Copper Leaching from Copper-ethanolamine Treated Wood: Comparison of Field Test Studies and Laboratory Standard Procedures

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Copper-based compounds are some of the most important biocides for the protection of wood in heavy duty applications. In the past, copper was combined with chromium compounds to reduce copper leaching, but a recent generation of copper-based preservatives uses ethanolamine as a fixative. To elucidate the leaching of copper biocides from wood, Norway spruce (*Picea abies*) wood was treated with a commercial copper-ethanolamine solution with two different copper concentrations (c_{Cu} = 0.125% and 0.25%). The aim of this research was to compare the laboratory leaching standards (ENV 1250-2, CEN/TS 15119-1, and CEN/TS 15119-2) with the field leaching studies in ground and above ground. The results indicated that the first leaching peak appears in the initial phases of leaching, both in laboratory and field studies. The degree of copper leaching is also affected by the method of treatment; copper-ethanolamine preservative solutions, when applied with superficial treatments, are more prone to leaching than is vacuum-pressure treated wood. On average, between 25% and 36% of copper was leached from the impregnated wood after 42 months of exposure.

Keywords: Copper; Emissions; In-ground application; Above ground application; Laboratory; Norway spruce; Leaching

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INTRODUCTION

Copper-based active ingredients are the most important biocides for the impregnation of wood in heavy duty applications in the European Union (EU). The majority of other alternatives were removed from the market after the implementation of the Biocidal Products Directive (European Parliament and the Council of the European Union 1998 and 2012) in 2006. In addition to creosote, copper-based biocidal formulations are the only solutions allowed for the protection of wood in in-ground applications (Hughes 2004). Copper has been used for centuries, as it provides excellent performance for reasonable costs (Morrell 2006). Furthermore, the negative influence of copper compounds on the environment has been considered as acceptable (Englot 2006). Therefore it is expected that copper-based preservatives will keep their place in the field of wood protection.

Copper compounds are rarely used alone. They are combined with other additives, which enable the fixation of copper and improve its efficacy against insects and copper-tolerant fungi (Preston 2000). In the past, copper was mainly combined with chromium and arsenic (CCA), or chromium and boron (CCB). However, after the introduction of Biocidal Products Directive (European Parliament and the Council of the European Union 1998) in the EU and the voluntary withdrawal of CCA-treated wood for residential applications within North America, copper-ethanolamine based wood preservatives have been used instead (Freeman and McIntyre 2008). This wood preservative is still one of the most important wood protectants used all over the world. There are several varieties available on the market. To improve performance of these preservatives, they are supplemented with quaternary ammonium compounds, such as boron, azoles, and other secondary fungicides and insecticides (Lupsea *et al.* 2013a). A new generation of copper-based wood preservatives based upon micronized copper has also been introduced in the past few years. They are predominately used for the impregnation of permeable softwood species, such as southern yellow pine, but are less suitable for refractory wood species such as spruce. However, use of copper-ethanolamine systems is now much smaller than micronized copper for residential lumber uses in US. On the other hand, these preservatives are not approved in the EU as of yet, but will likely influence the market.

One of the main issues related to copper-based preservatives is leaching. Fixation of copper-chromium based wood preservatives is well understood and has been investigated in laboratory and field trials. This type of preservative has been in use for almost a century, and thus a lot of service data are available (Richardson 1997). Copper-ethanolamine wood preservatives have been in use for a considerably shorter time, and therefore offer much less available data. There are different types of copper-ethanolamine wood preservatives on the market. The most important difference is in the selection of the co-biocides, as well as the use of additives that reduce leaching and improve penetration (Freeman and Mcintyre 2008). Users of the copper-ethanolamine treated transition poles reported some unexpected failures after rather short periods of time. Past laboratory studies showed that some brown rot fungi (Humar *et al.* 2002) and soft rot fungi (Thaler *et al.* 2013) can influence the solubility of copper. It seems that oxalic acid, which is formed by several brown rot fungi, can interact with copper-ethanolamine complex. This forms a water-soluble compound, which is then easily leached from wood. However, this mechanism is significant for wood in in-ground use, but not for wood in above-ground applications. Copper leaching from wood treated with copper-ethanolamine is predominately linked to the depolymerisation of lignin caused by ethanolamine that is not complexed with copper. Very few investigations related to copper leaching from copper-ethanolamine treated wood have been reported. Evans (2002) reported that between 65% and 80% of the copper was leached from the copper-ethanolamine treated wood within five years of in ground exposure. However, only the final result is reported in this study; thus, the leaching dynamics is not explained. Tao *et al*. (2013) performed a medium-term leaching study based on the collection of the leachates. This study indicates that the highest loss of active ingredients appears in the first period of exposure, and afterwards, leaching decreases slowly through the following month of exposure. As field leaching studies are rather time consuming, laboratory leaching studies have been performed more frequently. They are the basis for environmental assessments and for estimating the performance of new wood preservatives.

