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LABORATORY STUDIES OF CCA-C LEACHING: INFLUENCE OF WOOD AND SOIL PROPERTIES ON EXTENT OF ARSENIC AND COPPER DEPLETION

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Laboratory Studies of CCA-C Leaching:
Influence of Wood and Soil Properties on Extent of As and Cu Depletion

by

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Abstract

The extent which a wood preservative leaches is important for efficacy studies and environmental concerns. However, little information exists on the effect soil properties have on leaching. This study investigated leaching of stakelets which had been cut from five different southern yellow pine (SYP) sapwood boards then treated with CCA-C to a target retention of 6.4 kgm^{-3} (0.4 pcf). All stakelets were leached for 12 weeks by a common laboratory method in five different soils or water, with five replicate stakelets per board/soil. The physical and chemical properties of the five different soils were determined and the average leaching of the individual components of CCA was correlated with the various soil properties. Unfortunately, migration of a soil component (likely iron) into the stakelets from at least one of the five soils interfered with Cr determination by X-ray fluorescence; consequently, Cr depletion was not studied. Stakelets cut from one board tended to have lower Cu and As losses than the average of the other four boards for all five soils and water, and stakelets from another board tended to have higher Cu losses. Stakelets from all five boards had similar initial Cu and As levels, suggesting that the board effect was not due to differences in initial retentions. Cu loss was approximately equal to or greater than As loss for stakelets exposed to all five soils, but for wood leached in water the As loss was about twice the Cu loss. The soil property which was most statistically correlated to Cu loss was % Base Saturation (r^2 of 77%), with Soil Acidity (pH) also important as a single predictor, and the Cr and Cu Soil Contents important as secondary predictors. The relationship between % Base Saturation (or Soil Acidity) and % Cu leached was not linear, however. A negative correlation was observed between Soil Cu Content and the metal leached from wood. The best factor to predict As loss was the Soil Cu Content, with Exchangeable K and % Silt also contributing to give an overall r^2 of 72.3%. The % Organic Matter and the Soil As Content were also important as secondary predictors. We conclude that depletion of CCA is extremely complex and that Cu and As depletion appears to be influenced differently by the soil properties. Furthermore, extent of leaching can vary between different wood samples of the same species and even samples cut from the same board; thus, leaching data are not precise. Recommendations are given for a standard laboratory method for ground-contact leaching.

Keywords: CCA-C (Chromated Copper Arsenate-type C); Depletion; Leaching; Soil

Introduction

When treated wood is placed in soil, complicated leaching/depletion and chemical reactions (biodegradation of organics, metals complexing with organic compounds in the soil, etc.) occur which lowers the biocide level in the wood. Leaching of a biocide is important both for predicting the long-term efficacy of treated wood and determining potential environmental contamination.

Depletion is extremely complex and controlled by many factors. For example, greater leaching usually occurs when treated wood is placed in soil as opposed to water (Nicholas 1988; Cooper and Ung 1992; Wang et al. 1998) and, consequently, the chemical and physical properties of soil have an effect. The type of microbes present, which is heavily influenced by the soil properties (and collection method for laboratory studies), can also affect depletion. Furthermore, extent of depletion among duplicate samples can vary widely, even when samples are treated at the same time and installed in only one site or soil type (Schultz et al. 2002). Thus, data can be extremely variable which makes it difficult to statistically determine which soil factors influence leaching of a particular biocide or provide an estimate how much biocide may leach from wood.

The development of effective and safe wood preservatives requires considerable laboratory and outdoor tests, including leaching studies. However, no standard leaching protocol for wood in soil contact exists. The objective of this study was to leach treated wood samples by a common method at various government, university and company laboratories, with each lab using local soil. From the results obtained we hoped to identify factors important when developing a standard for soil-contact laboratory leaching. Southern yellow pine (SYP) sapwood treated with chromated copper arsenate (CCA-C) was selected, since SYP is the major wood treated and CCA-C is currently the major wood preservative in the U.S. (Micklewright 1999). Five different soils were used, along with a water-leach as a control treatment. The chemical and physical properties of the soils were determined so that the soil properties which have the greatest affect on leaching could be determined.

