# LEACHING AND DURABILITY OF COPPER TREATED SCOTS PINE (*PINUS SYLVESTRIS* L.) WOOD

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**Abstract**
Scots pine (*Pinus sylvestris* L.) is the most common wood species in Latvia. It is classified as not durable, therefore additional protection against microorganisms is needed prior its use outdoors. Presently Cu-containing wood preservatives are commonly used, but the biggest drawback is the poor Cu fixation, therefore raising concerns about the impact on the environment. Three types of specimens were used to carry out the experiments – untreated, Latvian originated Scots pine; Scots pine commercially treated with preservatives that belong to a group of Cu-boron-triazole (CBA) products; and Scots pine, impregnated with micronized-Cu solution using a standard full cell process. In order to make sure that all of the specimens are equal in their components, elemental analysis was performed and content of nitrogen (1.2 – 2.5 g $kg^{-1}$), carbon (485.5 g $kg^{-1}$), oxygen (456.0 g $kg^{-1}$) and hydrogen (55.6 g $kg^{-1}$) was determined. The treated specimens were leached according to the European standard EN 84. For micronized-Cu impregnated Scots pine the total Cu content in leachates obtained by atomic absorption spectroscopy was 0.15 mg $g^{-1}$ of wood, and 0.06 mg $g^{-1}$ of absolute dry matter with CBA preservative impregnated Scots pine wood. Subsequently, according to the European standard EN 113, treated Scots pine blocks were exposed to brown-rot fungus C*oniophora puteana* and to white-rot fungus *Trametes versicolor* for 16 weeks. Mass loss for wood treated with micro-Cu was 48.4% (484 g $kg^{-1}$) and 1.5% (15 g $kg^{-1}$) respectively, but for CBA – 49.5 % (495 g $kg^{-1}$) and 1.2% (12 g $kg^{-1}$). Both samples proved to be inappropriate for outdoor use (use class 3).
**Key words:** copper, leaching, Scots pine, fungal decay.

## Introduction

Wood is a very valuable material, being rather inexpensive and easy to process, it has good mechanical properties and aesthetic appeal. But as every material does, it has some drawbacks. The strongest drawback being, microorganisms degrade wood during its usage, especially, when this material is used outdoors. Among the microorganisms, brown-rot fungi cause the most considerable damage during the wood service life (Irbe et al., 2006). Scots pine (*Pinus sylvestris* L.) is the most common wood species in Latvia and according to European Standard EN 350-2 (1994) its sapwood is considered to belong to durability class 5 - naturally not durable. To prevent wood from biodegradation, wood protecting substances are used, water-born solutions being the most popular among them. Chromated copper arsenate (CCA) was the most frequently used solution historically, however, since 2003 (Commission Directive 2003/2/EC, 2003) two main components of this substance – $Cr^{6+}$ and $As^{5+}$ are prohibited because of the toxicity to human health and the environment (Shibata et al., 2007). Only $Cu^{2+}$ which was also a CCA component is allowed today, and thus many Cu based wood preservatives have been developed. Cu has many advantages – it is relatively easy to create waterborne formulations, analyze and determine its penetration in wood; additionally Cu slows wood degradation by UV radiation and water. Preservatives contain Cu as the main fungicide, along with additional organic fungicides, protecting wood from such fungi species as *Serpula*, *Antrodia* and *Postia* that benefit from presence of Cu (Grantiņa-Ieviņa, 2013). Usually quats, azoles or borates are used as additional fungicides. These preservatives contain amines or ammonia as Cu soluble and complexing substances (Temiz et al., 2006; Hasan et al., 2010). Nordic Wood Preservation Council (Salminen et al., 2014) has approved many preservatives, among them Cu-boron-triazole (CBA) products that can be used for treatment of wide range of softwood species.

