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INCREASED EMISSIONS OF CU/CR/AS FROM OLD CCA TREATED POLE DUE TO FUNGAL EXPOSURE

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ABSTRACT

Waste wood, impregnated with inorganic preservatives, is due to the toxic ingredients from wood considered as hazardous waste. Leaching of Cu, Cr and As is even more prominent in the case of fungal infestation. In order to elucidate these processes CCA treated pole, which was in service for 50 years, was collected and ground into the particles of five millimetres. Particles of CCA treated wood (15 g) were put into experimental jars of 750 ml and inoculated with four different brown rot fungal strains, CCA tolerant (*Antrodia vaillantii, Leucogyrophana pinastri*) and CCA sensitive (*Poria monticola, Gloeophyllum trabeum*) for four weeks. After that percentage of colonization was determined using respiration measurements. The overgrown particles were immersed in 500 ml of water for 24 hours. The concentration of remaining Cu, Cr and As in particles was determined using X-ray fluorescence spectroscopy. The respiration measurements indicate that CCA sensitive and CCA tolerant fungi overgrow the particles almost to the same level. Also proven that the exposure to copper tolerant and copper sensitive fungal strains significantly increases leaching of Cr and As from the specimens.

KEYWORDS: CCA, leaching, pole, emissions, wood decay fungi

INTRODUCTION

Preservative treatment of wood has many beneficial aspects, but the most important one is that it prolongs the useful service life of wood products exposed in extreme environments, markedly reducing the need to harvest our forests while improving the reliability and safety of a variety of structures. While preservative treatments can extend the useful life of a wood product 20 to 40 fold compared to untreated wood, eventually, even this durable material must be removed from service. The same chemicals that protect wood against degradation can have negative environmental impacts at the end of the product's useful life (Morrell 2004).

Despite the fact that the incineration is politically and technically preferred option in the majority of the European countries, some countries still landfill wood. However, disposal is still a preferred option in Denmark (Helsen and Bulck 2004) and the US (Jambeck et al. 2004).

The purpose of this paper is to estimate maximum possible leaching from disposed or landfielded CCA treated wood, particularly after colonization by CCA tolerant fungi. These organisms excrete copious amounts of oxalic acid that makes fixed biocides in wood leachable (Humar et al. 2004), what can cause contamination of the soil and ground water.

MATERIAL AND METHODS

CCA treated pole that was in service for almost 50 years was collected. According to the data of electrical company (Elektro Primorska), this pole was treated with a CCA preservative according to the sap replacement method (Boucherie) procedure. The above ground part of the pole without visual signs of microbial decay was used for experiments. The collected material was ground to the particles that can pass MESH 50 sieve. In order to homogenise them, the particles were thoroughly mixed after grinding. Subsequently, a portion of material was leached with water for 10 days. The water was replaced daily. A ratio of particles volume to water volume was 1 : 10. The amounts of biocides in wood were determined using X-ray fluorescence spectroscopy (XRF) before and after leaching.

15 g of leached particles of CCA treated wood were mixed with untreated wood (50 : 50) and put into 750 ml jars, steam sterilised, and moisturized to reach 133 % moisture content. Afterwards, wooden material was inoculated with four different brown rot fungal strains, CCA tolerant (*Antrodia vaillantii, Leucogyrophana pinastri*) and CCA sensitive (*Poria monticola, Gloeophyllum trabeum*), and put into growth chamber for four weeks (Table 1). Infested wood blocks of 18 cm^3 served as inoculums.

Tab. 1: Brown rot fungi used.CCA tolerance was estimated by Pohleven and co-workers (2002).

Fungi	Origin	Estimated CCA tolerance
Antrodia vaillantii	University of Ljubljana ZIM L037*	Highest
Leucogyrophana pinastri	Buckinghamshire Chilterns University College UK	High
Poria monticola	BAM 102	Low
Gloeophyllum trabeum	University of Ljubljana ZIM L017*	Lowest

* Raspor et al., 1995

After four weeks of fungal growth, effectiveness of colonization was determined using respiration measurements. The jars were sealed with the ventilation lids, using silicon vacuum paste to enhance the seal. The initial CO_2 concentration, and the one after one hour were measured using the equipment that consisted of membrane pump (flow rate 0.5 l/min), IR carbon dioxide sensor (0-3000 ppm, accuracy ±5 ppm) and 16-bit A/D converter for computerized data acquisition (ECHO d.o.o. Slovenia). The ECHO system was a closed-circuit system and permitted measurements of changes in CO_2 concentrations over time. Following respiration measurements, leaching was performed. The infested particles were immersed in 500 ml of water for 24 hours. The concentration of remaining Cu, Cr, Zn and As in air-dried particles (MC = 7 %), was determined using XRF.

RESULTS AND DISCUSSION

Chemical analysis of the pole revealed that significant amounts of Cr (3573 ppm) and As (1933 ppm) were detected in wood. Surprisingly, almost no copper was present in the treated pole. The concentration of Cu in treated pole was only tree times higher as it is reported for untreated wood (Fengel in Wegener 1989) (Table 2). There are several possible explanations for such a low copper content. The preservative might not be properly fixed, which could have resulted in higher copper leaching. Secondly, at the area where this pole was in use, high precipitation rates between 2000 in 2500 mm of annual rainfalls are reported (ARSO 2004). High precipitation level presumably results in more extensive leaching. As quite high zinc levels were determined, copper in the preservative might has been replaced by or combined with Zn compounds as well.