Experimental

Stakelets measuring 14 mm square by 250 mm long were cut from kiln-dried, defect free southern yellow pine (SYP) (*Pinus spp*.) sapwood. Thirty individual stakelets were cut from each of five different boards, for a total of 150 stakelets. The five boards were randomly selected from boards used to prepare field stakes or small wafers for laboratory decay tests. The stakelets were equilibrated to a moisture content of approximately 8% before treatment with CCA-C to a target retention of 6.4 kg/m^3 (0.4 pcf) by a full cell process (15 minutes vacuum at 26 inches Hg then 150 psig pressure for 60 minutes). After treatment the stakelets were stored in plastic bags for seven days at room temperature to prevent redistribution of the biocide during air-drying/free water movement (Schultz et al. 2003), then unbagged and allowed to air dry. A 100 mm long section was then cut from each stakelet to determine the initial CCA retention prior to leaching. The retention sample was removed from the cut end of these sections to avoid the variation associated with the end grain of stakelets.

The test containers for soil leaching were plastic flower pots measuring 170 mm in diameter by 160 mm deep, with drain holes in the bottom. The bottom of each pot was covered with a plastic screen prior to adding the soil, and the drain hole plugged with a rubber stopper. Five replicate pots were used in each location/laboratory (USDA/Forest Products Laboratory, soil from Wisconsin [FPL]; Arch Wood Protection Inc., soil from Georgia [Arch]; Michigan State University, [MI]; Osmose, Inc., soil from New York [Osmose]; and soil from Mississippi State University=s Dorman Lake plot [MSU]. At each laboratory five replicate stakelets from one particular board were inserted vertically into the soil of each of five replicate pots so that one end of the stakelet was flush with the top of the soil. This was then repeated for all 25 stakelets leached at each laboratory. Distilled water was then slowly added to the pots until there was an excess present. The water-saturated soil was left for 24 hours, then the excess water was drained from the bottom of the pots by removing the rubber stopper. Additional water was added twice a week to maintain a high soil moisture content, with a loose-fitting cover used to prevent drying. The pots were stored in the participating laboratory at room temperature during the exposure period. In addition to the soil exposure, a set of 25 treated stakelets (five replicates from each of the five boards) was soaked in distilled water to provide a comparison with the soil leach test [Water]. After 12 weeks of exposure, the stakelets were removed from the pots, lightly scrubbed, rinsed briefly with distilled water and blotted with a damp towel. The sticks were allowed to air dry, then a 50 mm section from each stakelet cut to determine the CCA content after leaching.

The soil from each of the five participating laboratories was analyzed for the physical and chemical properties by previously-described procedures (Schultz et al. 2002), with the particle size distribution, pH and % Organic Matter (Table 1), chemical analysis (Table 2) and heavy metals (Table 3) of the soil at each participating laboratory determined.

A 50 mm section from the initial (unleached) and a leached 50 mm sample from each stakelet were individually ground in a Wiley mill to 20 mesh, and each wood sample was analyzed three times using different wood each time, with the three analyses averaged together, to determine the individual CCA components (Cr, Cu and As, oxide basis) by X-ray fluorescence (ASOMA model 8620 bench-top instrument). Unfortunately, some component in the FPL/Madison soil apparently migrated into the stakelets and interfered with the Cr analysis, since an average **gain** of 48% Cr content after leaching was obtained from the 25 stakelets. This same component may have also interfered with Cr analysis in the stakelets exposed to one or more of the other four soils; consequently, Cr depletion was not be studied. This effect may have also affected results in prior leaching studies which used bench-top X-ray fluorescence instruments to quantify the Cr content of CCA-treated wood which had been in soil.

Statistics for this preliminary paper were carried out using stepwise regression on MINITAB software, with an F value-to-enter (or remove) of 4.00, and assuming a linear relationship.

