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IMPACTS OF WOOD PRESERVATIVE LEACHATES

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Summary

While it is assumed that new preservatives such as ACQ (alkaline copper quaternary) and CA (copper azole) have lower health and environmental impacts than CCA, relatively little work has been done to assess the leaching characteristics and eco-toxicity effects of these preservatives. This paper is focused on the leaching of CCA, ACQ and CA preservative components**,** influence of wood species and two acrylic coatings and the rate and mechanism of adsorption of wood preservative components in three different types of soil (loamy sand, clay and organic amended soil). Ecotoxicity of soil and water contaminated by naturally leached preservative components from CCA, ACQ, and CA treated wood were also evaluated.

There was higher leaching of Cu from ACQ and CA treated wood than from CCA treated samples. CCA components were more effectively bound in soil than copper from copper amine systems. Coating treatments reduced leaching of all elements from 32 to 91 %.

The presence of preservative components in the soil decreased the yield and increased their accumulation in ryegrass. ACQ leachate showed higher toxicity to germination of ryegrass seeds and *Daphnia magna* toxicity; it had a lower effect on ryegrass growth than CCA leachate. Reaction of ACQ leachate with sandy soil components resulted in reduced toxicity to *Daphnia magna.* None of the contaminated soils had a measurable effect on earthworms, although there was some preservative uptake in the worms. CCA and ACQ had similar effects on soil microflora/fauna respiration. CA leachate had lower toxicity to *Daphnia magna* and similar toxicity to other organisms as ACQ.

1. Introduction

Pressure treated wood contains chemicals that may be toxic not only to target organisms (wood degrading fungi and insects) but also to non-target flora and fauna. Although, investigation of chromated copper arsenate (CCA) wood preservatives has demonstrated excellent resistance to leaching, small amounts of Cu, Cr and As are released during the service life of wood products. Because of these concerns, there have been several recent studies of CCA leaching (Stilwell and Gorny, 1997; Lebow et al, 1999; Lebow et al, 2004; Kennedy and Collins, 2002; Taylor and Cooper, 2003). These studies clearly indicated that leaching of individual elements is not proportional to concentrations in the original formulation. Also, most studies show that leaching rates of all elements are highest initially, and decrease significantly over time, although Khan et al. (2004) observed that the weathered wood leached relatively more overall arsenic.

There is less information on the leaching of alternative preservatives such as alkaline copper quaternary (ACQ) and copper azole (CA). Most leaching investigations were done in the laboratory comparing the influence of different factors on rate and loss of preservatives components (Lebow, 1996; Hingston et al, 2001). Stook et al. (2005) observed that ACQ treated wood leached more copper than CCA treated wood. According to Chung and Ruddick (2004), the loss of copper from ACQ preservative was less than 5% after 16 months of weathering. They observed that time of exposure is the most influential factor in the copper leaching followed by the volume of leachate and hours of sun exposure. Kennedy and Collins (2001) compared leaching of CCA and copper azole treated boards exposed to natural weathering for 10 months in Australia. Lebow et al. (2000) compared the leaching and soil and water levels of preservative components under and near a boardwalk treated with different preservatives. A few recently published papers looked at field leaching and weathering (Lebow et al, 2000; Kennedy and Collins, 2001; Chung and Ruddick, 2004; Choi et al, 2004; Taylor and Cooper, 2003). Direct comparison of results is difficult due to varying effects of numerous parameters.

There is considerable interest in using finishes to minimize leaching but little information is available on the type of finishes that should be applied for this purpose. Surface coatings and water repellents applied after treatments are effective in reducing preservative leaching, at least in the short term (Stilwell and Gorny, 1997, Stilwell and Musante, 2004, Taylor and Cooper, 2003).

Interaction of leachate by the process of adsorption with different chemical and physical components of soil and soil as a potential barrier against contamination of other compartments, did not receive much attention, although Kennedy and Collins (2001) applied natural leachate to soil lysimeters and found that most preservatives except borates were bound to the soil.

The individual toxicities of As, Cu and Cr to various organisms have been well characterized, but little information is available on the toxicity of multi-component leachates from CCA and other preservative treated wood to plants, soil invertebrates and microbes, and aquatic life.

This paper is focused on the leaching of CCA, ACQ and CA preservative components from above ground exposed lumber samples in Toronto, Ontario. Also, the influence of wood species and two acrylic coatings were examined. A second objective of this study was to evaluate the rate and mechanism of adsorption of wood preservative components in different types of soil in lysimeters exposed to leachate from wood exposed to natural weathering. Ecotoxicity of soil and water contaminated by naturally leached preservative components from CCA, ACQ, and CA treated wood were evaluated. Effects are compared for the different preservative leachates for plant seed germination and growth (rye grass - *Lolium perenne*), fresh water organisms (*Daphnia magna*), earthworms (*Lumbricus terrestris*) and soil microbes.

2. Methodology

Sample preparation and field leaching

Commercially treated southern pine (*Pinus* sp.) and jack pine (*Pinus banksiana*) lumber treated with ACQ, or CA and southern pine lumber treated with CCA were cut to dimensions 38mm x 140mm x 300mm and end-sealed with silicone sealant and placed in plastic containers for exposure to natural weathering in Toronto, Ontario, Canada. A second set of the treated wood samples was coated with two different acrylic treatments provided by a coatings manufacturer and exposed to weathering. The exposure began in April 2003 until April 2005 (24 months). All treatments were exposed in three replicates. Leachate was collected periodically (usually after 1 or 2 rain events) for chemical analysis and volume measurement. Before the exposure small cross sectional samples of each board were taken and % of As, Cr (CCA) and Cu (CCA, ACQ, and CA) were estimated by X-Ray fluorescence spectroscopy (Oxford Instruments Ltd.). Samples of leachate were analyzed for As, Cr (CCA) and Cu (CCA, ACQ, and CA) by ICP- AS (Perkin Elmer Optima 3000). Preservative component loss expressed as $\mu g/cm^2$ was determined from the collected leachate volume (mL), leachate concentration ($\mu g/mL$), and sample surface area (cm^2). Percent component leached was estimated from the initial % of components in wood, and μg lost (concentration of leachate x leachate volume). Sample surface area refers only to the top face that was exposed to leaching, providing a conservative estimate (worst-case scenario) of leaching per unit area.

CCA, ACQ, and CA southern pine treated samples were placed in perforated plastic containers and connected to soil lysimeters (Fig. 1.) containing one of three selected soils (loamy sand, clay, and organic amended soil). Lysimeters were constructed from PVC tubes (50cm long and 15cm in diameter) with glued funnel and mesh on the bottom. 500 g of silica sand were placed on the mesh on the bottom of each lysimeter, followed by 3kg of sieved soils (between 25- 30 cm long soil columns depending on soil type); another 500 g of silica sand was placed on the soil (Fig. 1). Sufficient headroom space was left in the lysimeters to avoid overflow. The leachate was able to pass through the soil column and preservative components that were not bound to the soil were measured in the water collected below. The amount of each component adsorbed by the soil was estimated from the "input" (average amount leached for each preservative type from the leaching studies above) and the "output" (amount collected in the container under each lysimeter).

Before leaching test all soil types were characterized using the chemical procedures shown in Table 1.

After 16 months of natural weathering and contamination with CCA, ACQ, and CA treated wood leachates, loamy sand, clay, and organic amended soils were removed from lysimeters. All soil columns were divided into three parts of equal volume (about 1kg of dry soil) (top- A, middle- B and bottom- C) based on different distribution of As, Cu, and Cr in soil, obtained in preliminary analyses (decreasing total concentrations of elements from zone A to zone C). In order to get enough soil for analyses, parts from the same depth of three replicate lysimeters were combined together. Soils were dried and sieved through 2 mm mesh for chemical analysis and ecotoxicology testing.

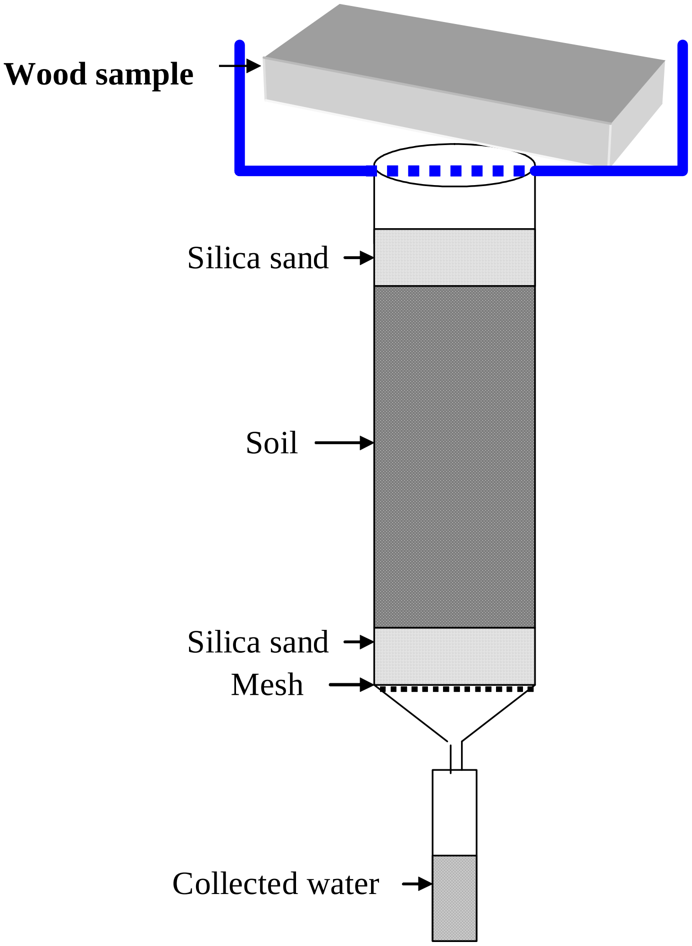

Fig. 1. Schematic diagram of lysimeter leaching setup

Total concentrations of As (CCA), Cu (CCA, ACQ and CA) and Cr (CCA) in soil were determined according to a modified version of Method 3050 (USEPA 1995; 1996). It consisted of digestion of 1g of soil with 18ml of $HN0_3$ at 120^oC for 2h in long glass tubes in a Tecator Digestor system. After cooling, 1ml of H_20_2 was added and the mixture heated for 15min. The resulting solution was filtered through Whatman No. 42 filter paper, diluted to 50ml and analysed by ICP-AES (Perkin Elmer Optima 3000).

