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Influence of Polyethylene and Oxidized Polyethylene Wax Emulsions on Leaching Dynamics of Boric Acid from Impregnated Spruce Wood

Utjecaj polietilenske i oksidirane polietilenske voštane emulzije na dinamiku ispiranja borne kiseline iz impregnirane smrekovine

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ABSTRACT • *Boron biocides belong to the most frequently used ingredients of commercial wood preservatives. They are very effective fungicides and insecticides, but they do not react with wood and thus leach from it in wet applications. This fact significantly limits use of boron compounds in the field of wood preservation. In order to reduce leaching of boric acid, the emulsion of polyethylene (WE1) and an emulsion of oxidized polyethylene (WE6) wax were combined with boric acid (c_B = 0.1 % or 0.5 % of boron). Spruce wood specimens were vacuum impregnated and afterwards leached according to the prCEN/TS 15119-1, EN 1250-2 and EN 84 procedures. The results showed that the boron leaching is predominantly influenced by moisture content of wood during leaching, and furthermore by the concentration gradient (frequency of water replacement). The fact that the prCEN/TS 15119-1 leaching procedure is less severe than other two methods is also reflected in the results. The results of the EN 84 and ENV 1250 test are comparable, while the results of the prCEN/TS 15119-1 testing are not in line with the other two methods. Considerable portions of boron are leached from wood in the first leaching cycles, already. WE6 wax emulsion (oxidized polyethylene wax emulsion) in combination with heat treatment reduces boron leaching to a certain extent. On the other hand, impregnation of wood with WE1 (polyethylene wax emulsion) does not reduce it and it even enhances it.*

Key words: *boric acid, leaching, wax emulsion, Norway spruce, wood preservation*

SAŽETAK • *Biocidi bora pripadaju najčešće upotrebljavanim sastojcima komercijalnih zaštitinih sredstava za drvo. Vrlo su učinkovita zaštita od gljiva i insekata, no ne vežu se s drvom i stoga su skloni ispiranju iz drva, posebno kada se takvo drvo primjenjuje u vlažnim uvjetima. Ta činjenica znatno ograničava upotrebu spojeva bora na području zaštite drva. U nastojanju da se smanji ispiranje borne kiseline, polietilenska emulzija (WE1) i oksidirana polietilenska voštana emulzija (WE6) kombinirane su s bornom kiselinom (c_B = 0,1 ili 0,5 % bora). Uzorci smrekovine vakuumski su impregnirani i nakon toga ispirani prema procedurama opisanim u prCEN/TS 15119-1, EN 1250-2 i EN 84. Rezultati su pokazali da na ispiranje bora najviše utječe sadržaj vode u drvu tijekom*

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ispiranja, a zatim gradijent koncentracije (frekvencija zamjene vode). Činjenica da je testiranje ispiranja prema proceduri prCEN/TS 15119-1 manje strogo od druge dvije metode odražava se i na rezultate ispitivanja. Rezultati ispitivanja prema procedurama EN 84 i ENV 1250 usporedivi su, dok se rezultati prema proceduri testiranja prCEN/TS 15119-1 ne mogu usporediti s rezultatima dobivenim drugim dvjema metodama. Znatan dio bora iz impregniranog drva ispire se već u prvom ciklusu ispiranja. WE6 emulzija (oksidirana polietilenska voštana emulzija) u kombinaciji s termičkom obradom donekle smanjuje ispiranje bora. Nasuprot tome, impregnacija drva s WE1 (polietilenskom emulzijom) ne smanjuje već, naprotiv, pojačava ispiranje bora.

***Ključne riječi**: borna kiselina, ispiranje, voštana emulzija, smrekovina, zaštita drva*

1 INTRODUCTION
1. UVOD

Wood preservation in Europe has changed significantly in the past 20 years. There were more changes in the past two decades than in the past 200 years (Connell, 2004). The most important factors that lead to these changes are: increased environmental awareness of the consumers and introduction of the Biocidal Products Directive (BPD 98/8/EC, 1998). It should be considered that there were 89 active ingredients available for wood preservation before introduction of the BPD, and there are only 40 that remained in the list of the approved active ingredients nowadays in the EU. It is forecasted that the number of the approved biocides for wood preservation will decrease further on (Suttie and Englund, 2008).

Boron-based compounds are one of the most important classical biocides that remained in the market after the implementation of the European Biocidal Product Directive (BPD 98/8/EC, 1998). Due to their broad spectrum of fungicidal and insecticidal properties, borates are considered to be more effective preservatives than copper- and zinc-based preservatives, the latter two performing better only because of their fixation in wood, and not because of their inherent fungicidal activity (Obanda *et al*., 2008). Between 200 ppm and 400 ppm of boron is necessary to inhibit the growth of fungi on nutrient medium. On the other hand, 650 ppm is required to inhibit the growth of copper sensitive species, and up to 1500 ppm of copper is required to inhibit the growth of copper tolerant species (Lesar and Humar, 2009). The use of borates is limited due to their high mobility and good water solubility, which results in insufficient fixation. The solubility and mobility of borates allows them to treat wood species that are difficult to treat with copper-based preservatives. Even when not applied on the whole cross-section, they redistribute by diffusion if sufficient moisture is available in wood to provide one of the most effective preservation systems available today (Peylo and Willeitner, 1999).

