species is faster. As a consequence of this factor, it can be deduced that penetration and movement of water into the pine wood should be faster than on spruce resulting in leach-susceptible preservative components like copper. There was no significant difference in chromium loss between the two wood species (Figure 3.58). The impact of wood species on the depletion of copper could be related to the higher mobility of copper in wood compared with chromium (Lebow, 1996). The results of my study demonstrate that the wood species had statistically significant influence on the copper depletion but less effect on the losses of chromium within 2 years of field exposure. Taylor and Cooper (2001) studied the effect of southern yellow pine (*Pinus* spp.), jack pine (*Pinus banksiana* Lamb.), and black spruce (*Picea mariana* Mill.) treated with two preservative concentrations and one commercial water-repellent on leaching rates. After one year, leaching results of CCA-treated lumber exposed above ground indicated significant differences between the wood species. In contrast, a laboratory study (Habicht et al., 2003) reported that wood species only minor influence the copper leaching rate.



3.58: Average percentage chromium remaining in the wood species after 2 years outdoor exposure. Error bars=standard deviation



3.59: Average percentage copper remaining in the wood species after 2 years outdoor exposure. Error bars=standard deviation

3.6.4 Comparison of laboratory and field tests

Laboratory leaching tests have traditionally been formed utilizing a small sample size under controlled conditions. Although these studies provided repeatable conditions and are useful for shorter test durations, they have little applicability to real exposure situations (Lebow, 1996). Studies have shown that smaller specimens have higher amounts or rate of leaching as a result of higher surface area to volume ratio (Hayes et al., 1994; Lebow, 1996). In addition, there is a uniform distribution of preservative components in small sample size whereas in larger dimensions (EN 252:1990), preservative distribution throughout the specimen becomes more non-uniform because of the inherent variability of wood. It appears that the leaching behavior of preservatives in larger specimens and exposed in service conditions will be different from that of the laboratory tests. These factors raise the issue of utilizing larger samples in the laboratory tests and compare their results to the field tests. Hingston et al., (2001) pointed out that direct comparison of laboratory and field trials are difficult due to the influence of different factors particularly the type of wood species, the retention levels of treated wood and exposure environments. Additionally, since the exact initial retention of preservative chemicals in the treated wood stakes is unknown, a calculation of the real loss of preservative components is difficult.

In the following, the results of the two laboratory test results (CEN/TS 15119-1) and (CEN/TS 15119-2) are compared to field test results. For comparison purposes, results of above ground section were compared to discontinuous water immersion and below ground section to continuous one.

First of all it is important to note that during the field test the migration/redistribution of metal components within the wood stakes was found in all treated stakes whereas this was not observed in the laboratory tests.

Figures 3.60 and 3.61 show the results of laboratory and field tests after 2 years of exposure in EN 252 pine sapwood. For comparison purposes, results of above ground section were compared to CEN/TS 15119-1 and below ground section to CEN/TS 15119-2 standard.

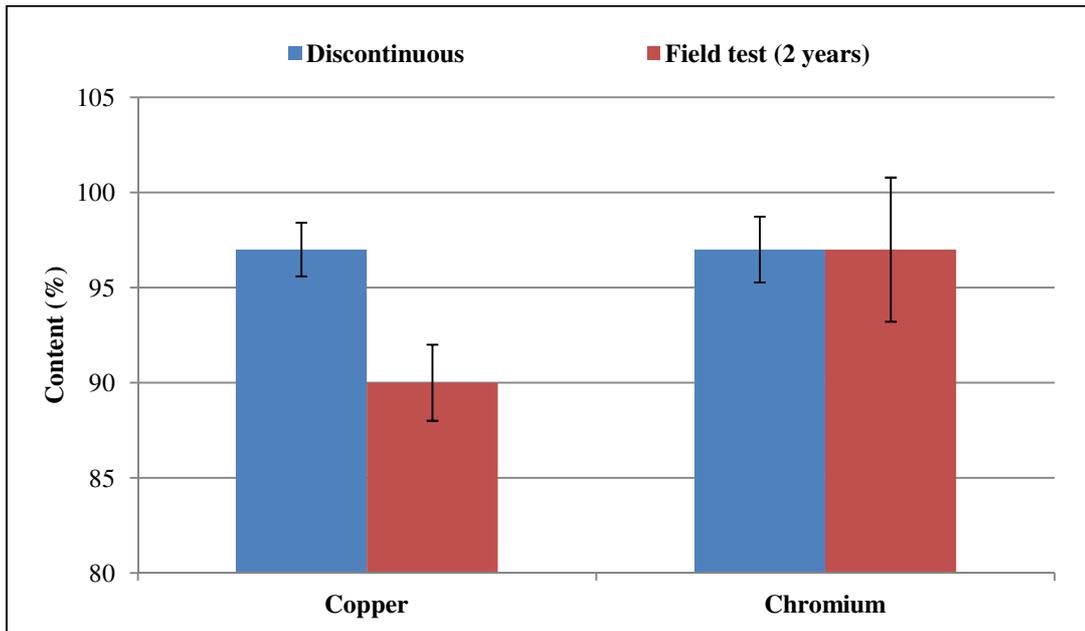


Figure 3.60: Residual metal contents in non-continuous experiment and field test exposure in EN 252 pine specimens after 2 years. Error bars=standard deviation