Table 1. - Physical and chemical characteristics of selected soils characterized before leaching test

Property		Procedure	Clay	Loamy sand	Organic amended
pH		Potentiometric method in H_2O	7.2	7.2	6.8
Texture (%)	Clay	Hydrometer	40	2	2
	Silt		34	18	10
	Sand		26	80	88
Organic matter (%)		1N potassium dichromate	0.5	1.4	12.1
CEC (cmol/kg)		0.1N HCl, autoanalyzer	10.7	3.2	37.5
Exchangeable (cmol/kg)	Ca	1N NH_4-acetate, pH 7, AAS	6.6	6.1	7.1
	Mg		0.5	0.2	0.6
	Na		0.5	0.4	0.3
	K		1.7	1.8	2.3
Fe (mg/kg)	Total	ICP-AES, digestion with H_2SO_4	29400	6925	12475
Fe (mg/kg)	Oxides	Citrate buffer	490	790	780
Mn (mg/kg)	Total	ICP-AES, digestion with H_2SO_4	500	325	155
Mn (mg/kg)	Oxides	Hydrohylamine hydrochloride	225	125	70
Total (mg/kg)	As	ICP-AES, digestion with HNO_3	1.0	0.5	7.3
	Cu		13.1	5.3	15.7
	Cr		14.6	7.4	10.2

Greenhouse ryegrass experiment and plant analyses

The greenhouse experiment was conducted at 20±5^{o}C with 12h average photoperiod. PVC pots (in total 30 pots; 3 controls and 3 lysimeter zones x 3 leachate types x 3 soils) without holes in the bottom (to avoid leaching of chemicals) were filled with 2kg of dried and sieved soil with addition of 0.5g/pot of NPK fertiliser (20:10:10) and arranged in a full block design on a greenhouse bench. Ryegrass (*Lolium perenne*), commonly used for cattle pasture, hay, and ensilage, was chosen as the test species. After seeding of 1 g of ryegrass seeds per container, the soil moisture was maintained at 75% of field capacity by daily adding distilled water after weighing each pot. Growth of the grass was monitored visually throughout the duration of the experiment. The above ground portions of plants were harvested two times, after 6 and 12 weeks. Roots were harvested 12 weeks after sowing. All plant material was rinsed and cleaned with distilled water and oven-dried at

75^oC for 48h. Weight of dry biomass was recorded. Dry biomass was ground to less than 1mm prior to digestion.

The two harvests of plant biomass and roots were digested with concentrated HNO_3 with addition of H_2O_2 and analysed for total concentrations of As, Cr and Cu by ICP-AES (Perkin Elmer Optima 3000).

Seed germination

The solutions used for seed germination testing were as follows:

- CCA, ACQ, and CA leachate (extensive soaking of treated sawdust in water)
- DDAC (5 mg/L)
- DDAC (10 mg/L)
- Amine (100 mg/L)
- Cu MEA (50 mg/L)
- DDAC+ Amine (10 mg/L+ 100 mg/L)
- DDAC+ Cu MEA (10 mg/L+ 50 mg/L)
- Amine + Cu MEA (100 mg/L+ 50 mg/L)
- DDAC+ Amine+ CuMEA (10 mg/L+ 100 mg/L+ 50 mg/L)

Whatman No. 42, 90 mm ashless filter paper previously moistened by the above solutions was placed in Petri dishes and 50 seeds of ryegrass were placed on the paper. The experiment was done in triplicate. The dishes were covered and held 10 days in the dark at 21^oC. Results were recorded as “normal”, “reduced” and “very reduced” growth and as percentage of germinated seeds.

Experiment with earthworms

The test animals were earthworms (*Lumbricus terrestris*) supplied by a local pet shop. Media were prepared by mixing 300g of different types of soil with 50g of corn meal as a source of food and 100ml of water (modified method suggested by Karnak and Hamelink, 1982). Approximately one half of the test medium was placed in test jars. The five worms per jar were individually examined, weighed as a group of five, placed onto the test medium, and covered with the remaining test medium. The jars were covered with parafilm with two holes on top for gas exchange and held in the dark at $12 \pm 2\ ^o C$. After two weeks the worms were removed from the test medium, individually examined, and weighed in groups of five. The physical condition of the worms was recorded as normal, moribund, or dead. One earthworm per treatment was digested with concentrated HNO_3 with addition of H_2O_2 for detection of total concentration of As, Cu, and Cr.

Aquatic ecotoxicity

Daphnia magna acute lethality test (48h LC50) was used for ecotoxicity testing of leachate from CCA, ACQ, and CA preservative treated wood in the water environment. Three different sets of samples were tested by the Ecotoxicity Laboratory of Stantec Consulting Ltd. (Guelph, Ontario). The first set of test samples was leachates that were produced under laboratory conditions by extensive soaking of treated sawdust in water (the worst case scenario). The second set was leachates after 17 months of natural weathering and the third was natural leachate from the CCA, ACQ and CA treated wood that passed through the loamy sand soil column after 2-3 rain events

The method involved placing groups of <24h old *D. magna* neonates into a range of leachate concentrations at 20±1°C. Observations for mortality were recorded at 48h. A daphnid was considered dead if there was no visible heartbeat upon microscopic examination.

Microbial activity

Carbon dioxide evolution from soil has been frequently used as measure of microbial activity (Waksman and Starkey, 1924) due to reported correlation between numbers of microorganisms and CO_2 evolved. PVC rings 12cm in diameter and 5cm in height were cut from tubes, sealed at one end with parafilm, filled with 200g of soil and 50ml of water and covered with parafilm from the other side. The rings were held in the dark for 14 days at 28°C. Released carbon dioxide was measured in triplicate by using LICOR 6400 with a soil CO_2 flux chamber.

3. Results and Discussion

Leaching of preservative components

Total cumulative arsenic, copper and chromium leaching per unit surface area and percent leaching losses for each treatment, species and coating system based on the average of 3 replicates are presented in Table 2.

The leaching of CCA components was not in proportion to their original concentrations in the treating solution, which agrees with earlier work by Fahlstrom et al. (1967) and Taylor and Cooper (2003). Elemental chromium accounts for approximately 24.4 % of the CCA- C oxides formulation, but chromium is the most leach resistant of all components. Elemental arsenic and copper account for approximately 22 percent and 14.4 percent of initial preservative content, respectively, but leach in greater amounts. These results confirm that chromium is deposited as low solubility components by an oxidation-reduction reaction.

As was the most leached element ($\mu g/cm^2$) from CCA treated wood after 24 months of exposure while leaching of Cu and Cr were 3-5 times lower (Table 2.) which agrees with work of other authors (Yamamoto et al, 1999; Kennedy and Collins, 2001; Choi et al, 2004; Yoon et al, 2005). Total cumulative losses of As, Cu (CCA) and Cr after more than two years of exposure averaged 2.3, 1.3, and 0.4 %, respectively (Table 2.). This is in general agreement with Kennedy and Collins (2001) who found similar Cu loss (1.2%) and slightly higher losses of the other components (4.4 % As and 0.9 % Cr) after 300 days exposure of CCA treated radiate pine decking in Australia. Very similar results were obtained by Taylor and Cooper (2003) with 2.5, 1.9 and 0.3% As, Cu and Cr leaching from 1% CCA solution treated southern pine samples after 351 days of natural weathering in Toronto.