However, boron compounds have been classified as substances of very high concern due to potential teratogenic effect according to the GHS (Globally Harmonized System). Therefore, the use of boron compound in "do it yourself" is only allowed, if the concentration of boric acid is not more than 5.5 %.

To increase the use of boron compounds as environmentally benign wood preservatives, several fixation systems have been developed to limit or decrease boron leaching. Some attempts have relied on limiting water penetration of treated wood using water repellents, monomer and polymer systems (Kartal *et. al.,* 2007). The most important solutions for limiting boron leaching are: combination of boron with glycerol/glyoxal (Taussaint-Davergne *et al.*, 2000), vinyl monomers (Yalinkilic *et al.*, 1999), silanes (Kartal *et. al.*, 2007), alkydes (Peylo and Willeitner, 1995), tall oil derivates (Temiz *et al*., 2008), and montan wax emulsions (Lesar *et al*., 2009). Despite numerous researches, there is no commercial solution available that could limit boron leaching below 25 % determined according to the standard ENV 1250-2 (2004).

In our investigation boron was combined with polyethylene and oxidized polyethylene wax emulsions. Our previous results showed that these waxes act synergistically with boric acid and improve its performance against fungi (Lesar *et al*., 2009; Lesar and Humar 2010). The treatment of wood with resin/wax water-repellent formulations greatly reduces the rate of water flow in the capillaries and significantly increases the dimensional stability of specimens exposed to wet conditions (Berninghausen *et al*., 2006, Kurt *et al*., 2008). The most important applications of waxes in wood industry are found in particleboard production. Paraffin emulsions are introduced to particleboards, thus reducing the water uptake and improving dimensional stability (Amthor, 1972). Nowadays, wax emulsions are added to the OSB boards for the same reason (Neimsuwan *et al*., 2008). However, there are reports that wax treatment can reduce the water capillary uptake in wood as well (Scholz et al. 2009). Furthermore, wax treated wood exhibited increased compression strength and hardness (Rapp *et al*., 2005). In addition, wax and oil emulsion additives are incorporated into aqueous wood preservatives to reduce checking and improve the appearance of treated wood exposed outdoors (Evans *et al.*, 2009). However, up to our best knowledge, this is the first report on the use of polyethylene wax emulsions for improvement of performance of boron-based preservatives.

There are several standard methods developed to evaluate biocides emissions from impregnated wood. The oldest ones DIN 52172-2 (1972), EN 84 (2002) and ENV 1250-2 (2004) were based on continuous leaching, where specimens were in contact with water within the majority of the leaching procedure. These standards were designed for testing wood preservatives in ground contact such as CCA (wood preservative based on Cu, Cr and As compounds) or CCB (wood preservative based on Cu, Cr and B compounds). Boron-based biocides are not used in such wet environments as copper-based preservatives. Thus novel leaching procedures were developed in past years, as in most of the cases hydrophobic properties of wood cannot be expressed if leached according to the continuous methods. The newly designed methods like prCEN/TS

Table 1 Selected properties of undiluted/commercial wax emulsions used
Tablica 1. Određena svojstva upotrijebljenih nerazrijeđenih/komercijalnih voštanih emulzija

Wax emulsion *Voštana emulzija*	**Dry content** *Sadržaj suhe tvari* %	**pH**	**Emulsion viscosity (4 mm 23 °C) ISO 2431** *Viskoznost emulzije* s	**Density** *Gustoća* g/m^3	**Melting point of solids** *Točka topljenja krute tvari* °C	**Average particle size** *Prosječna veličina čestice* nm	**Emulsifier system** *Sustav emulgatora*
WE1	36.4	9.9	20 – 36	1.00	130 – 135	100	Nonionic/anionic
WE6	38.2	8.9	20 – 60	1.00	126 – 133	100	Nonionic/anionic

15119-1 (2007) are designed for estimation of biocidal emissions from wood in use class III (above ground). These standards are significantly less severe, as specimens are in water contact only for the minor part of the leaching experiment. In the present research, boron emissions from impregnated wood were evaluated using continuous and non-continuous methods to prove or reject hydrophobic effect of montan waxes.

2 MATERIAL AND METHODS
2. MATERIJAL I METODE

2.1 Specimens preparation and impregnation
2.1. Priprema uzoraka i impregnacija

Samples (1.5 × 2.5 × 5 cm) made of Norway spruce (*Picea abies*) were vacuum/pressure impregnated with different preservative solutions according to the full cell process (20 min vacuum (0.05 bar), 3 hours pressure (8 bar), 10 min vacuum (0.1 bar). After impregnation, retentions of preservative solutions were determined gravimetrically. Preservative solutions used consist of emulsion of polyethylene (WE1) and an emulsion of oxidized polyethylene (WE6) wax and boric acid (c_B = 0.1 % or 0.5 % of boron). Wax emulsions were purchased from BASF (Germany). Concentrations (dry content) and basic properties of wax emulsions can be obtained from Table 1. Impregnation wax emulsions of two different concentrations were used. Namely, the emulsions WE1 25 and WE 6 25 contain 25 % of the original emulsions, while the emulsions WE1 50 and WE 6 50 contain 50 % of the original emulsions. Control specimens were impregnated with aqueous solutions of boric acid, only. Half of the specimens were dried above melting point of the waxes used (140 °C) prior to leaching. Specimens were dried for 3 hours, which ensured that even the centre of the specimens was heated above 135 °C for one hour as determined with temperature sensor EL-USB-TC Lascar electronics (United Kingdom). Specimens used for leaching according ENV 1250-2 (2004) and EN prCEN/TS 15119-1 (2007) had end sealed axial surfaces prior to leaching, while with specimens that were used for leaching according EN 84 (2002) method, axial surfaces remained unsealed during leaching.