One of the processes in material usage outdoors is leaching, in this process components of wood preservatives seep in the environment and therefore can pose a threat to it (Vetter et al., 2008). Leaching is a standardized procedure for accelerated ageing (EN 84, 1997) and is commonly used for impregnated wood testing. Insufficient fixation is the main drawback of Cu usage (Wang et al., 2013). Previously used chrome substances currently are replaced with amines, predominately, ethanolamine (Pankras et al., 2012) or micronized-Cu solutions (Matsunaga et al., 2008; Stirling et al., 2008; Xue et al., 2012) with poor fixation properties. Although Cu is an essential micronutrient for most living cells, in larger doses it acts as an algaecide, bactericide, fungicide, insecticide and moldicide (Freeman and McIntyre, 2008). Therefore raising concerns about environmental impact of treated wood in areas of agricultural use (Love et al., 2014).

The aim of this study was to compare Scots pine treated with Cu containing preservatives in terms of fixation and decay resistance.

**Materials and Methods**

The experiments were carried out in the Laboratory of Wood Biodegradation and Protection of the Latvian State Institute of Wood Chemistry from August 2014 till March 2015.

*Specimens*

All of the samples were tested keeping in mind that material should agree with the European Standard EN 350-2 (1994) Class 3 – to be used in a situation in which the wood or a wood–based product is not under cover, and not in contact with the ground. Three types of specimens were used to carry out the experiments – untreated Latvian originated Scots pine from sawmill; Scots pine wood treated with preservative that belongs to a group of Cu-boron-triazole products, containing 295 g $kg^{-1}$ $CuCO_3$, 45 g $kg^{-1}$ $H_3BO_3$, 2.3 g $kg^{-1}$ tebukonazol and 2.3 g $kg^{-1}$ propicionazol. For the third type Scots pine planks were conditioned and afterwards impregnated with micronized Cu containing solution (ethanolamine < 60 g $kg^{-1}$, CuO complex < 25 g kg $^{-1}$, alkildimethylbenzilamonnia chloride < 10 g $kg^{-1}$ and didecildimethyl ammonium chloride < 10 g $kg^{-1}$ using a standard full cell (Bethell) process (30 min vacuum 0.2 bar, 60 minutes pressure 10 bar, 15 min vacuum 0.5 bar). Afterwards samples, free of any physical defects, were sawn in 50 × 25 × 15 mm blocks for leaching and decay tests, part of the samples was chopped to sawdust with Retsch SM100 mill, mesh size 2 mm for elemental analysis.

*Elemental analysis*

Elemental analysis of the specimens was conducted according to standard LVS EN 15104 (2011) using Vario MACRO CHNS, Germany, carbon/nitrogen/hydrogen and sulfur analyzer with helium as carrier gas. Three replicates of 20-30 mg are packed in aluminium foil, weighted, $WO_2$ powder is added at ratio 1:3 and combusted in the presence of oxygen in a flowing helium stream. The original matrix of the sample is destroyed under these conditions and through subsequent catalytic reactions, the analyte components are formed into $CO_2$, $N_2$, $H_2O$ and $SO_2$. The oxygen content is calculated as shown in Equation 1:

$$1000g - (C + H + N + S) = O \quad (1)$$

where

C – total carbon concentration, g $kg^{-1}$

H – total hydrogen concentration, g $kg^{-1}$

N – total nitrogen concentration, g $kg^{-1}$

S – total sulfur concentration, g $kg^{-1}$

O – total oxygen concentration, g $kg^{-1}$

*Leaching*

Material preparation and leaching procedure was developed according to European Standard EN 84 (1997). The leaching procedure consisted of an initial impregnation with distilled water under 4 kPa vacuum for 20 min. The water was subsequently replaced 2 h after the impregnation, continuing at 24 h and 48 h, and another seven times in the next 12 days at intervals of not less than 1 day and not more than 3 days. The leachates were collected, their volume measured and stored in 5 °C until the Cu content analysis. The Cu content was determined by an atomic absorption spectroscopy. The atomic absorption was carried out using Atomic absoption spectophotometer SHIMADZU AA-6300.