Table 2. Total leaching ($\mu g/cm^2$) of arsenic, copper and chromium (average of 3 replicates – s.d. in brackets) after 24 months of weathering

Treatment	Coating?	Species	Retention (%)	Cumulative leaching ($\mu g/cm^2$)	Cumulative leaching (%)	Average reduction of leaching (%)
Control[1]- As	N	SP	-	7.2	-	-
Control[1]- Cu	N	SP	-	15.4	-	-
Control[1]- Cr	N	SP	-	5.2	-	-
As (CCA)	N	SP	0.41	130.3 (18.1) *	2.3 (0.3)	
As (CCA)	Y (1501)	SP		59.2 (27.0)* º	0.9 (0.4)	55
As (CCA)	Y (1500)	SP		12.3 (1.6)º ×	0.2 (0.02)	91
Cu (CCA)	N	SP	0.21	49.5 (2.3) *	1.3 (0.06)	
Cu (CCA)	Y (1501)	SP		28.7 (8.0)	0.5 (0.1)	42
Cu (CCA)	Y (1500)	SP		18.2 (2.9)	0.3 (0.04)	63
Cr (CCA)	N	SP	0.61	27.7 (6.6)	0.4 (0.09)	
Cr (CCA)	Y (1501)	SP		18.7(11.5)	0.2 (0.1)	32
Cr (CCA)	Y (1500)	SP		3.9 (1.1)	0.05 (0.01)	86
Cu (ACQ)	N	SP	0.40	223.7 (24.8) *	3.1 (0.3)	
Cu (ACQ)	Y (1501)	SP		126.9 (25.8)* º	1.3 (0.3)	43
Cu (ACQ)	Y (1500)	SP		38.8 (9.1)º ×	0.5 (0.1)	83
Cu (ACQ)	N	JP	1.51	1460.8 (262.1) *	4.6 (0.8)	
Cu (ACQ)	Y (1501)	JP		875.0 (244.3)* º	2.8 (0.08)	40
Cu (ACQ)	Y (1500)	JP		305.1 (253.3)* º ×	1.1 (0.9)	79
Cu (CA)	N	SP	0.54	818.4 (68.3) *	7.0 (0.6)	
Cu (CA)	Y (1501)	SP		479.6 (284.4)* º	3.6 (2.1)	41
Cu (CA)	Y (1500)	SP		83.0 (28.8)* º ×	1.9 (0.6)	90
Cu (CA)	N	JP	0.40	110.5 (22.0)*	1.8 (0.3)	
Cu (CA)	Y (1501)	JP		62.9 (16.8)*	0.8 (0.3)	43
Cu (CA)	Y (1500)	JP		45.9 (13.8)º	0.6 (0.2)	58

[1] Untreated wood

* LSD test at significance level 0.05 (relative to controls)

º LSD test at significance level 0.05 (relative to uncoated treatment)

× LSD test at significance level 0.05 (relative to coating 1501)

However, in the first six months of the experiment the most leached element from CCA preservative was Cu, which was then exceeded by As over longer exposure times. This behavior of Cu to leach significantly more at the early stage of exposure was also noticed in Taylor and Cooper (2003) and Choi et al. (2004) work. The lower amount of Cu in leachate compared to As amount after prolonged leaching may be explained by ion exchange reaction of mobile Cu onto the check surfaces (Cooper 1991). Choi (2004) also found higher amounts of Cu at the checked surface even though more arsenic was detected in the leachate.

The two new copper amine based preservatives ACQ and CA had much higher copper losses compared to CCA. Generally, higher leaching occurred from samples with higher copper retentions. Depending on the treatment, leaching of Cu from different preservatives was in the order:

ACQ JP > CA SP > ACQ SP > CA JP > CCA SP.

Leaching rates were relatively uniform with all treatments until the first winter (200 days after exposure), when Cu from CA southern pine (SP) started to have a slightly higher leaching rate (Fig. 2.). One replicate CA sample displayed unusually high leaching of Cu during this season that increased average loss per unit surface area. The probable explanation for the unusual increase in leaching from this sample was the development of splits in the sample. Choi et al. (2004) noticed that in material installed in the summer, checks soon formed and developed beyond the chemically penetrated zone during the first month of exposure. This also indicates that once Cu ion exchange sites are full, the excess continues to migrate with water movement. Similar results were obtained by Choi et al. (2004).

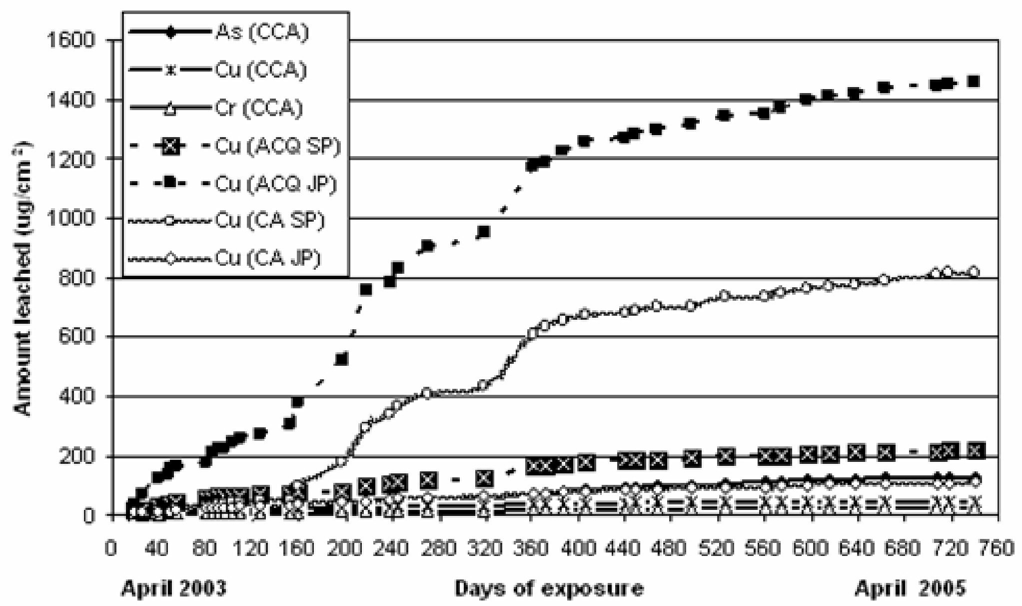

Fig. 2. Cumulative leaching per unit area of different wood preservatives (Average of three replicates)

Cu from ACQ jack pine (JP) showed a much higher rate of leaching from the very beginning of the experiment (Fig. 2). This is due to the very high retention in ACQ JP samples (1.51% CuO) in comparison with in ACQ SP samples (0.4% CuO). As noted by others (Yamamoto et al, 1999; Townsend et al, 2001; Temiz et al, 2005; Dubey et al, 2005), much higher leaching of Cu was noticed from ACQ than from CCA treated samples. The cumulative % of Cu leached from ACQ JP after 24 months of exposure was 4.6%. This is similar to results reported by Chung and Ruddick (2004) that total amount of Cu leached after 16 months of exposure was 3.95% relative to the weight.

However, for CA, SP samples leached more (7%) than JP samples (1.8%) despite their similar retentions (Table 2.). This may be related to higher permeability (Morsing, 2003; Morsing and Lindegaard, 2004) and more crack development in SP samples than in

JP samples. Jack pine is a difficult species to treat, resulting in shallow preservative penetration (Cooper, 2001) whereas southern pine is mostly permeable sapwood and achieves better preservative retention.

The amount of Cu leached from CA SP was higher than ACQ SP but was lower for CA JP than from ACQ JP (Fig. 2.). The Cu from CCA showed lower leaching in comparison with Cu CA as observed by Kennedy and Collins (2001). Different amounts of Cu CA leached in studies by Kennedy and Collins (600-700mg/m^2 or 2-3%) and Schoknecht (2005) (950mg/m^2 or about 6%) can be attributed to different test design, retentions, duration of exposure, environmental conditions (experiment locations) and wood species. Higher leaching of Cu from ACQ and CA treated samples can be explained by the different fixation mechanism in wood. There are indications that in contrast to As, Cu and Cr from CCA, Cu from ACQ and CA and the organic compound remain as separate chemicals with absence of binding reactions such as complexation of the components observed in CCA.

As a result of higher Cu concentration in the leachate from the alternative preservatives, higher % losses and losses per unit surface area are observed than from CCA treated wood. As noted in other reports (Taylor and Cooper, 2003; Yoon et al, 2005) rates of leaching of all preservatives decreased with time of exposure. The rate of leaching of all treatments was much lower in the second year of exposure than the first year of exposure (Figs. 2., 3. and 4.) and stabilization of leaching in the second year was evident.