2.2 Leaching procedures
2.2. Procedure ispiranja

Leaching was performed according to three different procedures: EN 84 (2002), ENV 1250-2 (2004), and prCEN/TS 15119-1 (2007). ENV 1250-2 (2004) procedure requires the shortest leaching time; it was completed in only four days. In order to further speed up the experiment, the following two modifications were made: instead of five, three specimens were positioned in the same vessels and water mixing was achieved with shaking on non-rotatory shaker (Kambič) instead of magnetic stirrer. To obtain three parallel leaching procedures, nine specimens per solution/concentration/treatment were put in three vessels (three specimens per vessel). Afterwards, samples in the vessel were positioned with a weight. 300 g of deionized water were added and the vessel with its content was shaken at the frequency of 60 min^{-1}. Water was replaced for six times in four subsequent days, as prescribed by the standard. Leachates from the same vessel were collected and compiled. The concentration of boron in leachates was determined after the first and fourth day of leaching.

EN 84 (2002) protocol requires vacuum pre-treatment of the specimens with water as the first step of leaching; specimens thus take up as much water as possible. Three samples, impregnated by the same treatment were positioned in the vessel and immersed into 300 g of deionized water. There was no water stirring during leaching. Water (300 g) was exchanged ten times in 14 subsequent days. Boron content in leachates was determined after the first day, the first and second week of leaching.

In contrast to ENV 1250-2 (2004) and EN 84 (2002), the prCEN/TS 15119-1 (2007) method is based on non-continuous leaching. The standard prescribes that specimens should be exposed to water for a relatively short period of time within three weeks. Specimens of the same shape and number were soaked in 300 mL of water for one minute only, and afterwards dried for two hours and then leached again for one minute and again dried and leached. This cycle was repeated after two days, in total for nine times in a three-week experiment. Boron content in leachates was determined at the end of each week.

2.3 Detection of boron
2.3. Detekcija bora

The Agilent Technologies (Palo Alto, USA) HP 4500 quadrupole ICP-MS with Burgener Mira Mist nebuliser was used as a detection system for boron. The spray chamber temperature was 4 °C. The plasma RF power was set to 1300 W. Plasma gas flow rate was 15 L·min^{-1}, auxiliary gas flow rate 0.7 L·min^{-1} and nebuliser gas flow rate 1.05 L·min^{-1}. Sampler and skimmer cones were made of nickel. Standard boron solutions for calibration curve were prepared by diluting a stock standard solution of boron (1000 mg·L^{-1}) (Merck, Germany). Samples were diluted 50-fold with MQ water before the analysis. The final standard and sample solutions contained 1 % (v/v) of nitric acid. The memory effect (as a consequence of introduction of solutions with high boron concentration) was eliminated by washing the system with 20 % (v/v) ammonia solution after each sample (Al-Ammar *et al.* 1999). The washout time was 60 seconds. Analytical grade nitric acid and ammonia solution (Merck, Germany) were used. NIST standard reference material 1643e (trace elements in water) was used to verify the accuracy of the measurements.

2.4 Moisture content
2.4. Sadržaj vode

In order to understand leaching mechanisms more precisely, moisture content of leached specimens were gravimetrically determined as well. It is believed that moisture content is a suitable indicator for boron diffusion processes. If wood moisture content is kept low, boron diffusion does not appear. Initial mass was derived from the mass of the oven dried wax treated samples considering (subtracting) mass of the epoxy sealer and wax. Mass of the wax and epoxy sealer was calculated from uptakes of impregnation solution/wax sealer considering dry content. Mass of the wax and epoxy sealer in wood cannot be determined by any other method, as some samples were heated above 140 °C, resulting in degradation of wood and epoxy sealer.

3 RESULTS AND DISCUSSION
3. REZULTATI I DISKUSIJA

As a result of impregnation process, specimens retained between 252 kg/m^3 and 555 kg/m^3 of preservative solutions (Table 2). These values are rather high, but it should be considered that specimens were made of sapwood, and that a rather severe impregnation process was applied. The highest loadings were observed with specimens impregnated with aqueous solution of boric acid (c_B = 0.5 %) without wax (555 kg/m^3) and the lowest with specimens that were impregnated with WE1 50 emulsion with 0.5 % of boron. This clearly indicates that the addition of wax emulsions reduces the penetration of preservative solution to spruce wood specimens. The emulsion particles are too big to penetrate the cell wall completely. With dry specimens, between 0.25 kg/m^3 and 2.77 kg/m^3 of boron (equivalent 1.43 and 15.84 of H_3BO_3 kg/m^3) remained in wood after impregnation (Table 2). These retentions are sufficient to protect wood against most common basidiomycetes in use class 2 or 3 (Freitag and Morrell 2005; Lesar and Humar, 2009). As there were considerably higher concentrations of wax in treatment solutions, it can be reasonably expected that there were higher retentions of wax determined in wood. The highest retentions of 49.9 kg/m^3 were determined with wood treated with preservative WE 1 50 with 0.1 % of boron (Table 2).