The advantages of laboratory leaching procedures are that one can obtain repeatable results in a rather short period. Secondly, the influence of various parameters, such as wetness, pH, and water composition, *etc.*, can be easily studied. In contrast, in nature wood is exposed to a mixture of biotic and abiotic factors that influence copper leaching. There are several laboratory leaching techniques available. The intention of this research is not to overview or examine all of them, but to compare the novel leaching techniques with leaching under outdoor conditions. The influence of some old methods on leaching of biocides from wood has been resolved in our past work (Lesar *et al.* 2008). The earliest of these were developed to study the chemicals interactions between wood and active ingredients, such as the DIN 52172-2 standard (1972), which prescribes that the wood specimens have to be split into small wood splinters. Even though this standard was not designed for any particular application, it has been very useful for assessing the chopper-chromium binding capability in wood; however, the method is not suitable for assessing the leaching of chemicals from wood in above ground applications. The next generation of leaching standard was ENV 1250-2 (1995); this standard was the first one to include a short drying period. In the last decade, there has been a considerable public interest in the leaching of toxic chemicals from pretreated wood. Existing standards do not reflect the conditions in these particular applications. Therefore, a new generation of standards based upon the OECD recommendations (Health and Safety Division Environment Directorate 2007) have been developed. One standard for above ground applications, CEN/TS 15119-1 (2008), prescribes shorter leaching periods, which simulates short rain events followed by drying phase, while another standard applications, CEN/TS 15119-2 (2013), prescribes longer leaching periods, which simulates in-ground leaching, and is based on simple immersion tests.

The prime objective of this paper was to elucidate copper leaching dynamics from wood exposed in in-ground and above-ground applications and compare it to different standardized procedures used to estimate the emissions of biocides from treated wood to the environment. Assessment of leaching is important for two reasons; first, the active ingredients should remain in wood as long as possible, as this ensures sufficient service life (Hingston *et al.* 2001); and second, leaching studies are important to elucidate the emissions of hazardous chemicals from wood. This issue will become more and more important. Furthermore, field leaching studies can also provide essential information for the modeling of leaching and service life of pretreated wood (Tiruta-Barna and Schiopu 2011).

EXPERIMENTAL

For impregnation, a commercial copper-ethanolamine wood preservative solution (Silvanolin®, Silvaprodukt, Slovenia) was used. The preservative solution consisted of five ingredients: copper(II) hydroxide/carbonate, ethanolamine, alkyl diethyl benzyl ammonium chloride, octanoic acid, and disodium octaborate tetrahydrate (Humar and Pohleven 2008). There were two concentrations used. The aqueous solution of the highest concentration (c_{Cu} = 0.25%) was predominantly used for in-ground applications (class 4), while the preservative of the lowest concentration (c_{Cu} = 0.125%) was used for above-ground uses (class 3). The copper-to-ethanolamine ratio of Silvanolin® was 1:6, while the concentration of the alkyl diethyl benzyl ammonium chloride was the same as the concentration of copper. The experiments were performed on Norway spruce sapwood (*Picea abies* (L.) Karst.). Five different tests were performed: three laboratory test studies and two field test studies. Although spruce wood is very difficult to impregnate, the experiment was performed on Norway spruce wood as this is the most important construction material in the Central Europe, and impregnated spruce wood is a preferred material for outdoor use as well.

Laboratory Tests

For the laboratory leaching study, uniform specimens were prepared. The dimensions (1.5 × 2.5 × 5.0 cm) and orientation of the specimens were according to the ENV 1250-2 (1995) standard requirements. Transverse surfaces of the samples were end sealed, due to the requirements of the standard. They were vacuum-pressure impregnated according to the full-cell process (Thaler *et al.* 2012). This process consisted of 20 min of vacuum (2×10^4 Pa), 180 min of pressure (8×10^5 Pa), and 5 min of vacuum (2×10^4 Pa). Afterwards, impregnation uptake of preservative solution was determined gravimetrically. Impregnated specimens were conditioned in a closed chamber for the first two weeks after the treatment, in a half-closed chamber for the third week, and in the open for the fourth week, according to ENV 1250-2 (1995). Leaching was performed according to three different procedures: ENV 1250-2 (1995), CEN/TS 15119-1 (2008), and CEN/TS 15119-2 (2013).