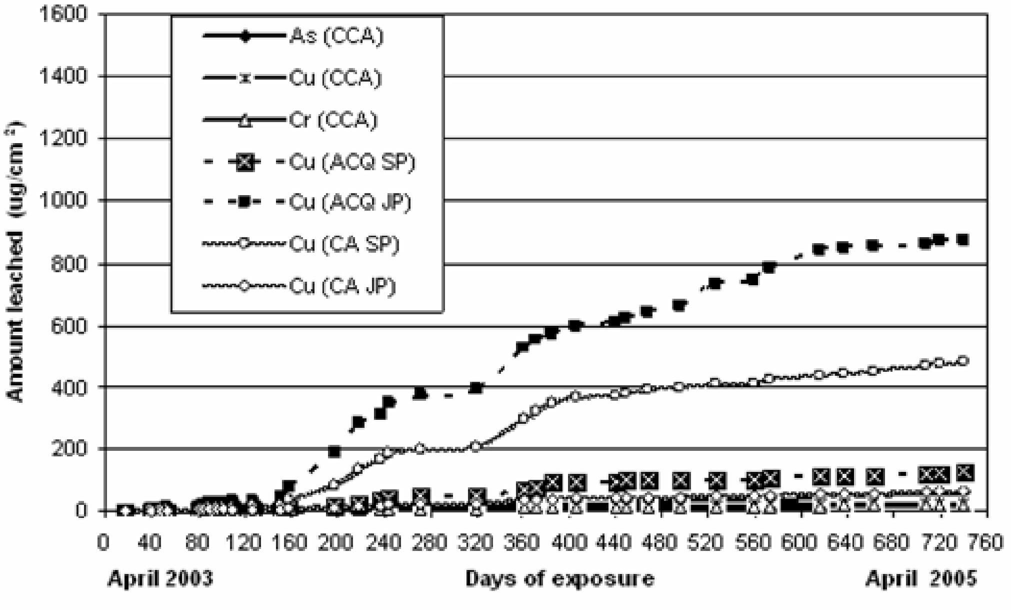

Fig. 3. Cumulative leaching per unit area of different wood preservatives coated with 1501

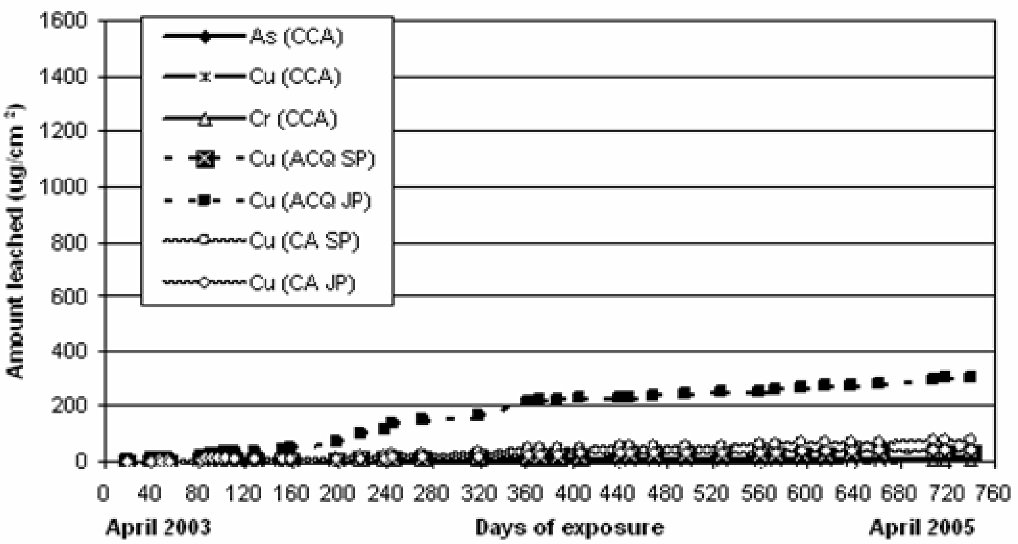

Fig. 4. Cumulative leaching per unit area of different wood preservatives coated with 1500

Effect of coatings

Application of acrylic coatings to wood specimens had a dramatic effect on leaching. Both finishes were effective, reducing the cumulative leaching after 2 years of all elements from 32 to 55 % for the coating designated 1501 and 58 to 91 % for the coating designated 1500 (Table 2.) in comparison to leaching from uncoated specimens. This corresponds with a few authors who all agree that different types of coatings significantly reduce leaching of wood preservative components in comparison to leaching from unfinished specimens (Lebow et al, 2002, 2003; Stilwell and Gorny, 1997; Cooper et al, 1997; Cooper and MacVicar, 1995). The coatings were effective because they limited the movement of water into and out of the treated wood.

For coating 1501, reduction of leaching was relatively uniform with all treatments until the beginning of winter (160 days after exposure), when Cu from CA SP and ACQ JP started to have higher leaching rates (Fig. 3.). The probable explanation for higher leaching after some time was checking and other coating failures with extended exposure. In contrast to uncoated specimens where ACQ JP treatment show high leaching from the very beginning of the experiment as a result of high retention, applying of 1501 coating delayed this increase for 5 months (Fig. 3.).

As for uncoated samples, the most leached element (µg/cm^2) from CCA treated wood coated with 1501 acrylic coating after 24 months of exposure was As while leaching of Cu and Cr were 1.5 – 4.5 times lower (Table 2.). For coating 1501 the total cumulative losses of As, Cu (CCA) and Cr after more than two years of exposure averaged 0.9, 0.5, and 0.2 %, respectively (Table 2.). In the first six months of the experiment the most leached element from CCA preservative was Cu, which was then exceeded by As over longer exposure times. As for uncoated samples, ACQ and CA had much higher copper losses compared to CCA and leaching of Cu from different preservatives for the coating designated 1501 was in the order:

ACQ JP > CA SP > ACQ SP > CA JP > CCA SP.

Coating 1501 had the largest effect on reducing arsenic leaching (55%) followed by copper (42%) and chromium (32%) (Table 2.). The 1501 type of coating resulted in a very uniform reduction of Cu leaching in ACQ and CA treatments (40- 43%).

The 1500 coating resulted in lower rates of leaching of all components compared to samples coated with 1501 coating, especially in the initial six months after exposure (winter time) (Fig. 4.). For coating 1500, the reduction of leaching was uniform with all treatments until the beginning of winter (160 days after exposure), when only Cu from ACQ JP started to have higher leaching rate (Fig. 4.). Peeling and crack development were responsible for the leaching increase after the summer of 2003. In order to prolong reduction of leaching, both coatings would need further development to assure longer service life. In contrast to uncoated and 1501 coated samples, leaching of Cu from different preservatives for the coating designated 1500 was in the order:

ACQ JP > CA SP > CA JP > ACQ SP > CCA SP

The most leached element from CCA treated samples coated with 1500 was Cu, followed by As and Cr. In this treatment As did not exceed Cu leaching as it did with the uncoated samples and coating 1501 (Fig. 4.). Coating 1500 also reduced As leaching most effectively (91%) but the reduction in leaching of Cr (86%) was larger than Cu (63%) while CA JP 1500 coating treatment had the least effect (58%) on reducing Cu leaching compared to other samples finished with 1500 type of coating.

Adsorption of preservative components in soil

In Figs. 5. - 9. adsorption of wood preservative components in different types of soil in the soil lysimeters are shown. The extent of accumulation of wood preservative components in the lysimeters depended on soil type. Organic amended soil adsorbed the highest amount of all elements in comparison with other examined soils. Clay soil showed moderate adsorption of Cu (CCA and ACQ), and Cr (CCA). This was expected because organic amended and clay soils had much higher cation exchange capacity (Table 1.) and organic matter in soil is a very important factor increasing the adsorption of chromium and copper (James and Bartlett, 1983; Wittbrodt and Palmer, 1995; Sharma and Foster, 1994; Ashley, 1996). Loamy sand soil showed much lower capacity for adsorption of Cu (CCA and ACQ) and Cr (CCA) wood preservative components than clay and organic amended soil. However, adsorption of As (CCA) and Cu (CA) were higher in loamy sand than in clay soil.

In the first five months of the experiment, the rates of accumulation of all elements in the soils were low and there was not much difference between soils. The initial As adsorption rate in that period was in order organic amended > loamy sand > clay soil and remained the same until the end of the first 14 month period. The initial adsorption rates of Cu (CCA, and ACQ) and Cr were in the order clay > organic amended > loamy sand soil but after 5 months of experiment, adsorption in the organic amended soil exceeded adsorption in the clay soil. The initial adsorption rate of Cu (CA) was in the order organic amended > clay > loamy sand soil but after 5 months of experiment, adsorption in loamy sand soil exceeded adsorption in clay soil.

After 5 months, the rate of adsorption in organic amended soil dramatically increased, consistent with the increased amounts in the leachate (Fig. 2.). However, the rate of adsorption in loamy sand and clay soils remained relatively low in all treatments. Arsenic adsorption in the loamy sand and clay soils reached a maximum after 5 and 9 months of exposure respectively (Fig. 5). Capacity of organic amended soil to adsorb As was not reached in the examined period (16 months).

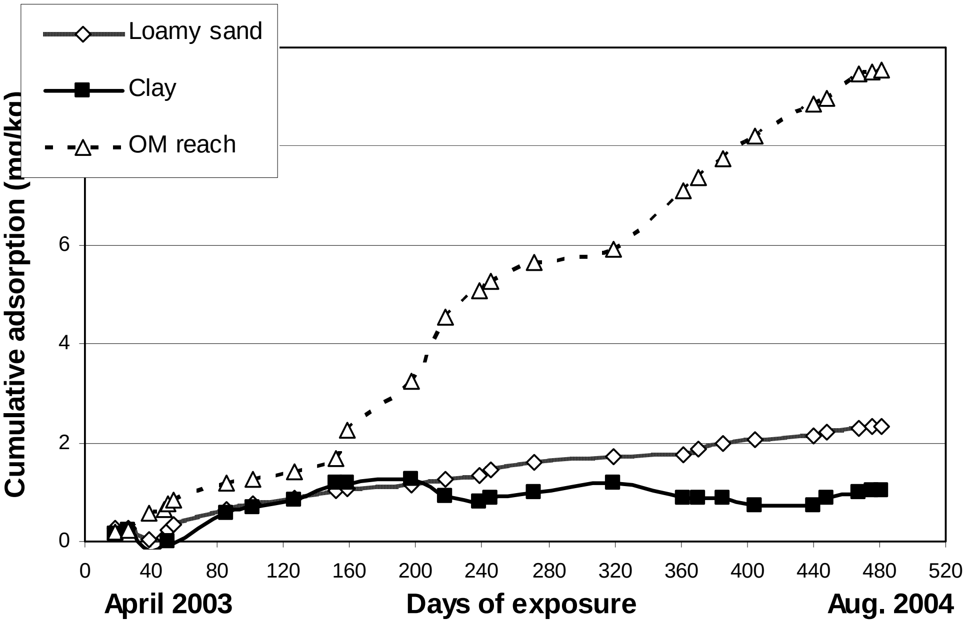

Fig. 5. Cumulative adsorption of As (CCA) in different types of soil in lysimeters

The adsorption maxima for Cu (CCA, ACQ and CA) and Cr for all examined soils was not reached but the rate of accumulation was much higher in organic amended soil than in loamy sand and clay soil (Figs. 6. - 9.). After about six months, there was a rapid increase in the accumulation of Cu (CA) in organic amended soil (Fig. 9.) which resulted in 10 and 5 times higher adsorption than in clay and loamy sand soils, respectively by the end of the study.