Our results reconfirmed that boron does not react with wood, and therefore leaches from wood considerably. The data presented in Tables 3, 4 and 5 clearly show the leach of 10 % to 100 % of retained boron from wood, depending on the methods applied. In line with our expectations, the standard procedure EN 84 is the most severe one, while the prCEN/TS 15119-1 method is the least rigorous. One of the factors that influence the intensity of boron leaching is moisture content. The highest average moisture content of the specimens was measured at the end of the EN 84 procedure (87 %), followed by ENV 1250-2 method (54 %) and prCEN/TS 15119-1 protocol (29 %). Moisture content and boron leaching are tightly correlated, which indicates that migration of boron in wood with higher moisture content is more distinctive (Figure 1). Concentration of the boron in preservative solutions without wax does not influence the fixation determined according to the prCEN/TS 15119-1 and ENV 1250-2 procedure. On the other hand, with specimens leached according EN 84 procedure, more prominent leaching was determined with specimens impregnated with lower concentration of aqueous solutions of boric acid (78 %) compared to the specimens treated with the one of the highest concentration (89 %). Additionally, comparison of the boron leaching according to the ENV 1250-2 and according to the EN 84 revealed that concentration gradient influences boron leaching as well. Despite of the fact that EN 84 leached specimens were vacuum impregnated with water at the beginning of the leaching, higher boron emission are determined with ENV 1250-2 leached specimens, where water was re-

Table 2 Uptake of treatment solutions, retention of wax and boron at vacuum/pressure of impregnated Norway spruce wood specimens (standard deviations are given in the parentheses)
Tablica 2. Unos otopine za impregnaciju, zadržanje voska i bora u impregniranim uzorcima smrekovine (u zagradi su dane standardne devijacije)

Emulsion *Emulzija*	c_{wax}* %	c_B** %	**Solution uptake** *Unos otopine* kg/m^3	**Retention** / *Zadržanje* kg/m^3 **Wax** / *vosak*	**Boron** / *bor*
/	0	0.1	493 (111)	0	0.49 (0.14)
		0.5	555 (88)	0	2.77 (0.44)
WE 1	25	0.1	329 (75)	30.9 (7.1)	0.33 (0.08)
		0.5	351 (89)	33.0 (8.4)	1.75 (0.44)
	50	0.1	274 (105)	49.9 (21.0)	0.27 (0.12)
		0.5	252 (54)	45.9 (9.9)	1.26 (0.27)
WE 6	25	0.1	339 (86)	31.9 (8.1)	0.34 (0.09)
		0.5	307 (72)	28.9 (6.8)	1.54 (0.36)
	50	0.1	249 (43)	47.5 (8.3)	0.25 (0.04)
		0.5	257 (50)	49.2 (9.6)	29.29 (0.25)

* Concentration of the original emulsion in the respective solution / *koncentracija izvorne emulzije u odgovarajućoj otopini*
** Concentration of boron in the respective solution / *koncentracija bora u dogovarajućoj otopini*

placed for three times during the first day of leaching, than with EN 84 leached specimens where specimens are soaked in the same water for the whole period (Tables 4 and 5). This clearly indicates the influence of concentration gradient on boron leaching. Half of the specimens were heated prior to leaching. Heat treatment itself does not have considerable influence on boron leaching with specimens impregnated with boron-based aqueous solutions without wax emulsions. It was expected that a film of melted wax would be formed on the surface of the samples and on the surface of the cell walls. It was presumed that this film would be a barrier that would limit water as well as boron diffusion. However, our presumptions were not confirmed.

During the first week of leaching according to the prCEN/TS 15119-1 protocol, consisting of nine one-minute immersion phases, between 5 % and 11 % of boron was leached from impregnated specimens. The differences between various treatments are not significant. Furthermore, leaching rates decrease within the second and third week. This result is reasonable, as during the first week, particularly, boron deposited on the surface layer is leached from wood. However, analyses of wood moisture contents revealed that moisture content of respective wooden specimens during the whole process of leaching were comparable (Table 3). It was expected that the addition of wax emulsions into aqueous solution of boric acid would reduce boron leaching from impregnated specimens. From the results presented in Table 3 it can be seen that there was some reduction in boron leaching in certain treatments observed, but it was not as distinctive as expected. In general, from specimens that were impregnated with preservatives based on wax emulsions and boric acid, and not heated prior to leaching, no reduction of boron leaching was observed. Between 11 % and 16 % of boron leached from all impregnated, unheated specimens. On the other hand, with specimens that were heated up to 140 °C, some reduction of leaching was observed. This difference was the most notable with specimens impregnated with preservatives based on emulsion WE1 25. For example, from heated Norway spruce specimens impregnated with WE1 25 (c_B = 0.1 %) 10 % of the retained boron compounds was leached, while 50 % higher leaching rates were determined at parallel specimens that were not heated prior to leaching (Table 3). It seems like that heat treatment causes redistribution and more uniform formation of film than air drying of wood treated with wax emulsions. From the results presented in Table 3 it becomes obvious that preservatives based on aqueous solution of the lowest wax concentration were more effective than the ones of the highest wax concentration. It can be presumed that the preservatives with the highest wax emulsion concentration were too viscose to achieve good penetration in wood.