The ENV 1250-2 (1995) procedure requires the shortest leaching time; it is completed in only four days. To further speed up the experiment, the following two modifications were made: (1) three specimens instead of five were positioned in the same vessel; and (2) water mixing was achieved by employing a non-rotary shaker (S-500×1100, Kambič d.o.o., Semič, Slovenia) instead of a magnetic stirrer. To perform three parallel leaching studies, nine specimens for each of the two concentrations were placed in three vessels (three specimens per vessel). Samples were secured with a weight to prevent them from floating. Distilled water (300 g) was added, and the vessel with its contents was shaken with the frequency of 60 rpm. Water was replaced six times in five subsequent days, as described by the standard ENV 1250-2 (1995) and illustrated in Table 1.

Leaching of the samples took three weeks in accordance to the modified CEN/TS 15119-2 (2013) test procedure. Three specimens were positioned in the container with 300 mL of deionized water. Water was replaced 9 times over the following 21 days (Table 1). In total, 9 specimens were leached in three parallel vessels.

In contrast to ENV 1250-2 (1995) and CEN/TS 15119-2 (2013) test methods, the CEN/TS 15119-1 (2008) standard is based on non-continuous leaching. This method prescribes that the specimens should be exposed to water for a relatively short period of time within three weeks. To obtain comparable results, three specimens with end-sealed transverse surfaces were immersed into 300 g of distilled water for 1 min and afterwards dried for 2 h. Each leaching day consisted of three leach-dry cycles as described above. Nine leaching days were present during the 21-day experiment. Distribution of the leaching days is shown in Table 1. Copper content was determined at the end of each leaching day. After the leaching the copper content in leachates was determined by X-ray fluorescence (XRF; Twin-X; Oxford Instruments, UK). For the leachates having concentrations lower than 10 ppm as analyzed by XRF, leachates were reanalyzed with atomic absorption spectroscopy (Varian SpectrAA Duo FS240; Varian Inc.; Walnut Creek, CA). The copper concentrations determined with both techniques in the range between 10 and 7 ppm were compared, and if there was notable difference present, analyses were repeated. XRF measurements were performed with a PIN detector (U = 26 kV, I = 112 µA, t = 360 s). There was no preparation of leachates required. Again, nine parallel specimens per solution/concentration were utilized in three leaching vessels. At the end of the leaching procedures, moisture content (MC) of the samples was determined gravimetrically. The percentage of leached copper was expressed as the ratio between the amount of retained copper determined gravimetrically from the uptake of preservative solution and the amount of copper in collected leachates.

Field Tests

For the first outdoor leaching experiment, cylindrical specimens (*r* = 1.6 cm; *h* = 1.8 cm) were prepared that fit the sample holder of the XRF device. Both impregnation and leaching take place through the top circular surface of the specimen; the remaining surfaces of the specimen were sealed with epoxy resin (Epolor; Color Medvode; Slovenia) prior to impregnation to prevent leaching. Samples were only impregnated with copper-ethanolamine solution of the highest concentration. Seven different impregnation methods were utilized (Table 3). These methods were chosen firstly, as they are commercially used, and secondly because they were well able to simulate a whole range of the different retentions (solution uptakes) and depth of penetrations. Afterwards, impregnation uptake of the preservative solution was determined gravimetrically. Dried and conditioned samples were then positioned on the sample holder and exposed to weathering 50 cm above-ground at the field test site in Ljubljana, Slovenia (46°2'55,57"N, 14°28'44,66"E) for a time period covering November 17, 2008 to November 10, 2009. Average temperature in Ljubljana is 10.2 °C, average precipitation is 1368 mm, and average number of rainy days is 155. Copper concentration on the surface layer of the samples was determined prior to exposure and was measured eight times during the exposure, usually after extensive rainfall. From the differences between copper concentrations, leaching rates were calculated. Samples were air-dried for three days prior to the analysis. For each treatment, five parallel specimens were milled together in a SM 2000 Retch mill (Retch GmbH; Haan, Germany), and three parallel tablets (r = 16 mm; d = 5 mm) were pressed with a Chemplex Sprectro pellet press (Chemplex Industries Inc., USA) from the milled material. The copper content in the tablets was determined with a Twin-X XRF spectrometer. Total leached copper was expressed as the ratio between the amount of retained copper determined gravimetrically from the uptake of preservative solution and the amount of remained copper determined with XRF.