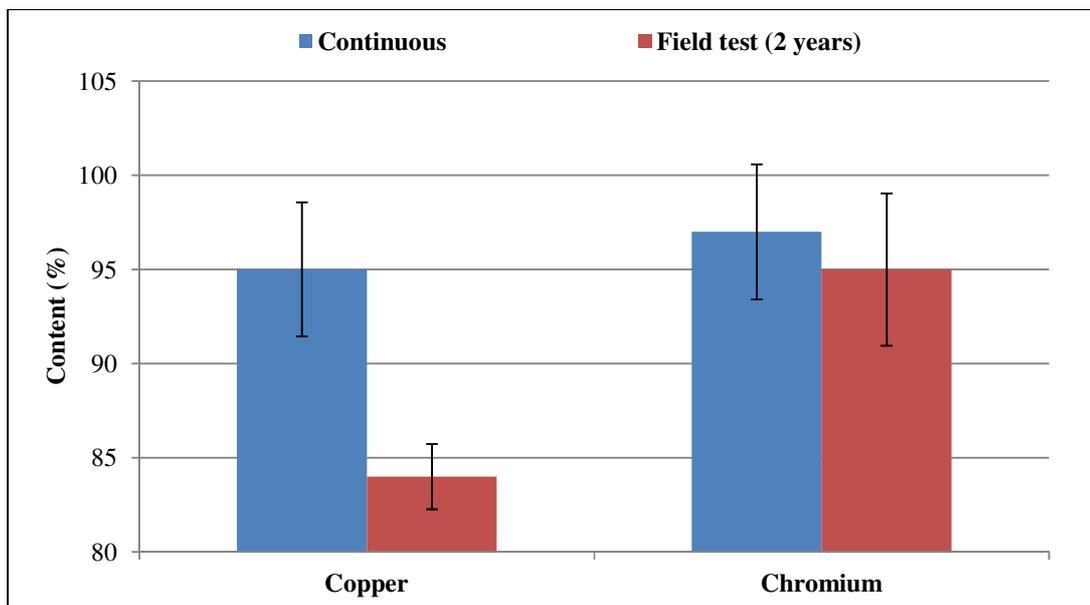


Figure 3.61: Residual metal contents in continuous experiment and field test exposure in EN 252 pine specimens after 2 years. Error bars=standard deviation

The residual content of chromium and copper of two different laboratory methods is higher than that of field test. There are a number of possible explanations for this difference. The treated stakes exposed in the field environment were subjected to more severe leaching as a result of the

intensity of rainfall, repeated wetting and drying cycles that may form checks and cracks on the specimens and direct UV light. In addition, water characteristics such as pH-value, temperature and inorganic ions have been reported to affect significantly the release of metals from treated wood (Cooper, 1991; Murphy and Dickinson, 1999), while in the standard laboratory protocols, the usually used deionized water may only remove the unfixed or poorly fixed metal components. Results also showed that chromium remaining content is higher than that of copper for both laboratory and field exposure.

In the case of non-standard pine sapwood size, after 24 months of outdoor exposure 90% of chromium and 86% of copper remained at the above ground section while higher values were found in the non-continual method, as 97% for chromium and 98% for copper (Figure 3.62). In below ground portion the amount of chromium and copper were 89 and 81%, respectively. The values of chromium and copper for continual immersion method were 96% (Figure 3.63). It can therefore be deduced that the metal depletion is greater in the field experiment (above and below ground) in comparison with both laboratory tests similar to that observed in standard specimens.