Leaching of the boron according to the ENV 1250-2 was more distinctive. It should be considered that specimens leached according to the ENV 1250-2

Table 3 Percentages of boron (B) leached from impregnated wood, determined according to the prCEN/TS 15119-1 procedure and moisture content (MC) of the specimens after respective leaching period (Standard deviations to the averages of triplicates are given in the parentheses)

Table 3. Postotak ispranog bora (B) iz impregniranog drva određen prema proceduri prCEN/TS 15119-1i sadržaj vode (MC) u uzorcima nakon odgovarajućeg vremena ispiranja (u zagradama su dane standardne devijacije srednjih vrijednosti triju mjerenja)

Wax type *Tip voska*	c_{wax} %	c_B %	**Heated** *Grijano*	**Leached B during 1st week** *Isprani bor B tijekom prvog tjedna* %	**Leached B during 2nd week** *Isprani bor B tijekom drugog tjedna* %	**Leached B during 3rd week** *Isprani bor B tijekom trećeg tjedna* %	**Sum of leached B** *Zbroj ispranog bora B* %	**MC after 1st week** *Sadržaj vode nakon prvog tjedna* %	**MC after 2nd week** *Sadržaj vode nakon drugog tjedna* %	**MC after 3rd week** *Sadržaj vode nakon trećeg tjedna* %
/	0	0.1	Yes	8 (3)	4 (0)	3 (0)	15 (3)	30 (1)	33 (1)	33 (1)
			No	8 (2)	4 (1)	3 (1)	15 (4)	35 (3)	38 (3)	37 (4)
		0.5	Yes	7 (1)	4 (1)	3 (1)	14 (3)	33 (5)	35 (4)	36 (4)
			No	7 (0)	4 (0)	3 (0)	14 (0)	33 (2)	34 (2)	35 (2)
WE 1	25	0.1	Yes	6 (3)	3 (1)	1 (1)	10 (2)	26 (1)	28 (1)	28 (1)
			No	7 (1)	4 (0)	5 (3)	16 (3)	27 (1)	32 (1)	31 (1)
		0.5	Yes	5 (2)	2 (3)	3 (1)	10 (4)	26 (1)	28 (1)	28 (1)
			No	7 (2)	4 (0)	3 (1)	14 (3)	27 (1)	31 (1)	30 (1)
	50	0.1	Yes	6 (0)	2 (1)	3 (2)	11 (1)	22 (1)	24 (1)	24 (5)
			No	8 (3)	3 (2)	2 (0)	13 (1)	26 (1)	28 (2)	30 (2)
		0.5	Yes	8 (3)	4 (0)	3 (1)	14 (4)	24 (1)	26 (1)	27 (1)
			No	8 (1)	4 (1)	3 (1)	15 (1)	26 (1)	30 (1)	28 (1)
WE 6	25	0.1	Yes	7 (0)	4 (0)	3 (2)	14 (2)	24 (2)	27 (4)	28 (1)
			No	8 (1)	2 (0)	1 (0)	11 (1)	27 (1)	29 (1)	29 (1)
		0.5	Yes	5 (0)	4 (0)	3 (0)	12 (4)	27 (1)	29 (1)	25 (4)
			No	8 (3)	4 (0)	3 (1)	15 (4)	28 (1)	31 (1)	29 (1)
	50	0.1	Yes	7 (1)	4 (1)	2 (0)	12 (1)	23 (1)	26 (7)	25 (2)
			No	11 (3)	3 (1)	2 (0)	16 (4)	26 (1)	27 (1)	27 (1)
		0.5	Yes	8 (0)	4 (2)	2 (1)	14 (3)	24 (2)	25 (4)	25 (1)
			No	7 (3)	3 (1)	3 (0)	13 (4)	27 (1)	29 (1)	28 (1)

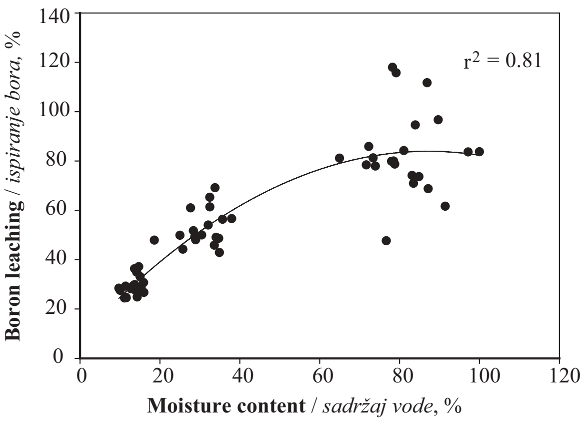

Figure 1 Correlation between wood moisture content and boron leaching
Slika 1. Korelacija između sadržaja vode u drvu i ispiranja bora