A second field test was performed on the larger specimens (1.5 × 2.5 × 30 cm) with unsealed surfaces. The specimens were vacuum-pressure impregnated with both concentrations of the copper-ethanolamine solution, as previously described. After impregnation, the uptake of preservative solution was determined gravimetrically. After drying and conditioning, samples were exposed to two different use class applications (class 3 and 4 use class as defined by standard EN 335 (2013)). Specimens (n = 60) undergoing the above-ground conditions were positioned horizontally 50 cm above the ground and exposed to weathering. The remaining specimens (n = 100) were positioned vertically in the soil, with the upper 5 cm left above the soil level. Exposure began on November 5, 2009 in the field test site in Ljubljana, Slovenia. Five parallel specimens were collected for each exposure period, oven dried (24 h at 103 °C), milled, and analyzed by XRF for copper content as previously described. During processing of the specimens, depth of the penetration and potential decay was assessed as well. Statistical analysis was performed with Statgraphics Centurion XVI software, version 15.2.11 (Statpoint Technologies, Inc.; Warrenton, VA).

RESULTS AND DISCUSSION

Laboratory Tests

Impregnation of the specimens with copper-ethanolamine compounds resulted in good uptake ranging between 514 kg/m^3 and 533 kg/m^3. Such high uptake indicates that the samples were fully penetrated with copper-based treatment solution. Full penetration was evident from the cross-section of the samples as well. Uptakes were in line with other literature data (Humar and Lesar 2009).

Copper compounds without fixation additives (*e.g.*, ethanolamine) are extremely prone to leaching. In four days of leaching according to the ENV 1250-2 standard (1995), the amount of copper leached from copper (II) sulphate treated wood was 20% to 36% (Lesar *et al.* 2008). The addition of ethanolamine considerably decreased the copper leaching, as shown in Table 1. Wood impregnated with the highest concentration of active ingredients lost an average of 3.4% of its copper content, while comparable copper leaching was observed for specimens impregnated at the lower concentration (*i.e.*, 4.7% loss of copper). Regardless of the concentration used during impregnation, the highest leaching rates were observed during the initial leaching periods. The concentration of copper in the leachates then continuously decreased. During the first leaching period, copper predominately deposited on the wood's surface is leached. Thus, even a short period of time was sufficient to remove copper deposited on the surface. The primary reason for copper deposits on the surface is due to fast uncontrolled drying or conditioning of freshly treated wood. This phenomenon can be slowed down with proper conditioning, but it is rather difficult to completely overcome it (Humar *et al.* 2007). One of the limiting factors for leaching could be the wood's moisture content. Moisture levels above the fibre saturation point (FSP) is required for effective diffusion of water-soluble active ingredients (Baysal *et al.* 2006). The final moisture content of the samples, which was considerably above the FSP (Table 2), indicated that this variable was not limiting the leaching process.

Table 1. Leaching of Copper from Copper-Ethanolamine Treated Norway Spruce Wood Determined According to Three Different Standard Procedures

c_{Cu} (%)	**Method**	**Leaching period***									**Sum**
		a	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	
		Leached Cu (%)									
0.125	15119-1	0.6 (0.2)	0.3 (0.1)	0.4 (0.2)	1.0 (0.4)	2.0 (0.6)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.7 (0.1)	5.0 (1.1)
	15119-2	4.3 (0.3)	0.9 (0.4)	0.6 (0.3)	0.5 (0.2)	3.1 (0.6)	0.0 (0.0)	1.6 (0.4)	0.8 (0.2)	0.0 (0.0)	11.8 (1.4)
	1250	0.8 (0.1)	1.4 (0.4)	0.5 (0.2)	1.1 (0.4)	0.4 (0.4)	0.5 (0.2)				4.7 (0.7)
0.25	15119-1	1.1 (0.7)	0.1 (0.1)	0.1 (0.0)	0.9 (0.5)	0.5 (0.2)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	2.7 (0.4)
	15119-2	2.8 (0.3)	0.3 (0.1)	0.2 (0.0)	0.7 (0.2)	1.4 (0.4)	0.2 (0.1)	0.0 (0.0)	0.0 (0.0)	0.4 (0.3)	6.0 (0.9)
	1250	1.5 (0.5)	0.1 (0.1)	0.4 (0.1)	0.2 (0.1)	0.2 (0.1)	1.0 (0.3)				3.4 (0.6)