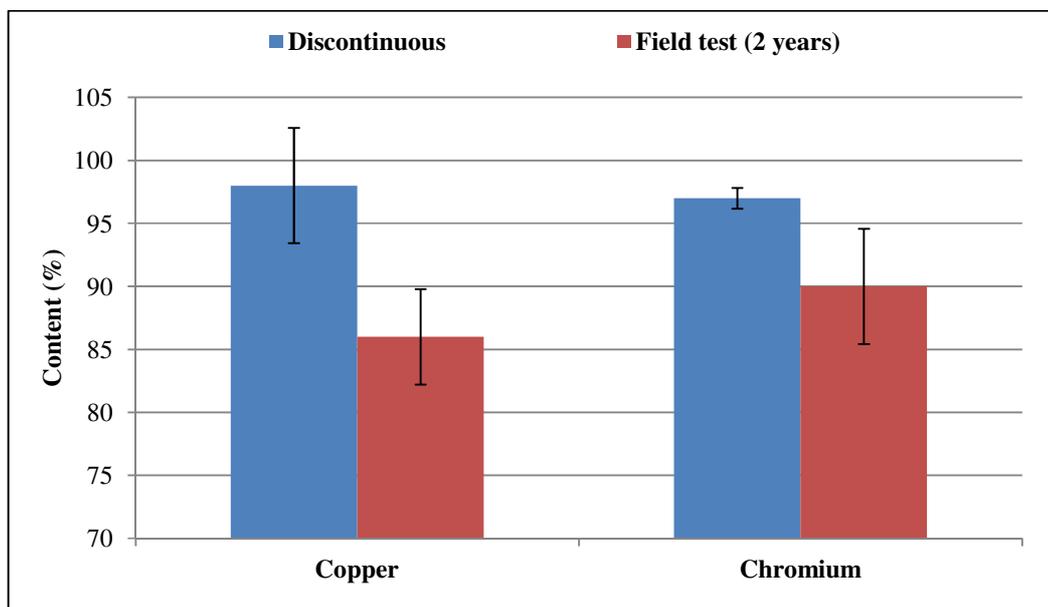


Figure3.62: Residual metal contents in non-continuous experiment and field test exposure in non-standard pine specimens after 2 years. Error bars=standard deviation

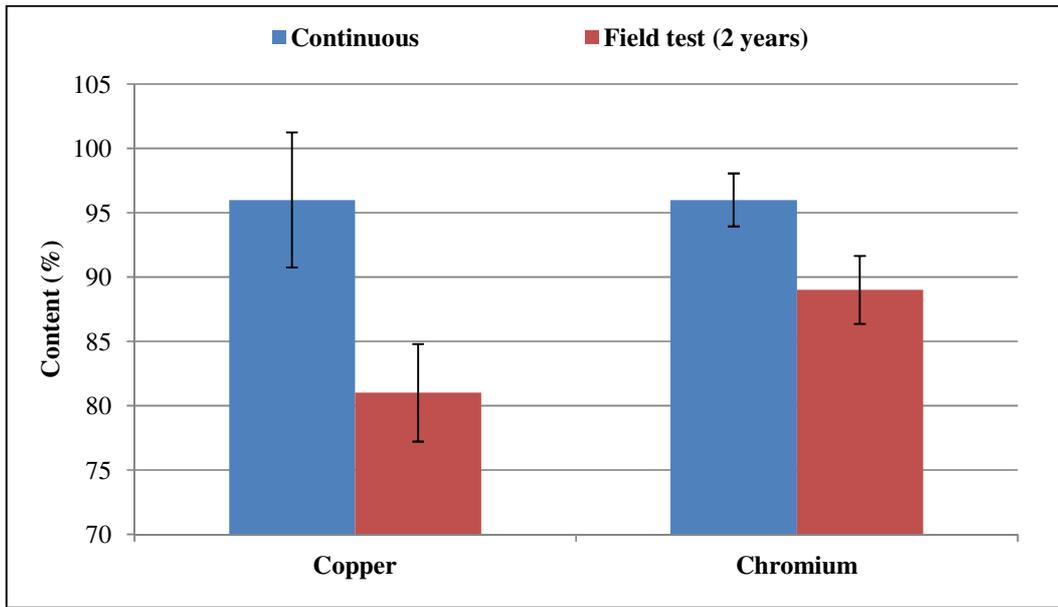


Figure 3.63: Residual metal contents in continuous experiment and field test exposure in non-standard specimens after 2 years. Error bars=standard deviation

Figures 3.64 and 3.65 show the results of the monitoring of laboratory tests and field test (after 2 years exposure) in spruce samples. Similar to standard and non-standard pine stakes, the loss of metal components in field exposure is greater than that of laboratory experiments.