procedure were in water contact for almost 80 hours, while specimens leached according to the considerably longer period than specimens leached according to the prCEN/TS 15119-1 protocol (27 min). This reflects in the MC of wood and leached boron. MC of wood at the end varied between 43 % and 69 %, which is considerably higher than MC values measured during prCEN/TS 15119-1 procedure (Tables 3 and 4). In contrast to prCEN/TS 15119-1 method, the difference in boron leaching was firstly evident during the first leaching day (7 hours of leaching). Boron leaching rates varied between 1 % (WE6 50 c_B = 0.5 %) and 69 % (WE1 50 c_B = 0.1 %) (Table 4). It was surprising that the highest leaching was not determined with control specimens (12.5 %), but on the contrary, with specimens impregnated with a combination of WE1 50 wax emulsion and boron of the lowest concentration. From these specimens in average 66 % of boron was leached during the first day. Heat treatment does not influence the leaching results in this case. This result is somehow surprising, but on the other hand in line with previous results (Grof, 2009). Our previous data clearly indicate that the surface of wood impregnated with this wax is not hydrophobic, as it supposed to be, but quite the opposite - hydrophilic. Therefore, these samples took up more water, predominately in the first leaching periods, which results in more prominent leaching of boron from wood. The reason for hydrophilic properties originates in the morphology of the wax surface on the wood. With WE1 treated wood there were small cracks on the surfaces of the wax impregnated wood samples (Lesar *et al.*, in press). The cracks acted as capillaries, which took up water and reduced the contact angles of the surfaces (de Meijer and Militz, 2000). The contact angle of water on vacuum dried WE6 treated wood was about 10°. This makes penetration of water into the wood considerably faster. However, polyethylene wax formed a compact thin film after curing above the melting point, which repelled water. Hydrophilic influence is not evident for WE6 impregnated wood, and therefore the lowest leaching rates were determined in the first hours of leaching (Table 4). After 4 days of leaching, differences between various treatments were less distinctive. The FTIR analysis of the waxes and boric acid showed that there are no chemical interactions between these two ingredients (Lesar *et al.*, in press). However, this issue will be addressed in the future studies. With specimens impregnated with WE1 50 emulsion of the lowest boron concentration, the highest boron leaching rates were determined (84 %). If moisture content and boron leaching are correlated (Figure 1) it is evident that with specimens of lower moisture content less boron was leached from wood. Therefore, with specimens with the one of the lowest MC (WE6 50 c_B = 0.5 %), the lowest leaching rates were determined as well.

However, during the third leaching protocol (EN 84), the most pronounced leaching rates were determined. This was expected, as EN 84 procedure is known as one of the most severe standard leaching procedures. Moisture contents of all specimens were very high. The highest one was determined with control specimens (113 %). Moisture content of all other specimens were lower, as the cell lumina was at least partly filled up with wax, which resulted in lower water uptake compared to control specimens. However, moisture contents of wax treated wood were still two to three times above fibre saturation point, which enables efficient diffusion (Morell and Freitag, 1995). EN 84 method was found less sensitive for determination of boron leaching from wood impregnated with hydrophobic treatments, as all specimens were vacuum treated with water prior to leaching, which diminished the hydrophobic effect. This can also be seen from our results. For example, from control specimens in average 83 % of boron was leached, while from the specimens impregnated with WE1 50 emulsion of the lowest boron concentration, the highest boron leaching rates were determined (98 %), similarly as observed at ENV1250-2 leaching (Tables 4 and 5). One of the reasons for low difference in boron leaching among different treatments is related to MC. As can be obtained from Figure 1, moisture content has more significant influence on boron leaching at lower MC, while at MC higher than 60 % this influence is not significant any more.

Comparison of the methods can be obtained from Figure 2. It can be clearly seen that there is a rather good correlation between moisture content of the specimens after leaching according to various procedures. The correlation varied between 0.68 and 0.38 (Figure 2A, B and C). On the other hand, there is less correlation between boron leaching determined according to various procedures. Although there is some correlation between B leaching ratios determined according to the EN 84 and ENV 1250-2, there is actually no correlation between prCEN/TS 15119-1 method and the other two continuous methods (Figure 2D, E and F). This is predominately due to different approaches. PrCEN/TS 15119-1 method is no-continuous, while the other two methods are the continuous ones.

4 CONCLUSIONS
4. ZAKLJUČCI

The results of the boron leaching studies indicate that boron leaching is predominantly influenced by moisture content of wood during leaching. If wood moisture content is kept low, boron leaching can be slowed down considerably. Considerable portions of boron are leached from wood in the first leaching cycles, already. WE6 wax emulsion (oxidized polyethylene wax emul-

Table 4 Percentages of boron (B) leached from impregnated wood determined according to the ENV 1250-2 procedure and moisture content (MC) of the specimens after respective leaching period. Standard deviations to the averages of triplicates are given in the parentheses.
Tablica 4. Postotak ispranog bora (B) iz impregniranog drva određen prema proceduri ENV 1250-2 i sadržaj vode (MC) u uzorcima nakon odgovarajućeg vremena ispiranja (u zagradama su dane standardne devijacije srednjih vrijednosti triju mjerenja)