Mean data (standard deviation)
*Leaching periods:
15119-1: a (day 1), b (day 3), c (day 5), d (day 8), e (day 10), f (day 12), g (day 15), h (day 17), i (day 19)
15119-2: a (day 2), b (day 3), c (day 4), d (day 5), e (day 8), f (day 10), g (day 12), h (day 15), i (day 19)
1250: a (1 h), b (3 h), c (7 h), d (24 h), e (32 h), f (96 h)

Final moisture content of the specimens leached according to CEN/TS 15119-1 (2008) was considerably lower. The average moisture content was 25%, regardless of the concentration of the copper-ethanolamine solution used (Table 2). Comparison of the moisture contents of the samples leached according to ENV 1250-2 (1995) and CEN/TS 15119-1 (2008) standards suggested that lower amounts of leached copper should be measured by CEN/TS 15119-1 (2008) *versus* ENV 1250-2 (1995). However, the results presented in Table 1 showed that comparable leaching rates were observed utilizing both aforementioned leaching procedures. The sample impregnated with a preservative solution of the lowest concentration (c_{Cu} = 0.125%) and leached according to the ENV 1250-2 (1995) averaged a 4.7% decrease in copper; similar copper losses were observed after three weeks for the CEN/TS 15119-1 (2008) standard (5.0%). These results showed that the moisture content of the wood samples and the copper leaching rates are not clearly correlated. We believe that the moisture content of the samples is important, but it is not the only parameter. Furthermore, it should be noted that the moisture content of the samples is not homogeneous throughout the cross-section. The outer layer has higher MC than the interior of the samples. Another parameter that influences copper leaching, besides MC, is the number of drying/wetting cycles. The MC of the specimens during CEN/TS 15119-1 (2008) test oscillated from an initial 10% to 12% to a final 25%. During drying, water transfers weakly bound copper from the central part of the specimen to the surface. Hence, the specimens leached according to the non-continuous standard (*i.e.*, CEN/TS 15119-1 (2008)) were in contact with water for only 27 min in total, whereas specimens leached according to the ENV 1250-2 (1995) standard were submersed for 79 h in total. This clearly indicated the importance of the drying phases. Drying and wetting phases thus resulted in comparable losses of copper for both procedures.

Table 2. Uptake of Preservative Solutions after Impregnation, and Moisture Content of the Samples at the End of the Leaching Experiment

c_{Cu} (%)	Method	Uptake (kg/m^3)	Final moisture content (%)
0.125	15119-1	533 (23)	25 (2)
	15119-2		95 (4)
	1250		71 (5)
0.25	15119-1	514 (27)	25 (2)
	15119-2		96 (6)
	1250		73 (4)

Mean data (standard deviation)

The most aggressive test in this study was the CEN/TS 15119-2 (2013) standard, which is evident from the higher copper leaching rates and final MC (95%) (Tables 1 and 2). This standard is designed to estimate biocide emissions of wood in in-ground applications. Thus, this wood is in contact with water for 19 days, which is considerably longer than the specimens tested by CEN/TS 15119-1 (2008) or ENV 1250-2 (1995), resulted in more prominent leaching.

The highest leaching rate was observed for specimens impregnated with the lowest concentration of wood preservatives. These specimens lost almost 12% of their impregnated copper levels, which was twice as much as observed for the other two test methods (Table 1). A bit less prominent leaching was found in the specimens impregnated with the wood preservative of the highest concentration (Table 1). Similarly as reported for the other two tests, the highest leaching rates were noted during the initial leaching phases. The reasons for this occurrence have been elucidated earlier. The reasons for higher leaching of copper from aqueous solutions of lower concentration were addressed in our previous studies (Humar *et al.* 2007). The prime reason for higher leaching from the samples treated with aqueous solutions of lower concentration is linked to the pH and buffering capacity.

Field Tests

The next step was the monitoring of copper leaching during weathering in order to obtain more realistic data. Samples were isolated after an extensive rain event or snow melting process, as shown in Tables 3 and 4. Similarly, as reported for the laboratory leaching, the first days of exposure resulted in the most prominent leaching. This was in agreement with other reported literature data (Tao *et al.* 2013). Samples that were vacuum-pressure treated with wood preservative of the highest concentration lost 6% of the impregnated copper within the first three weeks of exposure. The majority of the copper leached from vacuum-pressure treated specimens occurred in the first 199 days of weathering (Table 3). Afterwards, copper leaching became insignificant. In other words, the impregnated wood lost 21% of its infused copper within the first 199 days of exposure, and only lost an additional 2% in the subsequent 158 days (Table 3).