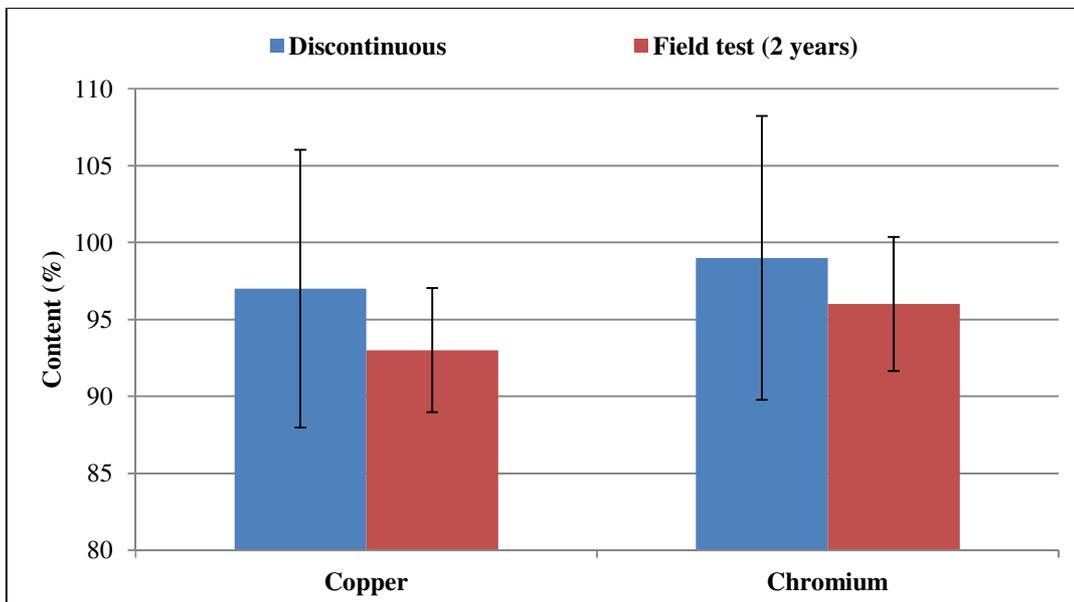


Figure 3.64: Residual metal contents in non-continuous experiment and field test exposure in EN 252 spruce specimens after 2 years. Error bars=standard deviation

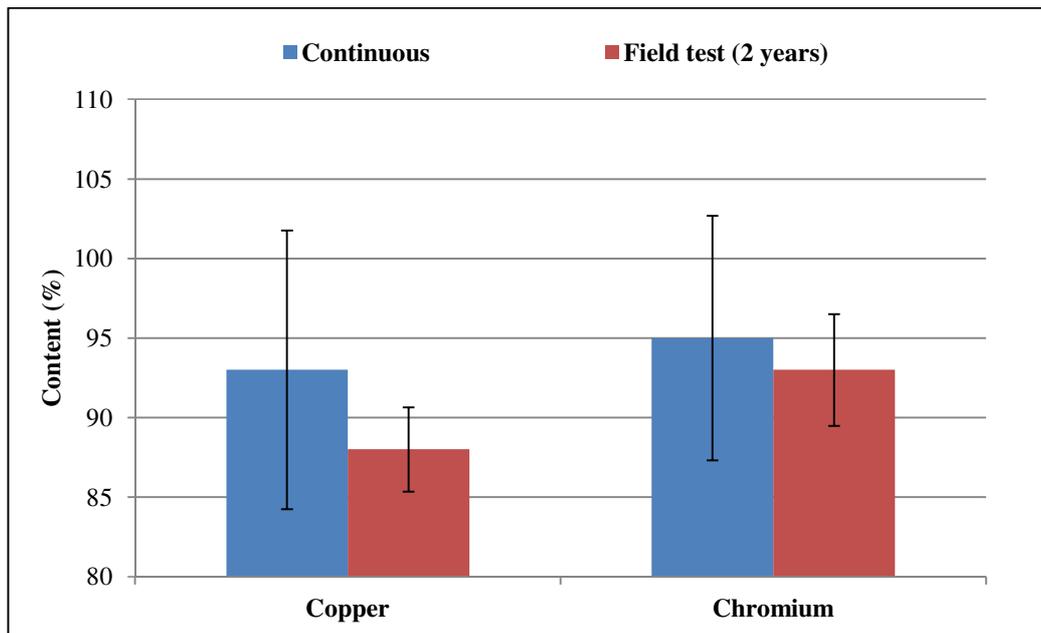


Figure 3.65: Residual metal contents in continuous experiment and field test exposure in EN 252 spruce specimens after 2 years. Error bars=standard deviation

The metal depletion in both laboratory experiments was lower than in the field exposure in all tested samples. Willeitner and Peek (1998) described the general requirements for realistic leaching tests:

- 1. as near to practice as possible,
- 2. easily to be handled and not too expensive,
- 3. comparable between test labs and test products and of high reproducibility,
- 4. short duration and should allow immediate interpretation of results.

The CEN/TS 15119-1 standard (as a discontinuous method) with modified sample size (EN 252) could be covered the options 1, 2 and 3. However, the short duration should be improved because only one-minute contact with water does not allow sufficient wetting and metal leaching. It is possible to achieve more realistic results by longer water immersion, for example 60 min as proposed in OECD Guideline (Melcher et al., 2004; Schoknecht et al., 2004).

