CWPA Proceedings, 2001, pp 165-176

Leaching of Chromated Copper Arsenate (CCA) During Above Ground Exposure: Treatment Effects

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Introduction

The efficacy of chromated copper arsenate (CCA) requires a balance between having the components soluble enough to be effective against target organisms throughout a product's service life, but also having low enough solubility to resist leaching (8, 9). Although CCA is considered leach resistant, small amounts of copper, chromium and arsenic are lost during the service life of most treated products (3, 9, 11). To date, most leaching research has consisted of laboratory studies comparing different factors on preservative loss or leaching rates (8, 9), and considerable discrepancies have been reported (6, 7, 9). Few studies demonstrate actual in-service leaching from treated wood during exposed conditions (9). In addition, leaching from CCA-treated wood subjected to above ground exposures has received little attention due to the assumption that leaching is less severe than from wood in continuous contact with soil or water (4).
This study examines chromium, arsenic and copper leaching from above ground, naturally exposed CCA-treated lumber. Leaching data were collected following 57 individual precipitation events from June 2000 to June 2001 (351 days) and related to wood species, initial preservative loading, water repellent treatment, washing treatment and exposure time.

Materials and Methods

For each variable tested, three replicate samples (38 x 137.4 x 200 mm) were prepared for each of three species: southern yellow pine (*Pinus spp.*), jack pine (*Pinus banksiana* Lamb.), and black spruce (*Picea mariana* (Mill.) B.S.P.). Samples of each species had similar growth rate and sapwood characteristics. The end-grain faces of each sample were sealed with silicon caulking prior to CCA treatment and after fixation to minimize end-grain penetration and leaching. Southern yellow pine dominates the CCA-treated lumber market in the United States, whereas jack pine and black spruce, together with balsam fir (*Abies balsamea* (L.) Mill.) comprise the spruce-pine-fir (SPF) group that dominates the CCA-treated lumber market in Canada.

Wood samples were impregnated with CCA-C preservative (48% chromium as CrO_3; 34% arsenic as As_2O_5; 18% copper as CuO) in a vacuum-pressure cylinder (retort) in two separate charges (1% and 3% CCA-C). Treatment included an initial vacuum (15 minutes at 13.3kPa), pressure treatment (45 minutes at 700kPa), and a final vacuum (15 minutes at 13.3kPa) to remove excess preservative. Fixation was achieved in a kiln set to 60^oC and 95% humidity for 36 hours. Preservative retention (kg/m^3) was calculated from the initial preservative concentration, uptake (change in sample mass), and specimen volumes.

Impregnation or surface application of water repellents has been shown to reduce leaching from wood above ground (2, 3, 5) by minimizing water contact. Spraying treated wood with high-pressure water immediately upon removal from fixation kilns is also thought to reduce the initial wave of leaching by removing surface deposits and unfixed CCA. A number of samples were washed with high-pressure distilled water, or received a commercial brush-on water repellent treatment (Thompson's Water Seal®) to evaluate these effects.

Forty-five wood samples [3 species x 2 CCA-C concentrations x 2 water repellent treatments (yes/no) x 3 replicates] + [3 washed samples/species at the 1% CCA-C concentration] were exposed above collection containers, allowing precipitation to contact samples and be collected, while preventing sample submersion in leach water.

Leaching rates were determined using Inductively Coupled Plasma (ICP) spectrometry (Perkin Elmer Optima 3000), following each event. Preservative component loss expressed as $\mu g/cm^2$ was determined from the collected leachate volume (ml), leachate concentration (µg/ml) and sample surface area (cm^2). Percent component leached was estimated from the initial wood retention (total µg/sample) 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.

Effects of treatment variables were evaluated for statistical significance by analysis of variance (ANOVA) of the effect of treatment factors on total cumulative losses, and least squared differences (LSD) multiple comparison test for significant differences between treatment parameters.