In this part of the research, different techniques were used for impregnation, which consequently resulted in different uptakes of preservative solutions (Table 3) and depths of penetration (Humar and Lesar 2009). Table 3 shows a clearly negative correlation between preservative solution uptake and copper leaching; the lower uptake of preservative solutions resulted in more intensive copper leaching (Fig. 1) ($r^2 = 0.63$). For example, the highest copper leaching was observed for specimens impregnated with 1 minute of immersion (79%), and the lowest copper leaching was observed at vacuum-pressure treated samples (23%). This difference was evident for all leaching periods. There are at least two important reasons for this occurrence. First, the copper on the surface is more exposed for leaching to occur than the copper inside the samples. Second, the erosion of the surface is attributable to weathering (Teaca *et al.* 2013). Lignin on the upper surface is predominately degraded due to photo-degradation reactions (Persze and Tolvaj 2012); thus, lignin-bound copper (Lupsea *et al.* 2013b; Zhang and Kamdem 2000) is simply washed away.

Copper leaching from the surface treated specimens is more prominent due to the greater exposure of its outer surfaces. This is also the reason for the insufficient performance of copper-ethanolamine surface treated wood in outdoor applications. However, it should be considered that copper leaching from copper-ethanolamine-treated lumber is a dynamic process, which can be simulated with rainfall intensity, time interval between two consecutive leachate-generating events, and rain pH (Tao *et al.* 2013).

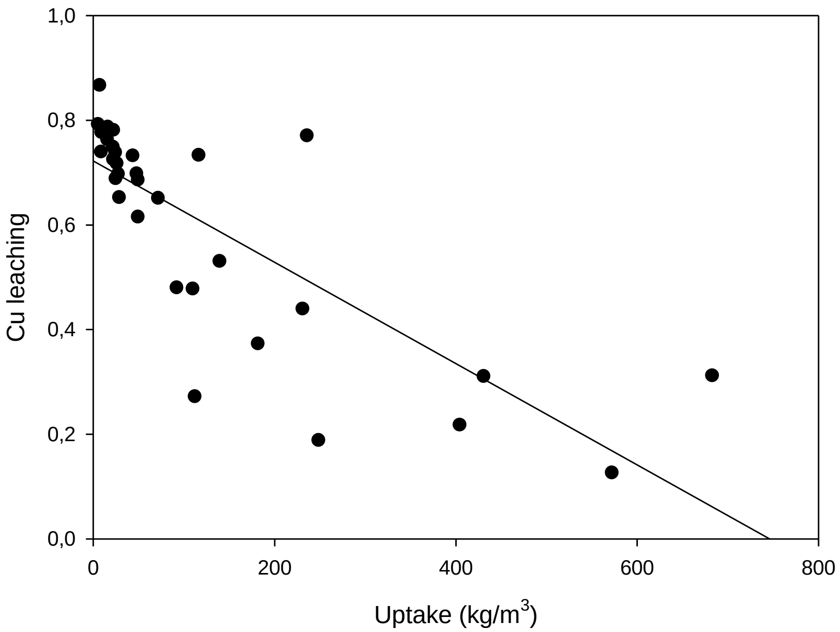

Fig. 1. Correlation between uptake of copper-ethanolamine preservative solution (c_{Cu} = 0.25%) and copper leaching after one year of exposure as determined by the non-destructive XRF analysis of the surface of the samples. Specimens were made of Norway spruce, round shaped (*r* = 1.6 cm; *h* = 1.8 cm).

Table 3. Influence of the Impregnation Procedure on the Leaching of Cu from Copper-ethanolamine (c_{Cu} = 0.25%) Treated Norway Spruce Wood during Outdoor Weathering. Specimens were round shaped (*r* = 1.6 cm; *h* = 1.8 cm).