The CEN/TS 15119-2 standard (as a continuous method) with modified sample size (EN 252) also could cover the four above requirements. However, it appears that the ratio of the water volume per surface area should be improved for larger sample (e. g EN 252) since this factor

plays an important role in metal emission and then in metal detection a low concentration. A ratio of 2 may be suitable instead of the ratio of 2.5 mentioned in the standard. This ratio can be also considered for the discontinuous method.

In developing a laboratory test method to estimate the depletion of metals from the treated wood in natural exposure, there is a need to determine the correlation between the two types of experiments.

In order to determine the potential of these laboratory methods to assess the depletion of metal components from treated wood in the field test a correlation was established between laboratory and field results. Tables 3.10, 3.11 and 3.12 show the correlation between chromium and copper content in the laboratory and field tests during outdoor exposure.

In all cases, analyses of the chromium and copper concentration in the leachate indicated that less than 1% of the metals were leached from treated during the leaching periods whereas more chromium and copper were depleted from the treated during field exposure. There are a number of possible explanations for the observed results. First, treated wood in service could be exposed to more severe conditions than during laboratory experimentation. Second, treated wood exposed under outdoor conditions subjected to the irregular wetting and drying cycles could create cracks. Cracking greatly increases the wood surface area which can lead to an increase of preservative depletion and redistribution (Choi et al., 2004; Taylor and Cooper, 2005). While one-minute contact with water in the discontinuous method may not lead to a generated concentration gradient of diffusion of metals from the inner to the outer treated layers. During the study visible cracks were observed on the wood surface and end-grain samples of the above ground section of standard and non-standard pine and spruce stakes. Third, as was observed in field exposure, a portion of metals migrated from the above ground to below ground sections in wood exposed outdoors, while as noted before, short time water immersion in the discontinuous method does not allow movement of metal ions within the wood. Fourth, a fraction of the release of preservative components in the field exposure may also be associated to photo-degradation by sunlight. A loss of approximately 0.03 mm of treated wood surface with CCA occurred by UV degradation (Feist and Williams, 1991; Williams et al., 2003). Based on this findings (i.e. considerable low metal leaching, $\%1<$), only the correlation was established between continuous and in ground contact results.

Based on the Pearson correlation analysis for residual copper content, the best correlation of the CEN/TS 15119-2 test and exposed in ground segments was observed after 8 months outdoor exposure. For remaining chromium, the best correlation was observed between the CEN/TS 15119-2 test and in contact ground segments after 8 months (Table 3.10).

In the case of the non-standard size, there was a high positive correlation between metal content during 2 years field exposure and percentage remained in the stake segments in the laboratory test. Based on the Pearson correlation analysis for residual copper, the best correlation was observed between the CEN/TS 15119-2 and in ground segments after 8 months. For chromium remaining, the best correlation between the CEN/TS 15119-2 and in contact ground segments was found after 12 months (Table 3.11).

In EN 252 spruce stake segments, based on the Pearson correlation analysis, for residual copper the best correlation between the CEN/TS 15119-2 and in ground segments was observed after 20 months. For remaining chromium, the best correlation of the CEN/TS 15119-2 and exposed out of ground segments was observed in contact ground segments was found after 8, 12 and 20 months (Table 3.12).

Results of this study showed that the residual metal content in field exposure could be assessed by using larger samples (EN 252 and non-standard samples) in the laboratory conditions with consideration of some modifications in time schedule and leaching process. For example, it is recommended that the immersion time of the dipping events can be longer than one minute in the discontinue method to better characterize the wetting and drying cycles of in-service treated wood. Also it should be mentioned that a migration/redistribution of metals within the wood stakes in the laboratory tests was not observed, whereas this was found in different intervals in field exposure. Therefore, these laboratory methods cannot be used directly for the natural leaching behavior of metal compounds.

Table 3.10: Correlation between laboratory and field test results for percentage of chromium and copper remained in EN 252 pine stake segments.

Field test/exposure time (month)	Laboratory test	
	CEN/TS 15119-2 (continual immersion)	
	Correlation coefficient (r)	Regression line
4	0.43	$y_{Cr}=0.69x+35.01$
	0.44	$y_{Cu}=0.51x+49.74$
8	0.64*	$y_{Cr}=0.73x+21.60$
	0.47	$y_{Cu}=0.35x+47.71$
12	0.49	$y_{Cr}=0.58x+38.24$
	0.27	$y_{Cu}=0.23x+62.28$
16	0.54**	$y_{Cr}=0.70x+19.42$
	0.36*	$y_{Cu}=0.33x+44.37$
20	0.57**	$y_{Cr}=0.42x+50.76$
	0.16	$y_{Cu}=0.10x+70.16$
24	0.47	$y_{Cr}=0.38x+58.32$
	-0.20	$y_{Cu}=0.14x+96.86$

* significant at the 0.05 level (at first 1*, then 2**)

Table 3.11: Correlation between laboratory and field test results for percentage of chromium and copper remained in non-standard pine stake segments.