*Fungal strains*

Two fungal strains were used in this study: the brown-rot fungus *Coniophora puteana* (Schum.: Fr.) Karst (BAM Ebw. 15) and the white-rot fungus *Trametes versicolor* (L.) Lloyd (CTB 863A). Isolates were maintained in Petri dishes on a medium containing 50g $kg^{-1}$ malt extract concentrate and 20 g $kg^{-1}$ agar (Fluka, Sigma-Aldrich). Mycelium plugs were transferred aseptically to Kolle flasks, containing the same medium as in Petri dishes, for the wood decay test.

*Decay test*

Moisture content was determined for treated and untreated sapwood blocks (50 × 25 × 15 mm) of Scots pine (*Pinus sylvestri*s L.). Afterwards specimens were exposed to *Coniophora puteana* and to *Trametes versicolor* for 16 weeks at 22 °C and 70% relative humidity. Before exposure to fungi treated Scots pine wood blocks were leached according to the European standard EN 84 (1997). The decay test procedures were done according to the European standard EN 113 (1996). Eight replicates for each of the fungus were taken. Subsequent to cultivation, blocks were removed from the culture vessels, brushed free of mycelium and oven dried at 103 ± 2 °C. The percentage of weight loss was calculated from the dry weight before and after the test.

The results were processed by mathematical and statistical methods calculating mean values and standard deviations of samples with Microsoft EXCEL 2010 software. The statistical difference between results was calculated using Student t-test. Values in the range of $p<0.05$ were considered statistically significant.

**Results and Discussion**

In order to ascertain homogeneity among untreated, commercial and impregnated Scots pine wood, the

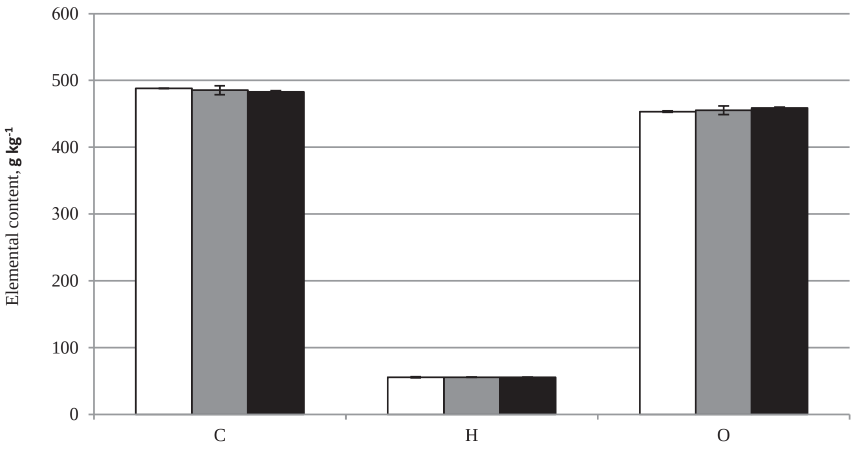


Figure 1. Elemental content of specimens:
□untreated Scots pine ■CBA ■Micro-Cu

elemental analysis was conducted. Figure 1 displays that there is only an insignificant difference among elemental content of all specimens. Scots pine wood contains 48.5 ± 0.25% (485.5 ± 2.5 g kg$^{-1}$) carbon, 45.6 ± 0.28% (456.0 ± 2.8 g kg$^{-1}$) oxygen and 5.56 ± 0.01% (55.6 ± 0.1 g kg$^{-1}$) hydrogen. Student test shows that there are statistically significant differences ($p<0.05$) among nitrogen contents in specimens of all types. The nitrogen content in untreated, commercially treated and impregnated Scots pine wood is 0.18 ± 0.01 % (1.8 ± 0.1 g kg$^{-1}$), 0.25 ± 0.04% (2.5 ± 0.4 g kg$^{-1}$) and 0.14 ± 0.02% (1.4 ± 0.2 g kg$^{-1}$) accordingly. Considering the small amount of nitrogen content in Scots pine wood, variety of wood material itself and the small samples needed for this analysis, the nitrogen content can be considered the same in all samples. H. Matsunaga et al. (2008) has analyzed southern pine boards treated with an aqueos dispersion of Cu carbonate and iron oxide particles (nano-Cu preservative). Energy-dispersive X-ray spectroscopy showed that wood cell walls contain 53% (530 g kg$^{-1}$) C, 40% (400 g kg$^{-1}$) O, 65% (65 g kg$^{-1}$) H and 0.5% (5 g kg$^{-1}$) N, which coincides quite well with the results obtained in this research.