Results

Preservative retention values for each CCA-C concentration level and species combination are presented in Table 1. Jack pine and black spruce are difficult to treat species resulting in shallow penetration (1), whereas southern yellow pine is permeable and achieved better preservative retentions. Jack pine and black spruce treated with 1% CCA-C did not meet the minimum desired retention level for above ground exposures (approx. 4 kg/m^3).

Treated samples were exposed above ground for 351 days commencing June 2000, and were immediately subjected to over twice the normal monthly precipitation (162

mm compared to 67 mm). However, total precipitation during the study period (685mm) was less than the average annual precipitation for Toronto (819mm).
Figure 1 shows average cumulative chromium leaching (μg/cm^2) for the five treatments of southern yellow pine. Clear differences in leaching rates are apparent between treatments, and were immediately evident during the first month of exposure. Leaching rates were high for southern yellow pine during the first month, followed by a declined to lower levels. Leaching rates for jack pine and black spruce (not shown) were relatively uniform until the winter months, when the rate slowed down. Samples treated with 1% CCA-C generated the highest cumulative leaching losses compared to samples treated with 3% CCA-C for all three species. In all cases, the water-repellent treatment significantly reduced component loss (30-65% reduction). Although not statistically significant, the washing treatment also contributed to lowering cumulative chromium loss.
Although the leaching rate for chromium was highest from southern yellow pine during the first month of exposure, the cumulative leaching curve presented in Figure 1 shows the rate declining during the second month of exposure. The curves for jack pine and black spruce displayed higher leaching rates during the first six months of exposure, resulting in higher total cumulative leaching losses during the study. Southern yellow pine also displayed a more pronounced increase in chromium leaching rate during the spring of 2001 compared to jack pine and black spruce.
Figure 2 provides an example of cumulative arsenic leaching for the five treatments of southern yellow pine. Cumulative arsenic leaching from southern yellow pine exhibited the same trend as chromium leaching discussed above. However, it is important to note the high leaching rate for the 1% CCA-C treatment during the spring of 2001. One replicate sample displayed unusually high leaching during this season that increased loss per unit surface area from less than 80 μg/cm^2 to over 130μg/cm^2. A possible explanation for the unusual increase in leaching from this sample after 6 months of exposure may be related to crack development in the end coating. A visible crack was noted in the end-coating material at the completion of the study. Although it has not been confirmed, the crack may have allowed precipitation to leach CCA from the end grain. Cumulative arsenic loss from jack pine and black spruce were higher from samples treated with 3% CCA-C compared to 1% CCA-C. In general, cumulative arsenic leaching is similar for all three species, with the exception of southern yellow pine treated with 1% CCA-C.
An example of cumulative copper loss is presented in Figure 3 for the different treatments of southern yellow pine. Figure 3 displays similar trends as those discussed for arsenic (i.e. rapid loss during the first month of exposure, followed by lower rates and increased loss in the spring of 2001). In addition, the water repellent treatment produced the largest effect on reducing copper leaching in contrast to chromium and arsenic leaching. Copper leaching losses were higher from samples treated with 3% CCA-C compared to 1% CCA-C, and the post-fixation power washing treatment had no consistent effect on leaching.
In general, cumulative leaching losses were initially high for the first month of exposure, followed by a decline to lower levels during the autumn and winter

months (see Fig.'s 1, 2, and 3). This trend repeated itself during the spring of 2001, when a second increase and stabilization of leaching was evident. This second wave of leaching is most likely a result of frequency and duration of rain events and associated higher temperatures during the spring season and not a reflection of treatment parameters.

Total average chromium, arsenic and copper leaching values for each treatment combination based on three replicates are presented in Table 2. Non-uniform variances between treatments violated an assumption of the ANOVA model, requiring log transformations to present multiple comparisons and significant differences. The transformations were verified by examining plots of residuals for homogeneity and normality. In general, jack pine and black spruce exhibited higher percent loss of CCA components compared to southern yellow pine, but displayed similar losses per unit surface area. Copper displayed the highest percent losses, reaching over 5% from black spruce samples treated with 1% CCA-C and exposed to 685mm of precipitation. Arsenic percent loss reached a high of 3.9% and chromium 1.6% loss for the same treatment type during the exposure period.