Field test/exposure time (month)	Laboratory test	
	CEN/TS 15119-2 (continual immersion)	
	Correlation coefficient (r)	Regression line
4	0.80 ^{**}	$y_{Cr}=1.08x-5.74$
	0.63 ^{**}	$y_{Cu}=0.79x+21.43$
8	0.83	$y_{Cr}=1.37x-43.59$
	0.77 ^{**}	$y_{Cu}=1.08x-15.16$
12	0.90 ^{**}	$y_{Cr}=1.16x-20.50$
	0.74 ^{**}	$y_{Cu}=0.63x+24.96$
16	0.86 ^{**}	$y_{Cr}=0.85x+1.17$
	0.74 [*]	$y_{Cu}=0.48x+30.66$
20	0.70 [*]	$y_{Cr}=0.76x+11.83$
	0.64 [*]	$y_{Cu}=0.42x+36.66$
24	0.67 [*]	$y_{Cr}=0.61x+10.00$
	0.53 ^{**}	$y_{Cu}=0.42x+41.40$

* significant at the 0.05 level (at first 1*, then 2**)

Table 3.12: Correlation between laboratory and field test results for percentage of chromium and copper remained in EN 252 spruce stake segments.

Field test/exposure time (month)	Laboratory test	
	CEN/TS 15119-2 (continual immersion)	
	Correlation coefficient (r)	Regression line
4	0.94 ^{**}	$y_{Cr}=0.82x+17.85$
	0.40 ^{**}	$y_{Cu}=0.30x+64.83$
8	0.95 ^{**}	$y_{Cr}=1.09x-10.09$
	0.22 ^{**}	$y_{Cu}=0.22x+69.12$
12	0.95 ^{**}	$y_{Cr}=0.72x+27.00$
	0.24 [*]	$y_{Cu}=0.15x+72.36$
16	0.92 ^{**}	$y_{Cr}=0.68x+27.77$
	0.34 ^{**}	$y_{Cu}=0.18x+66.14$
20	0.95 ^{**}	$y_{Cr}=0.66x+30.75$
	0.46 ^{**}	$y_{Cu}=0.24x+61.51$
24	0.92 ^{**}	$y_{Cr}=0.97x-0.42$
	0.45 [*]	$y_{Cu}=0.40x+48.76$

* significant at the 0.05 level (at first 1*, then 2**)

4. Conclusion

This study was performed to compare laboratory and field tests for the determination of residual chromium and copper content in pine sapwood and spruce stakes treated with commercial chromium and copper. Moreover, the distribution of the metals before and after exposure and also the effects of different factors on the distribution and metal depletion including exposure time, stake position (above and in ground sections), wood species and sample size were investigated.

The results are:

- The distribution of chromium and copper in the unexposed stakes was different not only between wood species but also within the same wood species. The metal gradient was higher in spruce than in pine sapwood stakes. Metal retention in the end grains was approximately 1.5 times higher in the spruce stakes than in pine sapwood ones.
- After two years of exposure in all cases, the highest chromium and copper were found at the end grain of the stakes due to higher initial content compared to inner segments whereas the lowest metal contents were observed at the groundline of the stakes which could be due to the presence of organic acids like humic acid and much water flow in this area.
- Increase in chromium and copper content in the exposed stake segments in relation to the unexposed ones may have been due to the migration/redistribution of the metals within the treated wood.
- Copper depletion in the below ground was higher as compared to the above section in pine sapwood and spruce stakes. However, no significant differences in chromium depletion were observed between above and below portions.
- Average percentage of remaining copper of the whole stakes of EN 252 pine, non-standard and EN 252 spruce were 87, 83 and 91%, respectively after two years of exposure and remaining chromium were 96, 90 and 95%, respectively.
- No significant differences were found in chromium depletion between the two wood species after two years of exposure whereas a significant difference was found in copper depletion.

- Evaluation of sample size on metal depletion showed that metal loss in the non-standard sample size was higher than in EN 252 stakes.
- In laboratory tests, for an equivalent time of CC-treated wood in contact with deionized water, metal depletion was higher in continuous water immersion than in discontinuous one. Also, in all cases metal depletion from CC-treated wood was in the order copper > chromium. The same finding was observed in the field test exposure.
- Results illustrated that 97, 96 and 99% of chromium remained in the full EN 252 pine, non-standard and EN 252 spruce stakes whereas the copper content corresponds to 96, 97 and 98% at the end of laboratory tests, respectively.
- Comparison laboratory and field results showed that residual metal content in both laboratory tests were higher as compared to the field exposure.
- The results of the study demonstrated the importance of the consideration of the larger specimens like EN 252 in developing laboratory leaching tests to better interpretation of the leaching effects on the behaviour of preservatives during outdoor exposure.
- Additional tests on EN 252 samples in various leaching media such as rainwater, and soil water should be used to determine the amount of metal leaching in comparison with field exposure.
- Monitoring the leaching under simulated rainfall would provide knowledge on the metal leaching and their redistribution. This study could yield a better understanding of the leaching and redistribution patterns of metals in laboratory tests and above ground applications.
- Finally, surface analysis may be used to examine the crack development during field exposure and to establish the relationship between crack formations and leaching behavior.