Impregnat. method		**Uptake (kg/m^3)**	**Penetration (mm)**	**Days of exposure**								**Final Cu leach. (%)**
				22	**36**	**71**	**105**	**199**	**253**	**325**	**357**	
				Leached Cu (%)								
soaking	1 min	8	< 1	22 (2)	35 (2)	38 (6)	44 (2)	70 (2)	74 (3)	80 (3)	79 (5)	79 (5)
	1 h	22	1.0	21 (3)	36 (4)	34 (7)	41 (6)	63 (5)	69 (6)	73 (4)	72 (6)	63 (5)
	4 h	23	1.2	15 (6)	29 (7)	32 (8)	37 (9)	64 (4)	70 (5)	74 (2)	74 (2)	74 (4)
	1 day	52	1.5	17 (2)	25 (4)	27 (4)	31 (3)	54 (4)	62 (4)	68 (4)	68 (4)	73 (3)
	3 days	129	2.0	18 (5)	21 (6)	20 (4)	23 (4)	37 (3)	33 (9)	37 (8)	39 (8)	45 (3)
Vacuum		151	3.5	9 (7)	16 (9)	15 (8)	13 (9)	31 (9)	33 (8)	38 (7)	42 (9)	34 (4)
Vacuum + pressure		468	10	6 (4)	7 (4)	8 (9)	14 (5)	21 (6)	21 (5)	24 (6)	23 (8)	30 (5)

Mean data (standard deviation)
Leaching was monitored non-destructively with XRF. In order to determine final Cu leaching, specimens were ground, pressed to the tablets, and analysed by XRF.

The final step of this experiment was the destructive analysis of copper content by the milling of the specimens and the XRF analysis of the compressed tablets (as previously described). Statistical comparison of the results were determined non-destructively by XRF analysis of the surface, and of the results from final destructive tests showed that there were no significant differences between the two methods.

Therefore, we believe that the non-destructive technique employed in this work is reliable and very convenient for monitoring of copper leaching.

The last experiment performed in this study was the most comprehensive one. Samples (1.5 × 2.5 × 30 cm) were exposed to weathering for time periods between 14 days and 42 months. During this exposure, no signs of fungal growth were observed on the samples, which suggested excellent preservation properties of copper-ethanolamine wood pretreatment. Similarly, as reported already, two weeks of exposure in ground was enough for the first signs of leaching. Exposure in soil for two weeks resulted in copper leaching of 5% (for c_{Cu} = 0.125%) and 14% (for c_{Cu} = 0.25%). Leaching in soil was higher than leaching according to CEN/TS 15119-2 (2013) due to the acidic pH and to presence of humic acids in the soil, which promoted copper leaching from the pretreated wood (Cooper *et al.* 2001). However, humic acids and acidic environment plays an important role only during the first periods of leaching, which is shown by the comparison of leaching from the specimens exposed above and in ground. First, the difference became apparent after one year of exposure, predominately with specimens impregnated with the lower copper concentration solution. The differences for specimens impregnated with the higher copper concentration solution were not as obvious. For example, when specimens were exposed to the weathering above ground for 42 months, 32% of the copper was leached above ground (use class 3), while 36% of copper emitted from the samples exposed in ground (use class 4) Table 5). Based on the previous studies (Thaler *et al.* 2013) and literature reports (Janin *et al.* 2009), microorganisms present are suspected to promote copper leaching. Our past laboratory investigation of leaching in the presence of soft rot fungi showed that during 40 weeks of exposure, up to the 80% of the impregnated copper is leached from the pretreated wood (Thaler *et al.* 2013). Furthermore, these results indicated that the drying and wetting cycles, when compared with temperature differences and UV radiation, was an important factor that influences the performance of wood treated with copper-ethanolamine based wood preservatives. Moisture variation during exposure is shown in Fig. 2. It is evident that the MC of the in-ground specimens was higher and more constant than the MC of specimens exposed above ground. However, moisture information is represented in a few points during the exposure alone; thus, this parameter cannot be interpolated over the whole period.

Table 4. Summary of the Rain Event during Respective Leaching Periods (Table 3), and Number of Days with a Snow Layer

	Days of exposure								**Sum**
	22	**36**	**71**	**105**	**199**	**253**	**325**	**357**	
Rain (mm)	47	0	66	126	330	338	155	150	1210
Days of the snow layer	22	14	31	16	4			2	89

Samples were exposed to weathering from Nov. 17, 2008 to Nov. 10, 2009

Additionally, as the leaching of active ingredients from wood exposed in ground and above ground was very similar, it should be considered whether two types of standards for leaching are necessary. However, even if these two standards may not be necessary for copper-ethanolamine based preservatives, they may be necessary for other wood preservatives. However, it should be considered that this research was performed on one wood species, with a single wood preservative, and on one location only; therefore it cannot be too generalized.