Tab. 2: Chemical elements determined in treated pole using XRF in comparison with literature data for untreated fir (Fengel and Wegener, 1989)

Element	Pole	Unimpregnated wood
	Concentration [ppm]	
As	1933,3	1-0,1
Ca	1144,0	1000-100
Cr	3573,3	10-1
Cu	3,6	1-0,1
Fe	15,4	1000-100
Pb	2,5	
Sr	4,6	100-10
Ti	19,0	100-10
Zn	218,7	100-10

We chose the most effective leaching method in order to determine the highest possible emissions from the material. Leaching from the particles is considerably more severe than leaching from the material of larger dimensions like described in EN 1250 procedure; therefore it was decided to perform the leaching from particles. After 10 days of leaching 13,6 % of Cr and 12,4 % of arsenic were leached from wood. Therefore, chromium content decreased from 3573,4 ppm to 3086,6 ppm and arsenic from 1933,3 ppm to 1693,4 ppm (Table 3). The reason for reported leaching presumably originates in the fact that wood structure was damaged during grinding, what increased relative surface of the material. However, these results show that even after 50 years Cr and As are still fixed in wood to quite high extent. Additionally, an impregnated pole in its original form does not represent significant threat to the environment. On the other hand, if we grind the pole, considerable leaching could follow. The most extensive leaching appeared during the first hours of leaching, and this leachate has a notable retardant effect on fungal growth (Hribar 2004).

The above-mentioned environmentally available free chromium and arsenic have significant retardation effect on fungi and prevents fungal growth on unleached particles. We have tried several techniques to inoculate the unleached particles and none was successful (Hribar 2004). However, even a short period of leaching enabled fungi to overgrow the particles made from an impregnated pole. All brown rot fungal strains overgrow the leached particles. Some fungi overgrow the particles made from the pole even to a higher extent as control ones. For example, fungus *A. vaillantii* growing on unimpregnated particles produces 850 ppm CO_2/h, while growing on particles made from the pole, the production of 1053 ppm CO_2/h was measured. Similar results were determined at particles exposed to CCA tolerant *L. pinastri* and CCA sensitive *G. trabeum* as well (Table 4). It seems that Cr and As in low concentrations even promoted growth of these fungal strains. On the other hand, fungus *P. monticola* grew better on control particles than on the ones made from the impregnated pole.

Tab. 3: Cr, Cu, Zn and As content before and after the leaching.

	Cr	Cu	As	Zn
	Concentration [ppm]			
Pole particles - unleached	3573,4	3,6	1933,3	218,7
Pole particles - leached	3086,6	5,2	1693,4	182,4

Tab. 4: Respiration of infested unimpregnated wood particles (Control) and particles made from the impregnated pole (Pole) overgrown by fungi for four weeks. Please note that particles made from the pole were mixed with untreated particles prior to the exposure at a ratio of 50 : 50.

Fungus	**Infested particles**	**Respiration [ppm CO_2/h]**
A. vaillantii	Control	850
	Pole	1053
L. pinastri	Control	361
	Pole	765
P. monticola	Control	1393
	Pole	477
G. trabeum	Control	1112
	Pole	1380

Table 5: Copper, chromium, zinc and arsenic content in leached particles made from the treated pole after being exposed to the wood decay fungi. Please note that particles made from the pole were mixed with untreated particles prior to exposure at a ratio of 50:50.

Fungus	**Cr**	**Cu**	**As**	**Zn**
	Concentration [ppm]			
Unexposed	1543,3	3,3	846,7	80,2
A. vaillantii	499,5	5,4	254,0	120,5
L. pinastri	926,3	5,6	500,3	140,2
P. monticola	1014,0	3,7	551,0	127,1
G. trabeum	1023,3	5,6	449,7	132,0

The most important part of this research was to elucidate the possible leaching from the impregnated pole due to fungal infestation. Overgrowth of the particles was successful what can be seen from table 4. All brown rot fungal strains examined increased leaching of the Cr and As from the impregnated particles. The highest leaching rate was determined at material overgrown by *A. vaillantii*, where approximately 68 % of Cr and 70 % of As compounds were leached. In contrast, the least prominent leaching was determined from the particles overgrown by *G. trabeum,* where 34 % of Cr and 47 % of As were removed (Table 5). Comparison of the data from tables 4 and 5 revealed that there is no significant correlation between the intensity of CO_2 production and leaching from the overgrown impregnated particles. For instance, at specimens overgrown by *G. trabeum* the most prominent production of CO_2 (1380 ppm CO_2/h) was measured, but in contrast the lowest leaching from the overgrown specimens were determined. We presume that leaching of the Cr and As compounds from infested particles has got more to do with the production of the oxalic acid than with the intensity of the fungal growth. If we compare the data for oxalic acid production (Takao 1965, Humar et al. 2001) and leaching we noticed quite a strong correlation. Fungi that excrete more oxalic acid (*A. vaillantii*) promote the leaching of the Cr and As more significantly than the ones that produce insignificant amounts of oxalic acid (*G. trabeum*).

However, the concentration of copper in the particles made of waste pole increased slightly from 3,6 to 5,2 ppm after leaching (Table 3). This variation is standard deviation limits and indicates indicates that particles are inhomogeneous. However, the concentration of copper after fungal exposure increases as the wood was decayed, but copper amount remained the same (Table 4).

CONCLUSIONS

During 50 years of pole service life, significant amounts of Cr and As species remained in the wood, while there was almost no Cu present in the pole. The remaining Cr and As in wood do not leach from wood significantly if the pole remained in the same shape. However, if decay by brown rot fungi appeared, leaching of the Cr and As significantly increased. The leaching is more prominent at fungal strains that excrete higher amounts of oxalic acid. If fungal decay would appear on the land field wood or material on the storage place, considerable emissions from the wood may occur.

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