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Appendices

Appendix 1

Mean Data -----

ID: 50ppm Cu, Cr	Seq. No.: 9	Sample No.: 9	A/S Pos: 9
Sample Qty: 1.0000 mL	Prep. Vol.: 1.0 mL	Dilution: 1.0:	1.
	Data: Original	Date: 15.09.10	09:20:49

Element	Mean Corr. Intensity	Mean Conc.	Calib Std.Dev. Units	Mean Conc.	Sample Std.Dev. Units	RSD
Cu 324.754	114227.2	51.3	0.16 mg/L	51.3	0.16 mg/L	0.32%
Cu 327.396	130619.6	51.6	0.16 mg/L	51.6	0.16 mg/L	0.31%
Cr 357.869	10173.0	49.8	0.11 mg/L	49.8	0.11 mg/L	0.23%
Cr 267.716	78721.7	50.9	0.21 mg/L	50.9	0.21 mg/L	0.42%
Cr 206.158	12452.8	50.3	0.11 mg/L	50.3	0.11 mg/L	0.23%

Mean Data -----

ID: 100ppm Cu, Cr	Seq. No.: 10	Sample No.: 10	A/S Pos: 10
Sample Qty: 1.0000 mL	Prep. Vol.: 1.0 mL	Dilution: 1.0:	1.
	Data: Original	Date: 15.09.10	09:22:45

Element	Mean Corr. Intensity	Mean Conc.	Calib Std.Dev. Units	Mean Conc.	Sample Std.Dev. Units	RSD
Cu 324.754	216840.0	97.7	0.30 mg/L	97.7	0.30 mg/L	0.30%
Cu 327.396	248135.7	98.4	0.32 mg/L	98.4	0.32 mg/L	0.33%
Cr 357.869	19657.9	96.4	0.17 mg/L	96.4	0.17 mg/L	0.18%
Cr 267.716	150437.6	97.5	0.28 mg/L	97.5	0.28 mg/L	0.29%
Cr 206.158	23968.0	97.1	0.19 mg/L	97.1	0.19 mg/L	0.20%

Appendix 2: Individual unexposed EN 252 pine sapwood data

Exposure time (month)	Segment	Chromium			Copper		
		Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %	Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %
0	A _(top)	1.88	2.02	107	1.09	1.17	107
	B		1.45	77		0.84	77
	C		1.82	97		1.05	96
	D		1.84	98		1.07	98
	E		1.82	97		1.06	97
	F		2.03	108		1.21	111
	G		1.86	99		1.10	101
	H		1.88	100		1.07	98
	I		1.97	105		1.10	101
	J _(bottom)		2.22	118		1.31	120
Mean	A-E		1.79	95		1.04	95
	F-J		1.99	106		1.16	106
	A-J		1.89	101		1.10	101

Exposure time (month)	Segment	Chromium			Copper		
		Analytical data	After analysis	Content	Analytical data	After analysis	Content
		(kg/m ³)	(kg/m ³)	%	(kg/m ³)	(kg/m ³)	%
0	A _(top)	1.98	2.30	116	1.14	1.29	113
	B		2.01	102		1.14	100
	C		1.84	93		1.04	91
	D		1.85	94		1.08	95
	E		1.62	82		0.95	83
	F		1.58	80		0.92	81
	G		1.71	86		1.00	88
	H		1.74	88		0.99	87
	I		1.72	87		0.97	85
	J _(bottom)		1.89	95		1.12	98
Mean	A-E		1.92	97		1.10	96
	F-J		1.73	87		1.00	88
	A-J		1.82	92		1.05	92

Exposure time (month)	Segment	Chromium			Copper		
		Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %	Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %
0	A _(top)	1.98	2.42	122	1.15	1.36	118
	B		2.24	113		1.27	110
	C		1.95	98		1.14	99
	D		1.95	98		1.13	98
	E		2.13	108		1.24	108
	F		2.03	102		1.19	103
	G		1.97	99		1.14	99
	H		1.93	97		1.11	96
	I		1.94	98		1.12	97
	J _(bottom)		2.40	121		1.41	123
Mean	A-E		2.14	108		1.22	106
	F-J		2.05	103		1.19	103
	A-J		2.09	105		1.20	104