Results and Discussion

The most logical soil component which might interfere with Cr determination of the samples leached in the Madison/FPL soil was iron, based on the periodic chart and it=s natural abundance in soils. To check this, 1.3% Fe(III) Sulfate was added to wood meal and analyzed by a bench-top X-ray fluorescence instrument. [Unfortunately, our ASOMA instrument had recently ceased functioning, and this experiment was run using a replacement (Oxford 3000) bench-top instrument]. An ACrO_3@ content of about 0.4% was obtained, which strongly suggests that iron caused the interferrence. [Thus, about 0.4 % Fe gave a reading of about 0.4 % CrO_3. Assuming that Fe is indeed the cause for the increase in Cr, based on the initial CrO_3 retention of about 3.2 kg/m^3 and almost a 50% increase in the Cr content, about 1.6 kg/m^3 of Fe, or 0.3 % Fe, may have somehow migrated into the stakelets exposed to the Madison/FPL soil. This is based on no Cr lost by leaching, so the actual amount of Fe may be higher. We will analyze some representative samples shortly to determine if Fe is actually present and measure the levels of Fe and Cr in these stakelets.] Based on the relatively neutral soil pH, iron would likely migrate into the CCA-treated stakelets by microbiological means (Ruddick 1992) rather than a simple physical diffusion. [If Fe did migrate into wood, by whatever means, this might lead to enhanced depletion of Cu and/or Cr in CCA-treated wood exposed to soil for an extended time (multiple months) via metal-exchange reactions. Alternatively, it is well known that Fe and As complex together. It may be possible that formation of a strong FeAs complex would deactivate As (Morris 1993)]. The possible Fe interference may have also affected Cr depletion data in the other soils examined in this and our prior study (Schultz et al. 2002), and other researcher=s leaching experiments.

Replicate stakelets (stakelets cut from the same board and exposed to the same soil) had considerable variability in depletion of Cu and As. This was expected, since prior studies also reported high variability (Wang et al. 1998; Schultz et al. 2002). Multiple analyses of the same stakelet gave similar results, thus, the variability was not due to the analysis method. To reduce the variability, the Cu and As depletions from the five individual stakelets were averaged (Table 4). The individual stakelet depletion data will be completely statistically analyzed at a later date.

Board Effect

The Cu and As depleted from stakelets cut from board 75 tended to be lower than the average overall depletion in the five different soils and water, while higher Cu losses than average were generally observed in stakelets from board 59. These trends were not due to the initial Cu and As retentions, since board 59 had the highest initial retention but board 75 the second highest (Table 4). A similar board influence on leaching of CCA [As and Cu only], DDAC or pentachlorophenol-treated wood in ground contact was observed earlier (Wang et al. 1998).

Soil vs. Water

Comparing Cu depletion in the five soils versus water (Table 4), in all cases more Cu was leached from wood exposed to soil than water. For As depletion, however, the differences between wood exposed to soil or water were less clear. Specifically, the % As leached from water and three of the five soils were similar, with slightly more As lost from one soil (MSU) and the highest As depleted in wood exposed to the MI soil. Wang et al. (1998) previously reported greater Cu than As lost from wood exposed to soil, while in water greater As than Cu was lost.

Table 1. Characteristics of Soils Examined.

Soil Location	Lab	Soil Texture (%)					
		Sand	Silt	Clay	pH (H_2O)	pH (KCl)	Organic Matter (%)
Wisconsin	USDA-FPL	17.9	67.2	14.9	6.68	5.82	2.13
Georgia	Arch	75.5	21.2	3.3	4.34	3.99	2.91
Michigan	Michigan State University (MI)	74.0	22.2	3.8	5.49	5.03	3.89
New York	Osmose	44.6	39.4	16.0	7.59	6.84	4.78
Mississippi	Mississippi State University (MSU)	11.4	56.0	32.6	4.81	3.72	2.40

Table 2. Exchangeable Cations and Base Saturation of the Soils.

Soil Location	Lab	Exchangeable Cations (Cmol/kg)							Base Sat. (%)
		Ca	Mg	K	Na	Exch. H+	Exch. Al*	Sum of Bases	
Wisconsin	USDA-FPL	7.59	4.10	0.16	0.05	3.50	0.00	15.40	77.27
Georgia	Arch	2.11	0.93	0.07	0.03	6.15	0.32	9.29	33.80
Michigan	Michigan State University (MI)	4.27	0.97	0.37	0.06	5.91	0.06	11.58	48.96
New York	Osmose	16.26	2.03	0.80	0.03	2.58	0.00	21.70	88.11
Mississippi	Mississippi State University (MSU)	5.66	4.49	0.39	0.12	15.6	5.45	26.26	40.31

* Not included in sum of bases.

Table 3. Heavy Metal Content of the Soils.