In terms of leaching losses per unit surface area, chromium displayed significantly higher leaching from samples treated with 1% CCA-C compared to 3% CCA-C for all three species. Arsenic and copper leaching produced the opposite trend, with total average leaching from 3% CCA-C treated samples resulting in significantly higher values than samples treated with 1% CCA-C for a number of treatments. The commercial brush-on water-repellent treatment was effective at significantly reducing total leaching for all treatments at the 3% CCA-C concentration level, with the exception of arsenic from southern yellow pine. Although not significant for all treatment types, similar reductions in total losses were observed for water repellent samples treated with 1% CCA-C. The highest chromium (20.5 $\mu g/cm^2$ from black spruce), arsenic (138.1 $\mu g/cm^2$ from SYP), and copper (68.4 $\mu g/cm^2$ from SYP) losses occurred from samples treated with 1% CCA-C.

The post-fixation washing treatment was not effective at reducing total leaching. The treatment displayed reduced CCA component losses for southern yellow pine samples only, whereas jack pine and black spruce samples exhibited higher losses from the washing treatment compared to unwashed samples. This increase is more likely a reflection of differences in localized preservative loadings between samples of the post-fixation wash treatment and unwashed treatment rather than the treatment effect alone.

Discussion and Conclusions

The leaching of individual elements is not in proportion to their original concentrations in the treating solution, which agrees with earlier work by Fahlstrom *et al*. (7). Chromium oxide accounts for approximately 48% of the CCA-C formulation, but is quite leach resistant. Arsenic and copper account for approximately 34% and 18% of the initial preservative solution respectively, and leach in greater quantities. Total losses from 57 rain events during 351 days of exposure ranged between 7.3 to 20.5 µg/cm^2 for Cr, 31.3 to 138.1 µg/cm^2 for As, and 19.1 to 78.6 µg/cm^2 for Cu (see Table 2).

Fahlstrom *et al*. (7) described leaching rate decreases to less than one-tenth of initial values within 18 hours and down to one-hundredth within 48 hours of water contact. Cumulative leaching trends for the results presented in this paper suggest that the rate decrease is much slower. The nature of periodic wetting and drying cycles associated with above ground exposures appears to extend the time requirement in which rate decreases are observed.

It would be logical to assume that lower initial preservative loadings would leach less when put into service, but the results presented in this study suggest otherwise. Percent loss of chromium, arsenic and copper were much higher from wood treated with 1% CCA-C compared to 3% CCA-C. The higher preservative loading produced lower percent loss of components, but displayed increased loss per unit surface area (µg/cm^2) of arsenic and copper.

Application of Thompson's Water Seal® reduced CCA leaching significantly, supporting earlier findings by Cooper *et al*. (3). Commercial water repellents should be recommended for all above ground applications of treated wood to minimize water contact, and subsequent leaching. Although results for the post-fixation washing treatment were inconsistent, treating facilities may wish to consider post-fixation power washing to ensure complete removal and recovery of surface deposits before treated wood is put into service.

The relationship between initial leaching and total leaching may be of use for the establishment of laboratory leaching standards. There is increasing desire to have standards of short duration and high reproducibility, that accurately simulate leaching during natural exposure. Although this would exclude effects of climatic variables, establishing a linear relationship between initial and final leaching losses may support the use of short duration leaching tests without compromises in accuracy.

Literature Cited

1. Cooper, P.A. 2001. Analysis of consumer lumber waste management options. Wood Preservation Strategic Options Process Manufacturers/Treaters Steering Committee. Consumer Waste Lumber Working Group. Unpublished.