Appendix 3: Individual unexposed non-standard pine sapwood data

Exposure time (month)	Segment	Chromium			Copper		
		Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %	Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %
0	A _(top)	2.10	2.16	103	1.22	1.32	108
	B		1.90	90		1.18	97
	C		1.93	92		1.13	93
	D		1.75	83		1.03	84
	E		1.55	74		0.92	75
	F		1.69	80		0.98	80
	G		1.78	85		1.05	86
	H		1.87	89		1.09	89
	I		1.87	89		1.12	92
	J _(bottom)		1.81	86		1.09	89
	Mean		A-E			1.86	89
F-J			1.80	86		1.07	88
A-J			1.83	87		1.09	89

Exposure time (month)	Segment	Chromium			Copper		
		Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %	Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %
0	A _(top)	2.04	2.31	113	1.18	1.44	122
	B		2.10	103		1.31	111
	C		1.97	97		1.15	97
	D		1.96	96		1.13	96
	E		1.47	72		0.85	72
	F		1.62	79		0.93	79
	G		1.87	92		1.05	89
	H		1.94	95		1.20	102
	I		1.99	98		1.24	105
	J _(bottom)		2.33	114		1.45	123
Mean	A-E		1.96	96		1.18	100
	F-J		1.95	95		1.17	99
	A-J		1.95	95		1.17	99

Exposure time (month)	Segment	Chromium			Copper		
		Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %	Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %
0	A _(top)	1.93	2.37	123	1.12	1.38	123
	B		2.33	121		1.36	121
	C		2.23	115		1.31	117
	D		2.41	125		1.43	128
	E		2.40	124		1.43	128
	F		1.96	101		1.15	103
	G		1.81	94		1.06	95
	H		1.84	95		1.06	95
	I		2.34	121		1.47	131
	J _(bottom)		2.32	120		1.48	132
	Mean		A-E			2.35	122
F-J			2.05	106		1.24	111
A-J			2.20	114		1.31	117

Appendix 4: Individual unexposed EN 252 spruce data

Exposure time (month)	Segment	Chromium			Copper		
		Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %	Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %
0	A _(top)	1.47	2.36	160	0.85	1.37	161
	B		1.65	112		0.92	108
	C		1.17	79		0.68	80
	D		1.18	80		0.68	80
	E		1.15	78		0.65	76
	F		1.11	75		0.62	73
	G		1.06	72		0.60	71
	H		1.29	88		0.73	86
	I		1.33	90		0.76	89
	J _(bottom)		2.34	159		1.39	163
Mean	A-E		1.50	102		0.86	101
	F-J		1.43	97		0.82	96
	A-J		1.46	99		0.84	99

Exposure time (month)	Segment	Chromium			Copper		
		Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %	Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %
0	A _(top)	1.20	1.88	157	0.69	1.13	164
	B		1.28	107		0.79	114
	C		1.10	92		0.69	100
	D		0.97	81		0.57	83
	E		0.89	74		0.49	71
	F		0.80	67		0.45	65
	G		0.88	73		0.53	77
	H		1.21	101		0.76	110
	I		1.25	104		0.80	116
	J _(bottom)		2.04	170		1.22	177
Mean	A-E	1.20	1.22	102	0.69	0.73	106
	F-J		1.24	103		0.75	109
	A-J		1.23	102		0.74	107

Exposure time (month)	Segment	Chromium			Copper		
		Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %	Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %
0	A _(top)	0.87	1.60	184	0.50	0.93	186
	B		0.88	101		0.49	98
	C		0.75	86		0.40	80
	D		0.65	75		0.37	74
	E		0.64	74		0.34	68
	F		0.63	72		0.36	72
	G		0.64	74		0.34	68
	H		0.80	92		0.42	84
	I		0.88	101		0.50	100
	J _(bottom)		1.58	182		0.92	184
Mean	A-E		0.90	103		0.51	102
	F-J		0.91	104		0.51	102
	A-J		0.90	0.90		0.51	102

Exposure time (month)	Segment	Chromium			Copper		
		Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %	Analytical data (kg/m ³)	After analysis (kg/m ³)	Content %
0	A _(top)	0.97	1.70	175	0.56	0.97	173
	B		1.00	103		0.52	93
	C		0.72	74		0.39	70
	D		0.63	65		0.35	62
	E		0.54	56		0.30	54
	F		0.53	55		0.28	50
	G		0.52	54		0.27	48
	H		0.71	73		0.40	71
	I		0.91	94		0.52	93
	J _(bottom)		1.64	169		0.95	170
Mean	A-E		0.92	95		0.51	91
	F-J		0.86	89		0.49	87
	A-J		0.89	92		0.50	89