Soil Location	Lab	Heavy Metal Content of Soils (ppm)								
		Fe	Mn	Zn	As	Cd	Cr	Ni	Pb	Cu
Wisconsin	USDA-FPL	16111	1248	50	7	0.047	20	18	15	11
Georgia	Arch	16611	579	31	2	0.006	89	18	8	15
Michigan	Michigan State University (MI)	6882	80	46	3	0.182	7	5	12	4
New York	Osmose	17267	612	306	10	0.337	22	35	297	32
Mississippi	Mississippi State University (MSU)	43436	1489	46	23	0.390	43	13	40	11

Table 4. Average % Cu and As leached from CCA-C stakelets after exposure to five different soils or water. Each individual board value is the average of five replicates. The % Cr leached could not be determined due to possible interference by Fe with the X-ray fluorescence instrument. For samples exposed to a water leach, an average of 5.0% Cr was lost.

Board I.D.	Metal	Average[a] Initial Rtn, kg/m^3	% Leached					
			Soil					Water
			FPL	Arch	MI	Osmose	MSU	
75	Cu As	1.33 2.11	10.9 7.3	24.7 9.3	21.3 20.2	7.0 10.2	23.4 14.9	4.2 8.7
17	Cu As	1.25 2.00	11.8 12.0	22.8 11.7	24.4 24.0	9.6 12.2	26.6 20.9	6.8 13.7
45	Cu As	1.22 1.94	14.4 12.1	22.4 11.4	21.8 18.9	11.7 13.6	22.3 16.7	6.9 14.3
30	Cu As	1.22 1.95	7.6 8.2	25.5 15.5	32.7 28.4	3.8 6.1	24.9 15.0	2.7 8.9
59	Cu As	1.42 2.27	16.6 13.0	26.5 5.0	32.1 35.4	9.6 11.7	27.2 16.4	9.9 16.4
Overall Average	Cu As	1.29 2.05	12.3 10.5	24.4 10.6	26.5 25.4	8.5 10.8	24.8 16.8	6.1 12.2

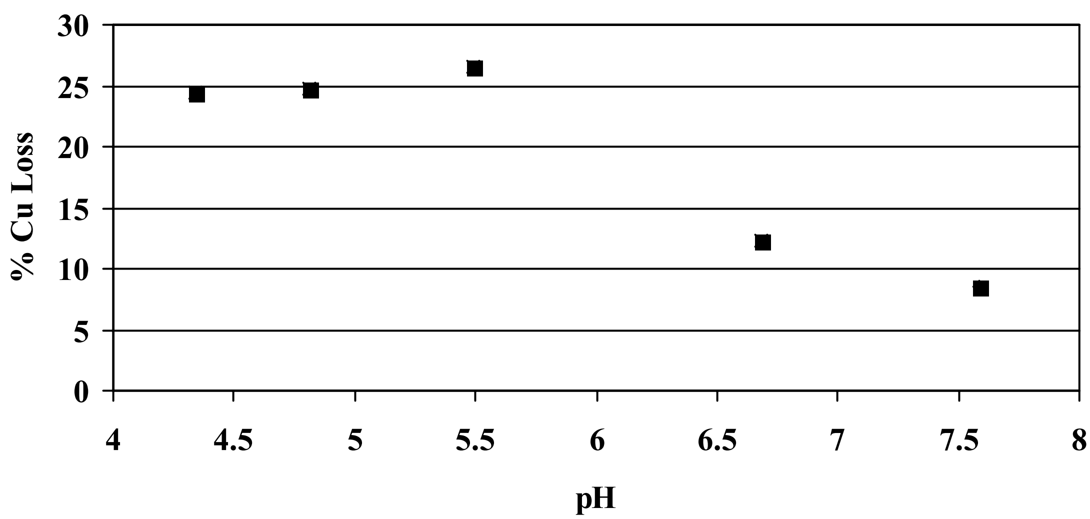
[a] Initial retention is the average of 25 samples.