2. Cooper, P.A., and R. MacVicar. 1995. Effect of water repellents on leaching from CCA treated fence boards. International Research Group on Wood Preservation. Stockholm, Sweden. IRG/95-40044.

3. Cooper, P.A., Y.T. Ung, and R. MacVicar. 1997. Effect of water repellents on leaching from CCA treated fence and deck units. International Research Group on Wood Preservation. Stockholm, Sweden. IRG/97-50086.

4. Cserjesi, A.J. 1976. Permanence of preservatives in treated experimental shake roofs. Forest Products Journal 26: 34-39.

5. Cui, F., and P. Walcheski. 2000. The effect of water-repellent additives on the leaching of CCA from simulated southern yellow pine decks. The International Research Group on Wood Preservation. Stockholm, Sweden. IRG/WP/00-50158.

6. Deroubaix, G., G. Labat, G. Le bayon, S. Legay, P. Marchal, C. Yrieix, E. Melcher, R.-D. Peek, S. De Geyter, J. Van Acker, W.J. Homan, D.J. Dickinson, R.J. Murphy, E. Suttie, A. Nurmi, A.C. Ritscloff, D. Rudolph, I. Stephan, D. Aston, E. Baines, and J.B. Simonin. 2000. Environmental risk assessment of treated timber in service: the environment focus group approach. International Research Group on Wood Preservation. Stockholm, Sweden. IRG/WP/00-50162.

7. Fahlstrom, G.B., P.E. Gunning, and J.A. Carlson. 1967. Copper chrome-arsenate wood preservatives: a study of the influence of composition on treatability. Forest Products Journal 17(7): 17-22.

8. Hingston, J.A., C.D. Collins, R.J. Murphy, and J.N. Lester. 2001. Leaching of chromated copper arsenate wood preservatives: a review. Environmental Pollution. 111: 53-66.

9. Lebow, S. 1996. Leaching of wood preservative components and their mobility in the environment. Summary of pertinent literature. General Technical Report. Forest Products Laboratory, United States Department of Agriculture, Forest Service. FPL-GTR-93: 36.

10. Morrell, J.J., and R. Rhatigan. 2000. Preservative movement from Douglas-fir decking and timbers treated with ammoniacal copper zinc arsenate using best management practices. Forest Products Journal 50: 54-58.

11. Murphy, R.J., and D.J. Dickinson. 1990. The effect of acid rain on CCA-treated timber. International Research Group on Wood Preservation. Stockholm, Sweden. IRG/WP/3570.

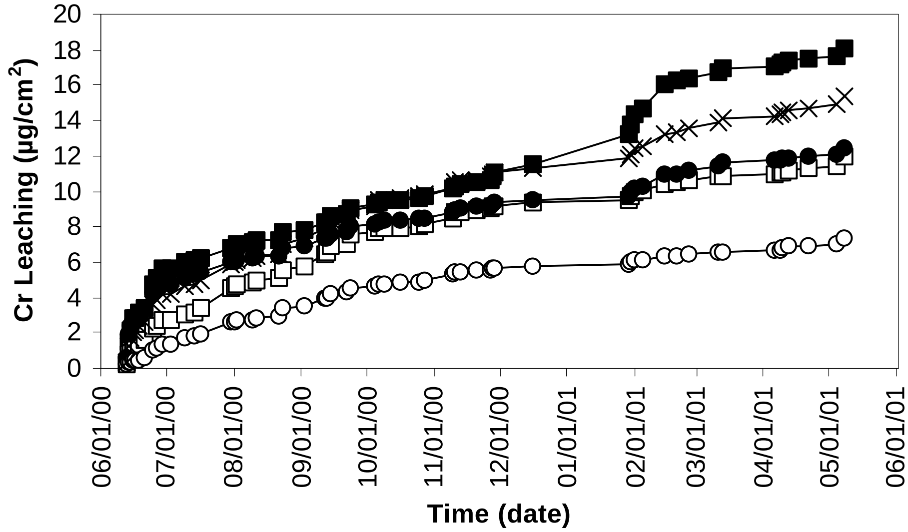
Table 1. Average CCA-C Preservative Retentions by Treatment Type.