Table 5. Influence of Exposure on Leaching of Cu from Copper-ethanolamine Treated Norway Spruce Wood exposed in Above Ground (use class 3) and in Ground Application (use class 4) after Periods Varying between 2 weeks and 42 Months. Specimen dimensions: 1.5 × 2.5 × 30 cm

c_{Cu} (%)	Use class	Months of exposure										
		0.5	**1**	**2**	**4**	**6**	**7**	**9**	**12**	**18**	**30**	**42**
		Leached Cu (%)										
0.125	3				1 (1)		5 (3)		4 (1)	2 (3)	17 (5)	25 (7)
	4	5 (3)	6 (3)	6 (4)	4 (3)	4 (3)		7 (4)	21 (5)	22 (5)	30 (4)	35 (4)
0.25	3				12 (3)		10 (4)		19 (6)	12 (3)	28 (5)	32 (2)
	4	14 (5)	13 (3)	14 (4)	12 (3)	15 (3)		19 (3)	24 (2)	26 (3)	33 (3)	36 (5)

Mean data (standard deviation)

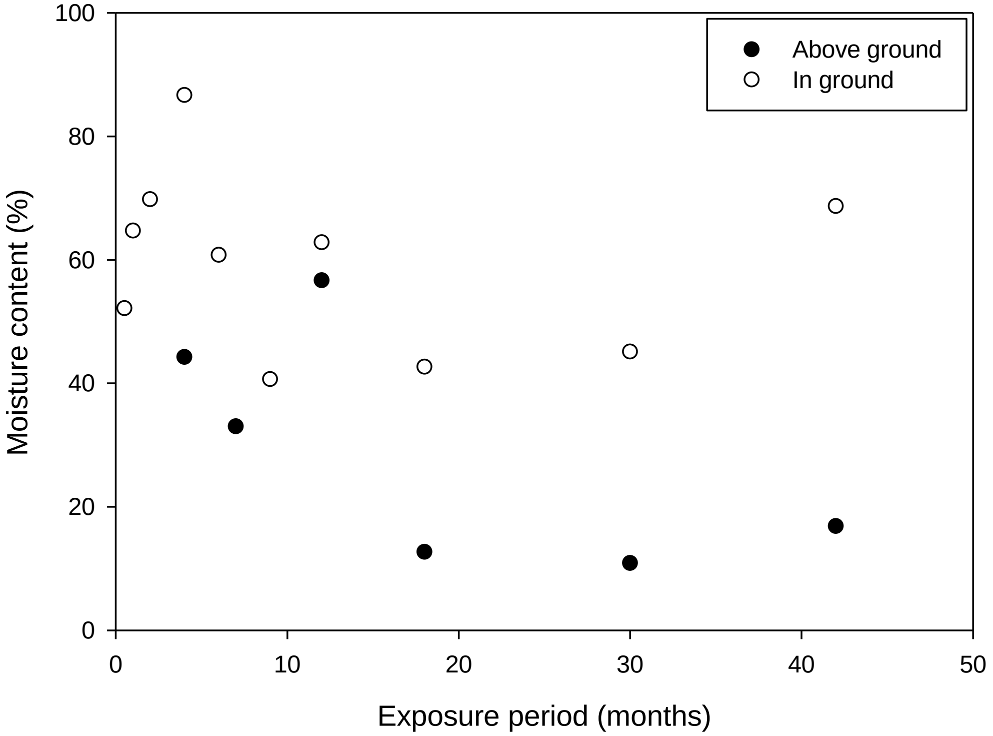

Fig. 2. Moisture content of the copper-ethanolamine treated samples during outdoor exposure. Specimens dimensions: 1.5 × 2.5 × 30 cm.

CONCLUSIONS

1. Copper-ethanolamine-based wood preservatives are effective. They react with wood and are slowly leached from wood. Laboratory and field studies revealed that the most prominent copper leaching appeared in the initial phases of leaching, when copper initially deposited on the surface of the specimens (unfixed copper) was leached from the wood.
2. Leaching of copper in above-ground and in-ground applications was comparable in most scenarios.

3. The method of treatment had the highest influence on copper leaching. Specimens that were treated with superficial treatments were more prone to leaching than vacuum-pressure-treated specimens.
4. Experiments were performed on the Norway spruce, the most important wood species for building applications in Europe. There might be different outcomes in the other wood species.

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