The Cu content in leachates obtained according to the European standard EN 84 (1997) is shown in Figure 2. For both specimens leaching rates are high initially and decrease significantly over time (after 200 h). This coincides with findings of A. Temiz et al. (2006). The total amount of leached Cu is 0.15 mg g$^{-1}$ absolute dry matter for Scots pine impregnated with micro-Cu. Less than twice the amount of Cu – 0.06 mg g$^{-1}$ absolute dry matter leaches from impregnated wood that belong to group Cu–boron-triazole products

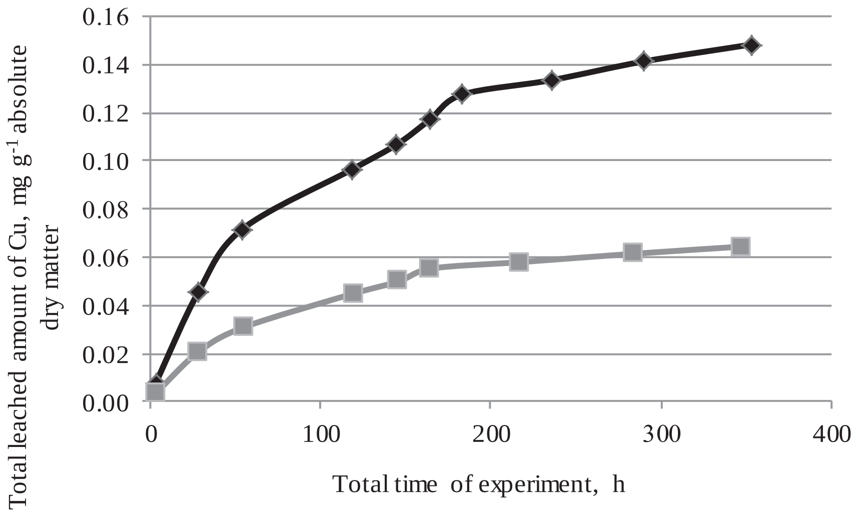


Figure 2. Total leached amount of Cu during artificial ageing:
Micro-Cu CBA

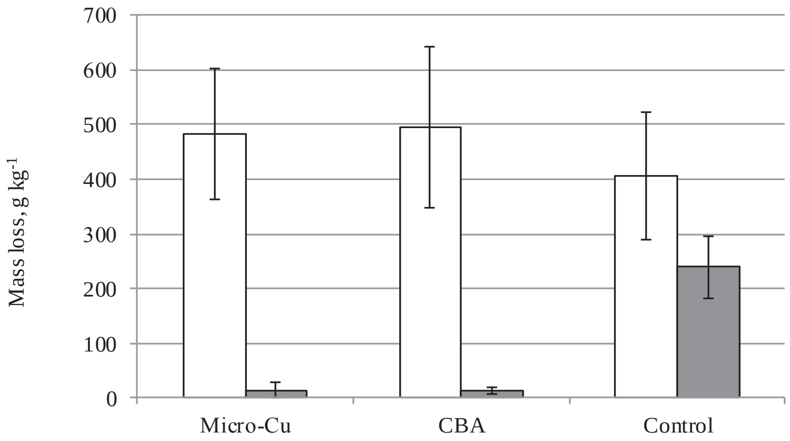


Figure 3. Mass loss of samples after fungi efficacy:
□ *Coniophora puteana* ■ *Trametes versicolor*

(CBA) according to (Salminen et al., 2014). These preservatives form complexes that do not involve cell wall components; they have different fixation mechanisms which leads to high Cu amount leached. Though M. Lupsea et al. (2013) states that Cu release is relatively high with respect to its initial content and Cu is bound on carboxyl and phenolic sites and forms soluble complexes with extractives. According to H. Matsunaga et al. (2008), these complexes aggregate into pits that connect cellular elements in wood and on the cell walls, suggesting that they are too large to penetrate them.