Soil Factors Related to Extent of Cu Leached

A stepwise regression of Cu leached from each of the five boards versus 19 of the chemical and physical properties from the five different soils (% Total Sand, % Silt, % Clay; pH/H_2O, pH/KCl, % Organic Matter, Exchangeable Ca, Mg, K, Acidity, and Al, Sum of Bases, % Base Saturation, and the Fe, Mn, Zn, As, Cr and Cu Soil Contents) was performed. The best single predictor of the extent of Cu leached was % Base Saturation, with a r^2 of 77.0%. A second predictor, the Cr Soil Content, then Astepped in@ to give an overall r^2 of 84.8%. When the model was reduced to only consider the Cu and As Soil Metal Contents but keeping all other properties listed above and the regression re-run, the Cu Soil Content was negatively related to the extent of Cu leached from the wood such that the higher the Cu Soil Content the less Cu leached. This result is similar to what we reported earlier (Wang et al. 1998). Apparently, the lower the Cu Soil Content the greater the gradient and the larger the Fickian diffusion potential for Cu migration from wood.

Not surprisingly, many soil properties are correlated to each other. For example, in Table 2 the five different soils have Soil Acidity (pH/H_2O and pH/KCl) closely related to % Base Saturation. Thus, regression of % Cu depleted versus only pH/H_2O or pH/KCl also gave respectable correlations, with r^2 of 71.7 and 66.2%, respectively. Other researchers have also shown Soil pH to be a significant factor in Cu leaching from wood (Wang et al. 1998, Edlund and Nilsson 1999). However, the pH effect is not straightforward; the presence of organic acids which can complex with Cu gives greater leaching than that obtained with inorganic acids (Warren and

Figure 1. Average % Cu leached versus soil pH.



Solomon 1990, Cooper 1991, Lebow 1996). In looking at a plot of the % Cu leached versus the soil pH (Figure 1), it appears that as soil becomes more acidic (lower pH) the amount of Cu leached at first increases. Once the soil pH has decreased to 5.5, however, greater acidity apparently causes no further increase in Cu leaching with the average % Cu loss remaining at about 25% as the soil pH decreases from 5.5 to 4.3. In contrast, Wang et al. (1998) and Edlund and Nilsson=s data (1999) suggest a linear relationship between pH and Cu depletion. [Since pH is a $\log_{10}$ function of the actual acidity (H^+ concentration), any direction correlation between soil pH and Cu loss would be expected to be a semi-log function].

Soil Factors Related to As Loss

A stepwise regression was performed on the % As leached from wood, with the most significant predictor a negative correlation with the Cu Soil Content (r^2 of 30.1%). Secondary predictors were Exchangeable K followed by % Silt, with an overall r^2 of 72.3%. Other secondary factors which were important included the % Organic Content and the soil=s As content.

The Fe Soil Content was not related to the extent of As leached. Since Fe and As can form strong complexes (Pettry and Switzer, 2001), one might expect that a high Fe Soil Content would give an enhanced As loss from CCA-treated wood.

Suggestions for Laboratory Leaching Method

Based on these results, we recommend that the following be considered when developing a standard method for ground-contact leaching for CCA-treated wood.

1. Wood samples be cut from at least four different boards, with multiple samples cut from each board.
2. At least three different soils be employed. The following soil properties appear to be important when selecting the soils: % Base Saturation, pH(H_2O), Exchangeable K, % Organic Content, % Silt, and the As, Cr and Cu Soil Contents.
3. Finally, in our prior lab study (Wang et al. 1998) and outdoor exposure study (Schultz et al. 2002), wood was exposed for up to 26 weeks and 66 months, respectively. In these studies it appears that additional exposure time did not greatly increase the amount of biocide leached. Thus, the 12 weeks of exposure in this laboratory study appears sufficient.

These recommendations are specific for leaching studies with CCA-treated wood. Recommendations for organic:copper mixtures, or totally organic systems, will require further study. Data already published (e.g. Edlund and Nilsson 1999, Wang et al. 1998) might suggest some of the important soil properties for Cu depletion in copper:organic systems. Also, this experiment used samples with small radial and tangential dimensions; thus, these data should not be used to predict depletion from commercial-size wood (Schultz et al. 2002).

Finally, this article is based only on laboratory leaching. Further studies are necessary to determine if a correlation exists between laboratory and outdoor ground-contact leaching. For example, this study suggests that the Cu and As Soil Contents are important. In a recent field-exposure study, however, no differences in extent of As and Cu leached was observed in two different sites which had two soils with significantly different Cu and As Contents (Schultz et al. 2002). In addition, another factor needing further study was if the use of water-saturated soil in these laboratory experiments - and thus possibly anaerobic conditions - affected the distribution and type of microorganisms present and, consequently, influenced the extent of leaching.

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