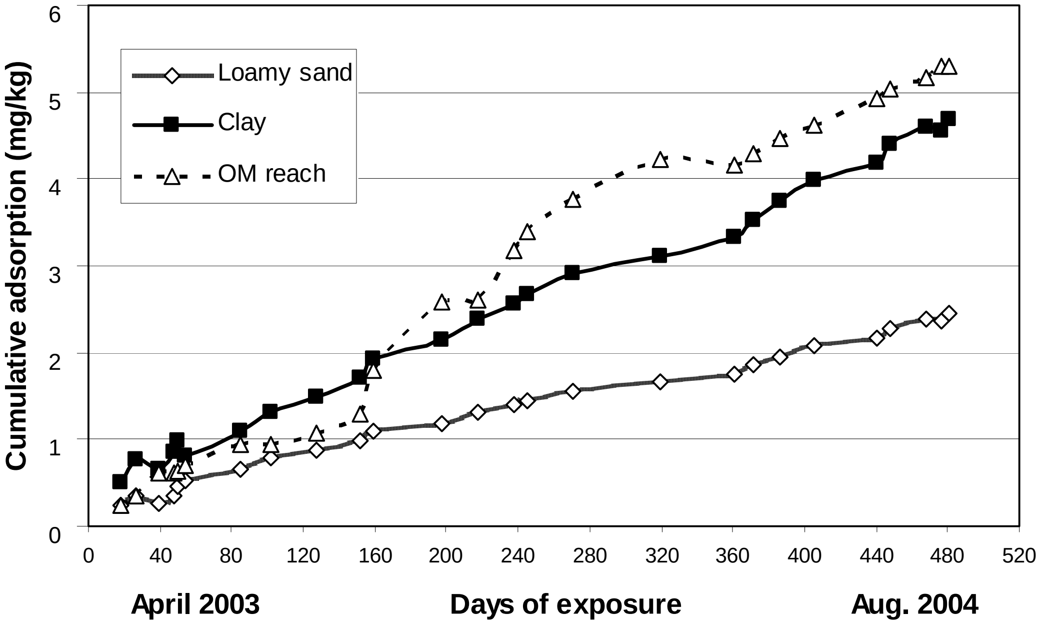

Fig. 6. Cumulative adsorption of Cu (CCA) in different soil types in lysimeters

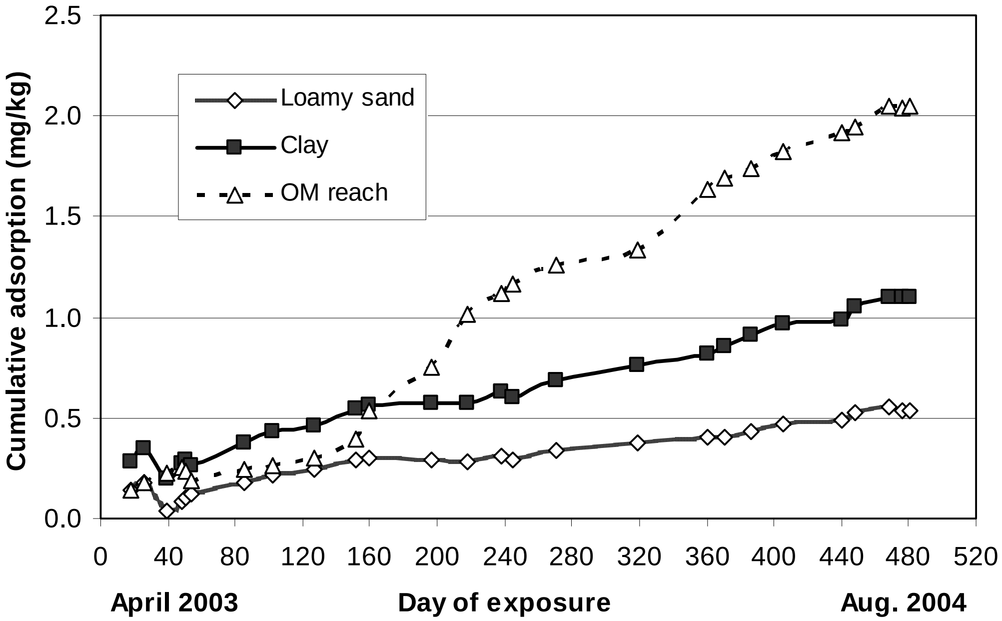

Fig. 7. Cumulative adsorption of Cr (CCA) in different types of soil in lysimeters