A. Temiz et al. (2014) has conducted a similar research – they reported that the total amount of leached Cu from CBA treated Scots pine wood was 470 mg $m^{-2}$. Recalculating units from mg $g^{-1}$ to mg $m^{-2}$ it is only 145 mg $m^{-2}$ in the current research. As N. Thaler et al. (2013) state that more intense leaching occurs from specimens with higher Cu content, because Cu deposits on the surface of the specimens and form Cu crystals in cell lumina, the difference between the results obtained by A. Temiz et al. (2014) and results in this research can indicate that initial Cu content was considerably higher in laboratory impregnated specimens than in commercially available ones.

It was expected that because of leached Cu amount there are going to be differences in mass loss of samples due to exposure to *Coniophora puteana* and *Trametes versicolor*. However, in Figure 3 it can be seen that mass loss after *Coniophora puteana* is 48 ± 12% (480 ± 120 g $kg^{-1}$) for wood impregnated with micro-Cu and 50 ± 15% (500 ± 150 g $kg^{-1}$) for CBA wood. This indicates that after leaching none of the chemical preservatives provided effective protection against *Coniophora puteana*. Coniophora puteana belongs to brown rot fungi that degrade wood cellulose and hemicelluloses, whereas lignin is modified (Janberga et al., 2013). The mass loss due to exposure to white-rot fungi *Trametes versicolo*r is 1.5 ± 1.5% (15 ± 15 g $kg^{-1}$) for with micro-Cu impregnated wood and 1.2 ± 0.7% (12 ± 7 g $kg^{-1}$) for CBA wood. This indicates that both of the chemical preservatives after leaching were effective against *Trametes versicolor*, probably because of non-evaporated ethanolamine in preservatives that causes depolimerisation of lignin (Humar et al., 2008) and prevents the growth of fungi.

A similar phenomenon has been observed previously. Cu leaching data and performance data were not clearly correlated in the experiment (Thaler et al., 2013), where Cu-ethanolamine impregnated Scots pine was exposed to terrestrial microorganisms, besides Cu-ethanolamine preservative exhibits good performance in soil (12% (120 g $kg^{-1}$) mass loss after 18 weeks with Cu concentration 0.125% (1.25 g $kg^{-1}$)). A. Temiz et al. (2014) also investigated Scots pine wood treated with CBA. Decay test was made according to the European Standard EN 113 (1996) and mass loss due to exposure to *Coniophora puteana* was 0.28% (2.8 g $kg^{-1}$) for unleached specimens. After accelerated ageing, according to the European Standard EN 84 (1997), mass loss was 0.19% (1.9 g $kg^{-1}$). These results are considered to fit durability class 3 according to the European Standard EN 350-2 (1994). These results significantly differ from the results obtained in this research, presumably because of the higher initial Cu content in the wood samples, as mentioned before.

## Conclusions

As expected, wood impregnation with micro-Cu or Cu-boron-triazole containing wood preservatives does not affect elemental composition of wood.

Both of investigated treatments proved to be inappropriate for wood materials that can be used outdoors (durability class 3, EN 350-2, (1994)) because of its sensitivity to brown-rot fungi C*oniophora puteana.* It is likely that concentrations of preservatives used on wood were too low. It is recommended to repeat the experiment using higher concentrations in order to provide sufficient protection. However, the treated wood met the requirements for the 3rd durability class due to mass loss after exposure to *Trametes versicolor*. It could be due to the altered structure of lignin after exposure to ethanolamine as lignin is the most affected wood component due to exposure to white-rot.

During leaching micro-Cu impregnated wood releases twice as much Cu than Cu-azole treated wood. However, it is not clearly perceivable, why there are no statistically significant differences between mass losses of both treated specimens, due to exposure to *Coniophora puteana*.

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