Wax type *Tip voska*	c_{wax} %	c_B %	**Heated** *Grijano*	**Leached B during 1st day** *Isprani bor B tijekom prvog dana* %	**Leached B during 2nd, 3rd and 4th day** *Isprani bor B tijekom drugog, trećeg i četvrtog dana* %	**Sum of leached B** *Zbroj ispranog bora B* %	**MC after 1st day** *Sadržaj vode nakon prvog dana* %	**MC at the end** *Sadržaj vode na kraju* %
/	0	0.1	Yes	12 (6)	21 (2)	33 (4)	42 (9)	61 (9)
			No	10 (3)	24 (8)	34 (5)	38 (9)	69 (9)
		0.5	Yes	15 (1)	18 (3)	34 (2)	41 (7)	66 (6)
			No	13 (3)	19 (9)	33 (5)	43 (5)	65 (9)
WE 1	25	0.1	Yes	10 (4)	24 (3)	34 (5)	34 (9)	49 (9)
			No	8 (2)	20 (9)	28 (5)	36 (9)	61 (9)
		0.5	Yes	11 (4)	25 (9)	36 (6)	30 (3)	56 (4)
			No	12 (1)	17 (0)	28 (6)	33 (5)	52 (9)
	50	0.1	Yes	69 (7)	22 (2)	91 (2)	31 (4)	62 (9)
			No	64 (7)	13 (5)	77 (6)	29 (9)	48 (6)
		0.5	Yes	10 (1)	22 (4)	32 (3)	24 (4)	54 (3)
			No	12 (1)	22 (4)	35 (3)	25 (8)	49 (1)
WE 6	25	0.1	Yes	10 (0)	25 (4)	35 (0)	18 (4)	43 (5)
			No	9 (1)	16 (2)	26 (4)	30 (4)	44 (9)
		0.5	Yes	11 (1)	27 (3)	38 (2)	41 (9)	57 (2)
			No	8 (1)	17 (1)	25 (3)	30 (7)	50 (2)
	50	0.1	Yes	8 (1)	20 (3)	29 (2)	24 (7)	49 (3)
			No	10 (1)	21 (1)	30 (3)	34 (9)	50 (9)
		0.5	Yes	1 (1)	28 (1)	29 (1)	26 (9)	48 (2)
			No	1 (1)	17 (1)	19 (1)	27 (5)	48 (2)

Table 5 Percentages of boron (B) leached from impregnated wood determined according to the EN 84 procedure and moisture content (MC) of the specimens after respective leaching period (Standard deviations to the averages of triplicates are given in the parentheses)
Tablica 5. Postotak ispranog bora (B) iz impregniranog drva, određen prema proceduri EN 84 i sadržaj vode (MC) u uzorcima nakon odgovarajućeg vremena ispiranja (u zagradama su dane standardne devijacije srednjih vrijednosti triju mjerenja)

Wax type *Tip voska*	c_{wax} %	c_B %	**Heated** *Grijano*	**Leached B during 1st day** *Isprani bor B tijekom prvog dana* %	**Leached B during 1st week** *Isprani bor B tijekom prvog tjedna* %	**Leached B during 2nd** week / *Isprani bor B tijekom drugog tjedna* %	**Sum of leached B** *Zbroj ispranog bora B* %	**MC after 1st day** *Sadržaj vode nakon prvog dana* %	**MC after 2nd week** *Sadržaj vode nakon drugog tjedna* %
/	0	0.1	Yes	12 (2)	34 (3)	32 (1)	78 (3)	82 (12)	118 (12)
			No	10 (2)	37 (1)	32 (3)	79 (4)	71 (15)	116 (10)
		0.5	Yes	9 (1)	38 (2)	43 (1)	90 (1)	69 (10)	107 (9)
			No	8 (1)	37 (2)	41 (1)	87 (2)	74 (9)	112 (11)
WE 1	25	0.1	Yes	13 (2)	36 (4)	24 (1)	74 (4)	38 (2)	78 (5)
			No	14 (4)	39 (3)	26 (5)	79 (1)	27 (3)	80 (9)
		0.5	Yes	10 (1)	30 (2)	32 (4)	72 (6)	54 (12)	86 (11)
			No	13 (3)	35 (5)	36 (2)	84 (2)	61 (13)	95 (13)
	50	0.1	Yes	17 (2)	36 (5)	45 (2)	97 (7)	46 (11)	84 (10)
			No	16 (3)	39 (4)	45 (5)	100 (8)	38 (10)	84 (12)
		0.5	Yes	12 (1)	38 (3)	34 (1)	83 (4)	33 (5)	71 (5)
			No	14 (4)	35 (2)	29 (4)	78 (5)	36 (7)	80 (13)
WE 6	25	0.1	Yes	19 (2)	29 (4)	23 (1)	72 (7)	38 (9)	78 (14)
			No	16 (1)	32 (2)	26 (4)	73 (7)	33 (11)	81 (8)
		0.5	Yes	9 (1)	36 (4)	37 (2)	81 (1)	49 (11)	84 (7)
			No	12 (3)	33 (4)	34 (1)	79 (6)	38 (13)	79 (8)
	50	0.1	Yes	23 (2)	42 (3)	21 (4)	85 (6)	40 (7)	74 (9)
			No	17 (1)	32 (2)	17 (4)	65 (5)	35 (8)	81 (12)
		0.5	Yes	11 (4)	37 (3)	35 (3)	83 (1)	42 (10)	74 (7)
			No	12 (1)	38 (3)	38 (2)	87 (5)	24 (4)	69 (9)