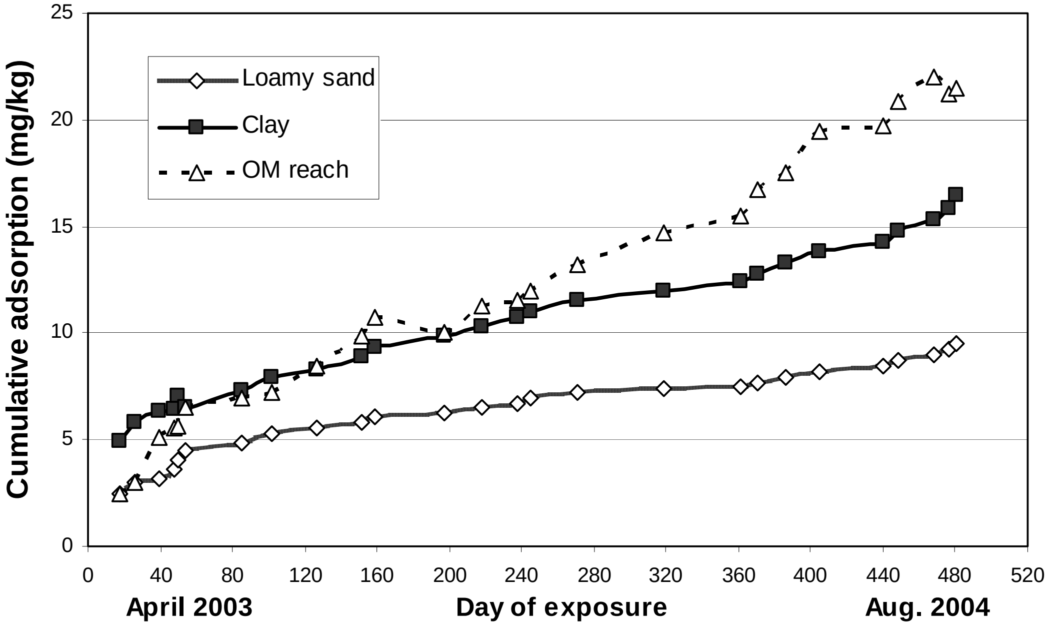

Fig. 8. Cumulative adsorption of Cu (ACQ) in different soils types in lysimeters

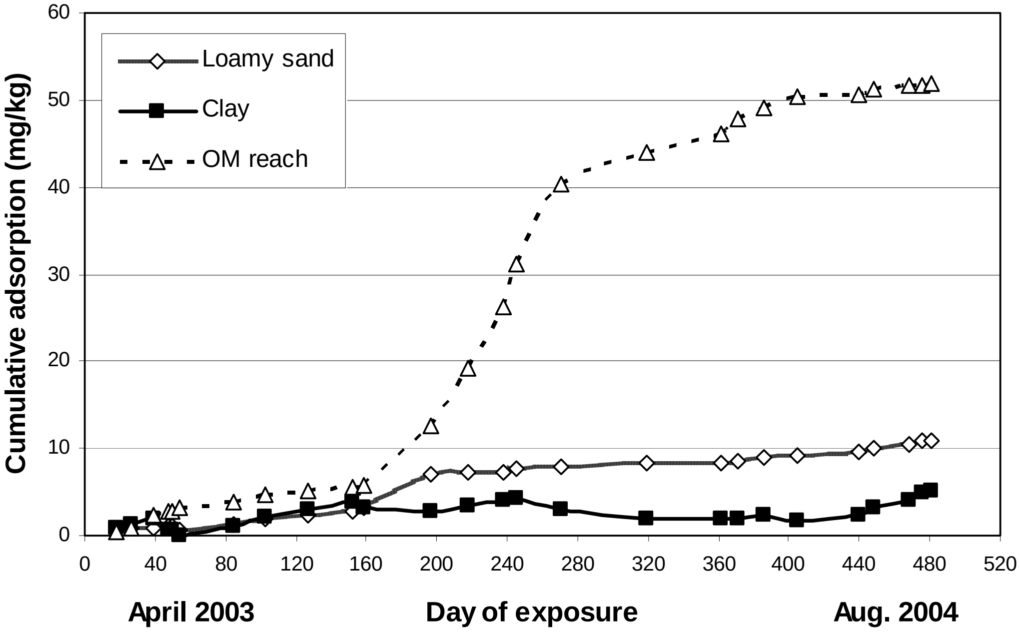

Fig. 9. Cumulative adsorption of Cu (CA) in different soils types in lysimeters

In Table 3. the percentages of adsorbed wood preservative components in different types of soil in lysimeters after 16 months of natural weathering are shown. Copper from CCA leachate was adsorbed in highest proportion in all soils in comparison with other ions, ranging from 43% in sandy soil up to 95% in organic amended soil. Cr (CCA) was adsorbed in significantly lower percentages (14 - 57% depending on soil type). This finding was partially in accordance with Melcher and Peek (1997) who observed that 97% of Cu and 94% of Cr (leachate containing CCF) stayed in soil. Also, Melcher and Wegen (1999) reported that more than 99% of the Cu and Cr added were adsorbed in the soil after addition of CCB leachate for almost 5 days. Cary et al. (2002) reported that 100% of Cu and As and 76% of Cr (applied in hexavalent form) had been retained within the large undisturbed soil lysimeters profile after 102 days of leaching with combination of natural and simulated rainfall. This discrepancy in results can possibly be explained by using of different wood preservatives formulations and soil with different physico-chemical characteristics, high leachates amounts and the extended natural leaching time in this study.

Table 3. Percentage of adsorbed wood preservative components in different types of soil in lysimeters (3 kg of soil) after 16 months of natural weathering (average of 3 replicates – s.d. in brackets)

		As	Cu	Cr	Cu (ACQ)	Cu (CA)
Added (mg)		48.6 (6.7)	16.8 (0.8)	10.6 (2.5)	83.7 (9.3)	403.7 (33.7)
Adsorption (mg)	**loamy sand**	6.9 (2.5)	7.2 (1.5)	1.5 (0.6)	28.5 (7.5)	33.0 (10.2)
	clay	3.0 (0.5)	14.1 (2.8)	3.3 (0.9)	49.2 (15.2)	15.0 (3.5)
	organic	28.8 (5.2)	15.9 (2.6)	6.0 (1.5)	64.5 (24.7)	155.4 (16.9)
Proportion (%)	**loamy sand**	14 (5.1)	43 (8.9)	14 (5.6)	34 (8.9)	8 (2.5)
	clay	6 (1.5)	84 (16.7)	31 (8.4)	59 (18.2)	4 (0.9)
	organic	59 (10.6)	95 (15.5)	57 (14.2)	77 (29.5)	38 (4.1)

Plant biomass and accumulation

The presence of preservative components in the soil decreased the yields of ryegrass in the first and second cuts and reduced ryegrass root growth in all three examined soils (Table 4.). A stimulatory effect was observed in the least contaminated zone (C) in clay and organic amended soil contaminated with ACQ and CA leachate, possibly due to nutritional effects of added Cu on plant growth Within contrast, Jin and Preston (1993), based on visual observations of tomato plant growth and chemical analysis, concluded that the influence of either ACQ or CCA treated wood in proximity to growing plants was minimal..

Table 4. Plant biomass (grams dry mass/pot)

Soil Type	Treatment and zone	First cut		Second cut		Roots	
		g/pot	%	g/pot	%	g/pot	%
Loamy sand	Control	0.95	100	4.33	100	3.68	100
Loamy sand	CCA- A	0.33	35	0.39	9	0.82	22
Loamy sand	CCA- B	0.38	40	0.78	18	0.96	26
Loamy sand	CCA- C	0.43	45	0.85	20	1.00	27
Loamy sand	ACQ- A	0.10	11	1.35	31	0.50	14
Loamy sand	ACQ- B	0.12	13	1.40	32	0.59	16
Loamy sand	ACQ- C	0.20	21	1.99	46	1.06	29
Loamy sand	CA- A	0.20	21	0.02	0.5	0.16	4
Loamy sand	CA- B	0.50	53	1.47	34	0.79	21
Loamy sand	CA- C	0.59	62	2.91	67	2.56	70
Clay	Control	0.04	100	1.20	100	1.15	100
Clay	CCA- A	0.02	50	0.04	3	0.04	3
Clay	CCA- B	0.03	75	0.07	6	0.08	7
Clay	CCA- C	0.04	88	0.42	35	0.16	14
Clay	ACQ- A	0.02	50	0.60	50	0.20	17
Clay	ACQ- B	0.03	75	1.00	83	0.35	30
Clay	ACQ- C	0.04	100	2.30	192	0.57	50
Clay	CA- A	0.01	25	0.09	8	0.13	11
Clay	CA- B	0.02	38	0.69	58	0.15	13
Clay	CA- C	0.07	175	0.74	62	0.19	17
Organic	Control	2.05	100	7.26	100	7.34	100
Organic	CCA- A	0.92	45	5.88	81	2.74	37
Organic	CCA- B	1.35	66	5.10	70	3.05	42
Organic	CCA- C	1.75	85	6.75	93	3.55	48
Organic	ACQ- A	1.18	58	3.40	47	1.53	21
Organic	ACQ- B	1.95	95	5.52	76	2.92	40
Organic	ACQ- C	3.07	150	7.65	105	6.24	85
Organic	CA- A	1.19	58	6.95	96	3.56	49
Organic	CA- B	1.26	61	7.05	97	3.53	48
Organic	CA- C	2.25	110	7.52	104	5.66	77

Much higher biomass was observed for the second cut than for the first cut in all soils with all preservatives (Table 4.). The best ryegrass growth occurred in the organic amended soil followed by loamy sand and clay soils, possibly due to low concentrations of micro and macronutrients in loamy sand and clay soils. Phyto-toxic symptoms of yellow leaves were observed in grass in all soils. In organic amended soil these symptoms appeared in the later phase of plant growth (after 4 weeks) compared to after 2 weeks in sandy and clay soils. The highest accumulation of As in ryegrass was from the loamy sand and clay soils (Table 5.). Cu and Cr accumulations were highest in rye grass grown on clay soil followed by loamy sand and organic amended soils. Uptake values were higher from contaminated than from control soils and decreased with lysimeter depth (from A to C zone) in agreement with Cooper et al. (1995) who found that the uptake of all CCA elements by ryegrass increased with increased soil contaminant level. In most cases, accumulation of elements was lower in the second cut (also higher biomass – Table 4.) than in the first cut. The highest concentrations of all elements were found in the roots, consistent with the observations of others (Cary et al, 1975; Lahouti and Peterson, 1979; Weaver et al, 1984). Taking into account that ryegrass is a common food for animals, the results should be compared with maximum tolerable limits (MTL) of 50 mg/kg As, 100 mg/kg Cu and 1000 mg/kg Cr for consumption by domestic animals as established by the U.S. National Research Council (NRC) (1996). In the first and second cuts of grass in all soil layers, the concentrations of As did not approach the suggested maximum tolerable limit but the concentration of As in roots exceeded the 50 mg/kg As limit in loamy sand and clay soils. The limit for Cu was exceeded more frequently than the As limit. In the first cut on clay soil (ACQ and CA), in second cut on loamy sand soil (CA) and even more often in roots in all three soils (ACQ, CA), the concentration of Cu approached or exceeded the suggested MTL of 100 mg/kg. The suggested limit for Cr (1000 mg/kg) was not approached in any treatment.

The fact that MTL values were most often exceeded in roots could only pose a threat under close grazing situations where animals would be consuming some roots. Of course, root feeding wild animals would potentially be most susceptible.