Species	CCA-C Preservative Concentration	Preservative Retention (kg/m^3)
Jack Pine	1%	2.57
Jack Pine	3%	6.47
Black Spruce	1%	1.70
Black Spruce	3%	5.43
SYP	1%	5.52
SYP	3%	13.94

Table 2. Total Leaching (µg/cm^2) and Percent Loss (%) of Chromium, Arsenic and Copper.

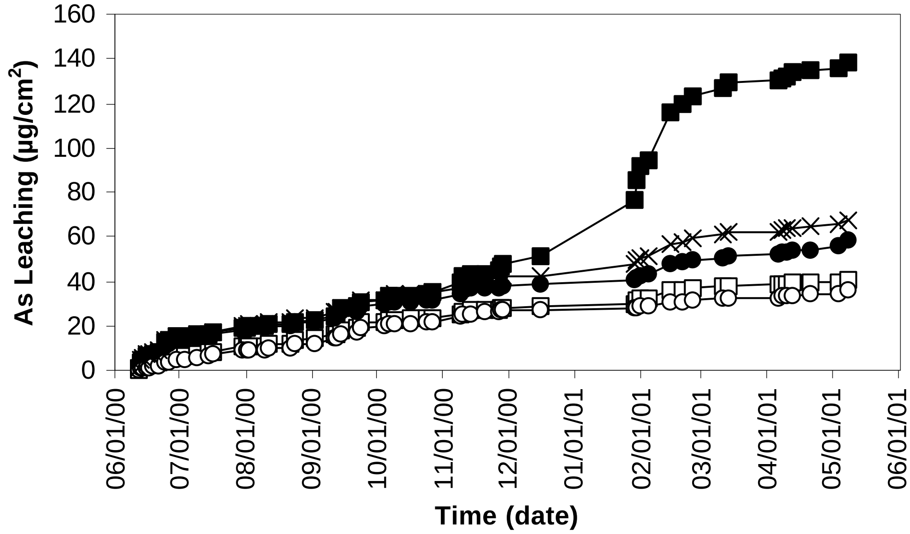
Species	Sample Treatment			Leaching Loss (µg/cm^2)			Leaching Loss (%)			
	CCA-C Pres. Conc.	Water Repellent	Post-fixation Wash	Total Mean Cr (st. dev.)	Total Mean As (st. dev)	Total Mean Cu (st. dev.)	Total Cr	Total As	Total Cu	Total CCA
Jack Pine	1%	no	no	19.1 A (4.06)	44.4 BCD (9.77)	39.2 CDEF (5.87)	1.3	3.4	4.1	2.6
Jack Pine	1%	yes	no	12.6 C (1.95)	33.3 CD (2.96)	28.3 G (10.28)	0.7	1.8	2.1	1.3
Jack Pine	3%	no	no	11.5 CD (1.43)	53.4 BC (11.49)	60.7 AB (9.87)	0.2	1.0	1.6	0.7
Jack Pine	3%	yes	no	8.8 DE (0.16)	32.3 CD (3.92)	31.2 EFG (6.87)	0.2	0.6	0.9	0.4
Jack Pine	1%	no	yes	18.5 A (1.36)	50.5 BC (11.77)	41.8 CDE (8.44)	0.7	2.2	2.6	1.5
Black spruce	1%	no	no	20.5 A (0.73)	43.4 BCD (1.19)	38.4 DEFG (5.64)	1.6	3.9	5.2	3.0
Black spruce	1%	yes	no	13.2 BC (0.79)	25.8 D (0.86)	19.1 H (2.43)	0.7	1.5	1.7	1.1
Black spruce	3%	no	no	11.8 CD (1.04)	64.6 AB (7.42)	63.1 AB (6.99)	0.2	1.4	2.0	0.9
Black spruce	3%	yes	no	7.3 E (0.75)	31.3 CD (4.74)	28.3 FG (5.36)	0.1	0.6	0.8	0.4
Black spruce	1%	no	yes	19.3 A (3.88)	49.8 BC (4.01)	47.4 BCD (7.02)	0.9	2.7	3.9	2.1
SYP	1%	no	no	18.0 AB (7.68)	138.1 A (128.23)	68.4 AB (23.86)	0.3	2.5	1.9	1.4
SYP	1%	yes	no	12.0 CD (2.59)	40.9 BCD (6.27)	32.6 EFG (3.25)	0.2	0.8	1.0	0.5
SYP	3%	no	no	12.4 C (3.24)	58.0 BC (29.17)	78.6 A (6.41)	0.1	0.6	1.0	0.4
SYP	3%	yes	no	7.4 E (0.59)	36.0 CD (12.11)	42.4 CDE (4.05)	0.1	0.4	0.6	0.3
SYP	1%	no	yes	15.4 ABC (0.39)	67.6 AB (19.85)	54.9 BC (5.61)	0.3	1.5	1.7	1.0