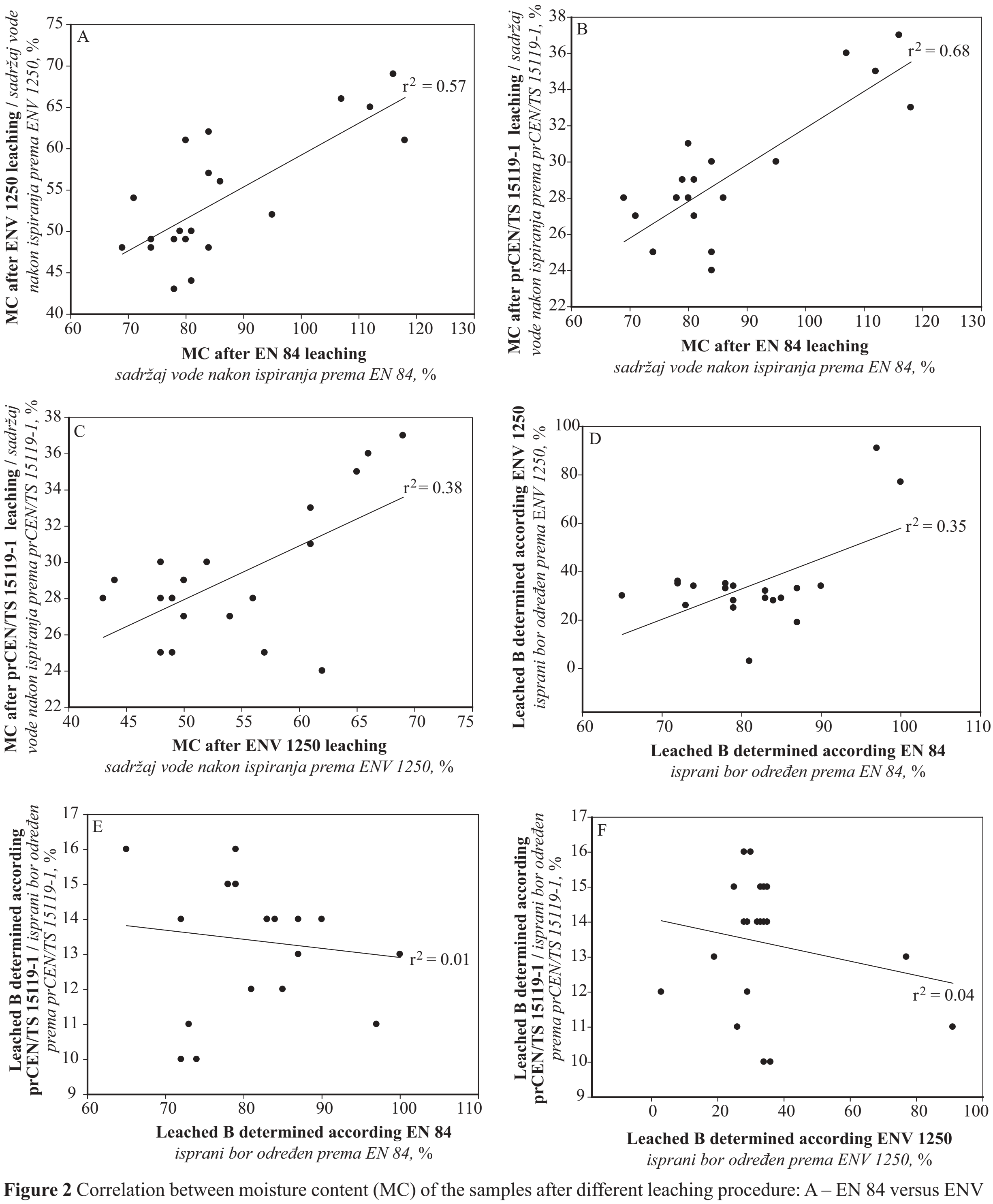

Figure 2 Correlation between moisture content (MC) of the samples after different leaching procedure: A – EN 84 versus ENV 1250-2; B – EN 84 versus prCEN/TS 15119-1; C – ENV 1250-2 versus prCEN/TS 15119-1. Correlation between boron leaching determined according various procedures is shown as well D – EN 84 versus ENV 1250-2; E – EN 84 versus prCEN/TS 15119-1; F – ENV 1250-2 versus prCEN/TS 15119-1.

Slika 2. Korelacija između sadržaja vode (MC) u uzorcima nakon različitih testova ispiranja: A – EN 84 i ENV 1250-2; B – EN 84 i prCEN/TS 15119-1; C – ENV 1250-2 i prCEN/TS 15119-1. Korelacija između vrijednosti ispranog bora određenih različitim metodama testiranja: D – EN 84 i ENV 1250-2; E – EN 84 i prCEN/TS 15119-1; F – ENV 1250-2 i prCEN/TS 15119-1.

sion) in combination with heat treatment reduced boron leaching to a certain extent. On the other hand, impregnation of wood with WE1 (polyethylene wax emulsion) did not reduce it and it even enhanced it.

The fact that prCEN/TS 15119-1 leaching procedure is less severe than other methods is reflected in the results. There is no correlation between boron leaching obtained according to this method and other two methods (EN 84 and ENV 1250-2). From the practical point of view, the method ENV 1250-2 is the most suitable one, as it is rather short and simple. On the other hand, prCEN/TS 15119-1 is the most suitable method for the estimation of the emissions in above ground applications. It provides information regarding leaching dynamics, but this method is rather long lasting and more expensive. In order to further improve the predictability of the applied methods, laboratory methods will be compared to field test results in future.

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