Table 5. Total concentration in soil and accumulation of As (CCA), Cu (CCA, ACQ, and CA) and Cr (CCA) in ryegrass (s.d. in brackets)

Soil type	Treatment and zone	Total in soil (mg/kg)			First cut (mg/kg)			Second cut (mg/kg)			Roots (mg/kg)		
		As	Cu	Cr	As	Cu	Cr	As	Cu	Cr	As	Cu	Cr
Loamy sand	Control	0.2	4.3	6.3	1	10	24	1	10	3	1	29	13
Loamy sand	CCA- A	18.2	19.7	8.0	47	16	62	25	19	9	58	44	16
Loamy sand	CCA- B	6.1	7.8	8.0	30	12	39	8	12	4	17	45	12
Loamy sand	CCA- C	2.7	6.0	6.3	7	10	39	4	9	3	14	38	10
Loamy sand	ACQ- A		58.4			41			23			166	
Loamy sand	ACQ- B		18.7			34			16			101	
Loamy sand	ACQ- C		10.0			21			14			37	
Loamy sand	CA- A		128.8			35			160			181	
Loamy sand	CA- B		44.8			22			24			128	
Loamy sand	CA- C		14.0			15			12			63	
Clay	Control	0.5	12.1	8.6	13	45	45	19	11	9	33	82	16
Clay	CCA- A	12.9	32.8	13.8	25	85	86	46	84	40	62	97	47
Clay	CCA- B	6.1	9.7	7.1	17	51	51	17	34	12	54	95	19
Clay	CCA- C	5.5	8.4	6.2	15	34	40	15	18	4	33	72	13
Clay	ACQ- A		73.7			230			23			117	
Clay	ACQ- B		13.2			206			16			97	
Clay	ACQ- C		8.4			45			13			88	
Clay	CA- A		114.5			199			66			246	
Clay	CA- B		38.9			181			20			267	
Clay	CA- C		27.3			47			24			211	
Organic	Control	3.3	13.2	7.6	0.3	7	2.5	0.1(0)	5 (2)	2(0)	0.2	42	10
Organic	CCA- A	24.1	26.9	15.5	8*	12*	2.9*	4(1)*	9(3)*	2(0)	25*	64*	18*
Organic	CCA- B	13.0	17.3	9.7	6*	12*	2.2	3(1)*	8(2)*	2(0)	20*	6*	11*
Organic	CCA- C	3.5	7.1	5.1	3	7	1.9	1(0)*	6(2)	3(1)	6*	37	8*
Organic	ACQ- A		50.3			18*			14(4)*			120*	
Organic	ACQ- B		36.5			12*			11(3)*			62*	
Organic	ACQ- C		11.3			10*			8(2)*			58*	
Organic	CA- A		203.9			23*			2(0)*			295*	
Organic	CA- B		19.3			13*			11(3)*			56	
Organic	CA- C		11.9			12*			8(2)*			54	

* LSD test at significance level 0.05 (relative to controls)

Seed germination tests

Percentage germination of ryegrass seeds and initial growth are shown in Table 6. Seed germination was not significantly reduced when exposed to CCA leachate (86% in comparison with 92% in control), and shoot growth appeared to be normal. Treatment with CA leachate resulted in a slight reduction in growth with significantly less seed germination. Extremely reduced growth and reduction in germinated seeds were noticed in treatment with ACQ leachate (Table 6.). Jin and Preston (1994) found that ACQ leachate only had a negative effect on tomato, grass and cucumber seed germination at high contamination levels while at low levels growth stimulation was observed. This discrepancy is probably the result of their testing of the commercial preservatives instead of leachate and their use of different plant species.

In order to determine which ACQ component(s) was (were) responsible for this negative effect on germination, additional experiments using preservative components in various concentrations were conducted. Results suggested that DDAC (5mg/L and 10mg/L) and monoethanolamine (100mg/L) used separately and combined, did not have as great a toxic effect as Cu MEA (50mg/L) by itself and combined with DDAC and amine or treatment with ACQ leachate. The greatest toxic effect was found only when all three components (DDAC, amine and Cu MEA) were combined in one solution, suggesting that some interaction among these three components may have increased toxicity (Table 6.).

Table 6. Germination of ryegrass seeds in solutions containing different wood preservative components (s.d. in brackets)

Treatment	Concentration of components	% of germinated seeds	Growth
Control	Distillate water	92 (5)	Normal
CCA- leachate (sawdust)	Cu- 1.52 ppm, Cr- 1.26 ppm, As- 5.52 ppm	86 (6)	Normal
ACQ- leachate (sawdust)	Cu – 51.3 ppm, MEA and DDAC n.d.	58(3)*	Very reduced
CA- leachate (sawdust)	Cu – 25.8ppm, MEA and TCA n.d.	75 (5)*	Reduced
DDAC	5 ppm	85 (5)	Normal
DDAC	10 ppm	83(8)*	Normal
Amine	100 ppm	88 (8)	Normal
Cu MEA	Cu 50 ppm, MEA 165 ppm	72 (5)*	Reduced
DDAC+ Amine	DDAC 10ppm, MEA 100ppm	80 (4)*	Normal
DDAC+ Cu MEA	DDAC 10ppm, Cu 50ppm, MEA 165ppm	70 (3)*	Reduced
Amine+ Cu MEA	MEA 100ppm, Cu 50ppm, MEA 165ppm	64(6)*	Reduced
DDAC+ Amine+ Cu MEA	DDAC 10ppm, MEA 100ppm, Cu 50ppm, MEA 165ppm	54 (3)*	Very reduced

* LSD test at significance level 0.05 (relative to controls)

Ecotoxicity effects on earthworms

The weights of earthworms before and after exposure to contaminated soil and concentrations of inorganic preservative components in their bodies are shown in Table 7. Earthworms in all treatments gained in weight after 2 weeks of exposure to contaminated soils. Earthworms in the organic amended soil showed the highest growth rate, followed by earthworms in loamy sand and clay soils. No deaths occurred and all five examined earthworms in all treatments were very active and in normal physical condition which supports Marchal and Poly (2005) finding that with the CCA and CA mesocosm, there is no adverse effects in the earthworm acute toxicity test.

As expected, the concentrations of As, Cu and Cr in bodies of earthworms in contaminated soils increased relative to the control. In addition to the earthworms' tissue some soil particles that remained in their digestive systems were extracted with acid, increasing total concentration of As, Cu and Cr. Concentrations of all elements decreased with decreasing total concentration in soil (from A-C zone).

Table 7. Weight of earthworms before and after exposure to preservative contaminated soils and concentration of As (CCA), Cu (CCA, ACQ, and CA), and Cr (CCA) in body

Soil type	Treatment and zone	Weight (g/5 individuals)			Concentration in body (mg/kg)		
		Before	After	Increase in weight (g)	As	Cu	Cr
Loamy sand	Control	25.9	32.2	6.3	0.3	1.6	0.5
Loamy sand	CCA- A	18.4	24.4	6.0	1.3	1.8	1.0
Loamy sand	CCA- B	25.8	28.9	3.2	0.5	1.5	0.7
Loamy sand	CCA- C	25.6	34.2	8.7	0.4	1.3	0.9
Loamy sand	ACQ- A	26.3	31.3	5.0		3.0	
Loamy sand	ACQ- B	31.2	34.1	2.9		2.1	
Loamy sand	ACQ- C	24.3	28.1	3.8		1.8	
Loamy sand	CA- A	28.8	33.0	4.2		11.6	
Loamy sand	CA- B	27.8	31.2	3.4		3.6	
Loamy sand	CA- C	32.0	34.0	2.0		1.3	
Clay	Control	34.1	38.8	4.7	0.6	1.7	0.9
Clay	CCA- A	24.4	28.1	3.6	0.5	1.9	0.5
Clay	CCA- B	24.6	27.2	2.6	0.4	1.2	0.7
Clay	CCA- C	25.9	30.1	4.2	0.5	1.2	1.0
Clay	ACQ- A	24.5	30.0	5.4		3.7	
Clay	ACQ- B	25.4	33.2	7.8		5.4	
Clay	ACQ- C	28.3	35.5	7.2		1.2	
Clay	CA- A	26.2	35.4	9.2		8.8	
Clay	CA- B	26.1	28.1	2.1		1.7	
Clay	CA- C	29.8	35.6	5.8		2.4	
Organic	Control	24.8	32.2	7.3	0.2	1.2	0.5
Organic	CCA- A	25.5	34.2	8.7	1.1	1.9	0.7
Organic	CCA- B	27.2	36.1	8.9	0.8	1.4	0.5
Organic	CCA- C	27.5	35.0	7.5	0.4	1.1	0.5
Organic	ACQ- A	26.9	35.4	8.4		3.3	
Organic	ACQ- B	28.6	36.2	7.6		1.4	
Organic	ACQ- C	25.3	31.7	6.4		1.5	
Organic	CA- A	24.5	31.6	7.2		11.4	
Organic	CA- B	28.8	37.7	8.9		1.3	
Organic	CA- C	24.0	30.0	5.9		1.5	

Ecotoxicity effects of leachates on Daphnia magna

LC50 results for *Daphnia magna* acute lethality test are shown in Table 8.

In treatments with leachates produced by intensive soaking of treated wood sawdust (CCA, ACQ, and CA), based on copper, the ACQ leachate, appeared to be more toxic than the CCA and CA leachates. The higher toxicity of the ACQ leachate could result from the DDAC or amine component in the leachate. Also, ACQ and CA had higher concentrations of Cu so it is clear that even though CCA leachate has a higher LC50 than CA and ACQ, the leachates of ACQ and CA are more toxic since it is more concentrated (Table 8). The dilution factor column in Table 8. calculated as 100/LSD50, indicated how many times the leachate would have to be diluted to reach the LC50 values.

The *Daphnia magna* test was also performed with leachates collected after 17 months of weathering of treated wood samples when according to published literature, the DDAC and tebuconazol (Morsing, 2003; Morsing and Lindegaard, 2004) concentrations in leachate get very low. Results showed that on the basis of copper concentration of the leachate, the LC50 toxicity was greatly reduced for ACQ and especially for CA. CCA LC50 leachate toxicity was not reduced by the extended weathering period as it was similar to that from the concentrated leachate suggesting that the arsenic and/or chromium components could increase its toxicity. These results show that the aquatic toxicity effect of ACQ and CA decreases with weathering time, probably due to reduction in the amounts of co-leachates.

Another possible reason for the reduction in toxicity could be chemical speciation changes occurring in wood over longer exposure times, causing Cu to change to a less toxic form such as $CuCO_3$ (De Schamphelaere et al, 2003). Also, this could be due to lower content of extractives in natural leachate after several months of exposure (Marchal and Poly, 2005).