Mean leaching values were compared statistically to determine effects of treatments. These mean values are significantly different (á = 0.05 Duncan's Multiple Range Test) if they do not share the same letter.



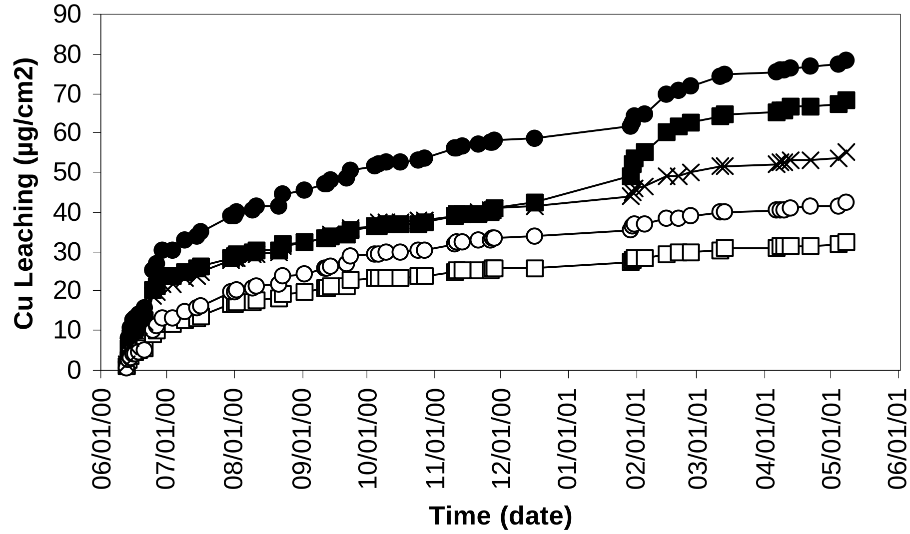
1% CCA-C
1% CCA-C, Water Repellent
x 1% CCA-C, Washed
3% CCA-C
3% CCA-C, Water Repellent

Figure 1: Cumulative Chromium Leaching from Southern Yellow Pine Lumber Exposed to Natural Above Ground Leaching Conditions.



1% CCA-C
1% CCA-C, Water Repellent
x 1% CCA-C, Washed
3% CCA-C
3% CCA-C, Water Repellent

Figure 2: Cumulative Arsenic Leaching from Southern Yellow Pine Lumber Exposed to Natural Above Ground Leaching Conditions.



1% CCA-C
1% CCA-C, Water Repellent
x 1% CCA-C, Washed
3% CCA-C
3% CCA-C, Water Repellent

Figure 3: Cumulative Copper Leaching from Southern Yellow Pine Lumber Exposed to Natural Above Ground Leaching Conditions.