CCA and CA leachates collected after passing through the loamy sand soil column, had concentrations below the LC50 concentration in *Daphnia magna* test (>100%) (Table 8.). It is important to note that this leachate was taken after only 2-3 rain events when concentration of all elements in leached water was the highest. Also, loamy sand soil had the lowest capacity to adsorb wood preservative components in comparison with other two examined soils. Thus, soil contact and adsorption is effective in reducing the aquatic toxicity of preservative leachates. This is in agreement with Melcher and Wegen (1999) who observed that Cu and Cr from CCB leachate after passing through a soil column did not show any toxicity against daphnids.

Only the ACQ leachate was above the LC50 concentration, but the corresponding toxic copper concentration was much higher than observed above, suggesting that the other components (DDAC, amine and/or wood extractives) may have been removed by the soil, reducing the toxic effect of the leachate considerably and that copper speciation in the soil resulted in greatly reduced toxicity. It is known that dissolved organic matter generally increase the leaching of Cu from CCA treated wood in direct soil-wood contact (Cooper et al, 2001a), form water-soluble chelates and complexes with Cu (Cooper and Ung, 1992; vanVeen et al, 2002; De Schamphelaere et al, 2003a), reduce the extractability of the soluble and exchangeable forms of metals (Halim et al, 2003), enhance the metal adsorption in soil (Arias et al, 2002) and reduce the toxicity of copper (Halim et al, 2003; De Schamphelaere et al, 2003a). Despite the low content of organic matter in loamy sand soil it seems that some of these processes had a role in Cu adsorption in lysimeters and in that way prevented its environmental mobility and reduced its toxicity.

Table 8. LC50 for *Daphnia magna* test with different leachate types

Preservative	**Element**	**Treatment**	**Concentration in leachate (mg/L)**	**LC50 (%)**	**Dilution factor**	**Concentration LC50 (mg/L)**
CCA	As	Soaking of the sawdust	5.52	3.86	26	0.21
	Cu	Soaking of the sawdust	1.52	3.86	26	0.06
	Cr	Soaking of the sawdust	1.26	3.86	26	0.05
ACQ	Cu	Soaking of the sawdust	51.3	0.054	1850	0.03
CA	Cu	Soaking of the sawdust	25.8	0.24	417	0.05
CCA	As	Natural leachate (after 17 months of weathering)	0.96	42.3	2.4	0.41
	Cu	Natural leachate (after 17 months of weathering)	0.11	42.3	2.4	0.05
	Cr	Natural leachate (after 17 months of weathering)	0.10	42.3	2.4	0.04
ACQ	Cu	Natural leachate (after 17 months of weathering)	0.68	11.4	8.8	0.08
CA	Cu	Natural leachate (after 17 months of weathering)	2.40	8.6	11.6	0.21
CCA	As	Passed through loamy sand soil column (2-3 rain events)	0.02	>100	<1	>0.02
	Cu	Passed through loamy sand soil column (2-3 rain events)	0.2	>100	<1	>0.2
	Cr	Passed through loamy sand soil column (2-3 rain events)	0.03	>100	<1	>0.03
ACQ	Cu	Passed through loamy sand soil column (2-3 rain events)	0.87	70.7	1.4	0.62
CA	Cu	Passed through loamy sand soil column (2-3 rain events)	0.13	>100	<1	>0.13

Microbial activity

Results of CO_2 respiration tests on control and contaminated soils are shown in Table 9. Microbial activity was the lowest in loamy sand and clay soils for both control and contaminated soils. Activity in the organic amended soil was very high. There was no measurable decrease in CO_2 respiration due to contamination by any of the preservatives in loamy sandy soil. In fact, in C zones contaminated with all examined preservatives, statistically significant increases of microbial activity were noted. This may be due to the stimulatory effect of added Cu on microbial function. In clay soil, there appeared to be a slight reduction in microbial activity in the more highly contaminated soils for all treatments but these were only statistically significant for the ACQ treatment in the first two zones (A and B) (Table 9.).

Table 9. Microbial activity in preservative contaminated soils (CO_2 respiration)

Soil type	Treatment and zone	Average CO_2 respiration (mmol/100g of soil)
Loamy sand	Control	0.1
Loamy sand	CCA- A	0.09
Loamy sand	CCA- B	0.1
Loamy sand	CCA- C	0.2*
Loamy sand	ACQ- A	0.1
Loamy sand	ACQ- B	0.09
Loamy sand	ACQ- C	0.17*
Loamy sand	CA- A	0.1
Loamy sand	CA- B	0.15*
Loamy sand	CA- C	0.26*
Clay	Control	0.19
Clay	CCA- A	0.14
Clay	CCA- B	0.18
Clay	CCA- C	0.20
Clay	ACQ- A	0.10*
Clay	ACQ- B	0.09*
Clay	ACQ- C	0.15
Clay	CA- A	0.13
Clay	CA- B	0.18
Clay	CA- C	0.19
Organic	Control	35.0
Organic	CCA- A	13.9*
Organic	CCA- B	9.5*
Organic	CCA- C	12.0*
Organic	ACQ- A	13.1*
Organic	ACQ- B	25.6*
Organic	ACQ- C	38.8*
Organic	CA- A	26.6*
Organic	CA- B	33.0
Organic	CA- C	47.0*

* LSD test at significance level 0.05 (relative to controls)

In organic amended soil, significant reductions in CO_2 respiration were observed in all soil lysimeter zones contaminated with CCA. There was no significant difference among zones (Table 9.). Also, the top two zones contaminated with ACQ and the top zone from the CA lysimeter had significantly reduced microbial activity. The lowest reduction of microbial activity was noticed in CA and the highest in CCA contaminated soil. There appeared to be a stimulatory effect in the least contaminated zone (zone C) for both the ACQ and CA contaminated organic soils.

4. Conclusions

The leaching of CCA components is not in proportion to their original concentrations in the treating solution. The most leached element from CCA preservative in the first six months of the experiment was Cu, which was exceeded by As after longer exposure times. Cu from ACQ JP showed a much higher rate of leaching than Cu from ACQ SP due to higher retention in ACQ JP than in ACQ SP samples. These results indicate that the leaching of copper from new wood preservative systems increases greatly with increased preservative retention and it is important that specified retentions are not significantly exceeded.

Coating treatments reduced leaching of all elements from 32 to 91 % depending on the treatment and coating. Identification of appropriate coating systems for treated wood will result in the potential to greatly reduce impacts of preservative leaching from treated wood.

The rate and extent of adsorption of wood preservative components in soil columns depended on soil type. Organic amended soil adsorbed the highest amount of all elements in comparison with other examined soils. Clay soil showed moderate adsorption of Cu (CCA and ACQ), and Cr (CCA) which was 2- 5 times lower than adsorption in organic amended soil. Loamy sand soil showed much lower capacity for adsorption of Cu (CCA and ACQ) and Cr (CCA) wood preservative components than clay and organic amended soil. However, adsorption of As (CCA) and Cu (CA) were higher in loamy sand than in clay soil.

Copper from added CCA leachate was adsorbed in highest percentage in all soil, from 43% in loamy sand up to 95% in organic amended soil indicating that Cu (CCA) poses little or no risk to ground water in soils with high CEC. Other elements from different preservatives can pose environmental impacts with various degrees.

After 16 months exposure to natural leachates from treated wood, soil columns had adsorbed significant amounts of all contaminants, occasionally exceeding OMOE, 1998 cleanup criteria for contaminated sites for As from CCA and Cu from CA in the top zone of the lysimeters. The soil columns had additional capacity to adsorb contaminants since there was a significant concentration gradient from top to bottom of the lysimeters.

The presence of preservative components in the soil decreased the yields of ryegrass in the first and second cuts and reduced ryegrass root growth in all three examined soils, except in the low contaminated zone (C) in clay and organic amended soil contaminated with ACQ and CA leachate where a stimulatory effect was observed possibly due to Cu nutritional effect.

Plant accumulation in all treatments was higher than from control soils and decreased with depth (from A to C zone). Concentration of As in roots exceeded the As maximum tolerable limit for consumption by domestic animals in loamy sand and clay soils but not in shoots. The limit for Cu in root and shoots was exceeded more frequently than for As. The suggested limit for Cr was not approached in any treatment.

Reduced growth and reduction in % of germinated ryegrass seeds were observed for treatment with ACQ leachate and in the case when all three components (DDAC, amine and Cu MEA) were combined in one solution, suggesting that some interaction among these three components may have increased toxicity.

No negative effect of wood preservative leachates on earthworms was observed despite some increased concentrations of As, Cu, and Cr in their bodies.

The *Daphnia magna* test results showed decreased toxicity of leachates to these aquatic organisms during the service of treated wood and reduced toxicity after leachates passed through the soil column, possibly due to changes in copper complexes and removal of DDAC, amine and/or wood extractives by soil components.

Microflora/fauna respiration was mostly affected by wood preservative leachate contamination in organic amended soil where general microbial activity was highest in comparison with other soils. In zones with the lowest contamination in loamy sand and organic amended soils, increases of microbial activity was noted possibly due to the stimulatory effect of added Cu on microbial function.

5. Literature

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