

Relative Leaching and Aquatic Toxicity of Pressure-Treated Wood Products Using Batch Leaching Tests

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Size-reduced samples of southern yellow pine dimensional lumber, each treated with one of five different waterborne chemical preservatives, were leached using 18-h batch leaching tests. The wood preservatives included chromated copper arsenate (CCA), alkaline copper quaternary, copper boron azole, copper citrate, and copper dimethyldithiocarbamate. An unpreserved wood sample was tested as well. The batch leaching tests followed methodology prescribed in the U.S. Environmental Protection Agency toxicity characteristic leaching procedure (TCLP). The wood samples were first size-reduced and then leached using four different leaching solutions (synthetic landfill leachate, synthetic rainwater, deionized water, and synthetic seawater). CCA-treated wood leached greater concentrations of arsenic and copper relative to chromium, with copper leaching more with the TCLP and synthetic seawater. Copper leached at greater concentrations from the arsenic-free preservatives relative to CCA. Arsenic leached from CCA-treated wood at concentrations above the U.S. federal toxicity characteristic limit (5 mg/L). All of the arsenic-free alternatives displayed a greater degree of aquatic toxicity compared to CCA. Invertebrate and algal assays were more sensitive than Microtox. Examination of the relative leaching of the preservative compounds indicated that the arsenic-free preservatives were advantageous over CCA with respect to waste disposal and soil contamination issues but potentially posed a greater risk to aquatic ecosystems.

Introduction

Manufactured wood products from many wood species (e.g., southern yellow pine, Douglas fir) require treatment with a preservative if they are to be used in environments where decay or rot is likely. Pressure treatment of wood refers to the process where wood is impregnated with preservatives under pressure (1). Wood preservatives primarily include

oilborne chemicals (creosote, pentachlorophenol) and waterborne chemicals. The main waterborne wood preservative used in North America in recent decades has been chromated copper arsenate (CCA). In 1996, CCA-preserved wood represented 79% of the U.S. wood preservative market (2). Environmental and health issues stemming from the chemicals in CCA-treated wood, primarily arsenic, have raised concerns over its use and disposal (3–7). The wood preservation industry and the U.S. Environmental Protection Agency (EPA) agreed to phase out the production of CCA-treated wood for many uses (predominantly residential) beginning in January 2004. Instead of producing CCA-treated wood for residential use, the wood-treatment industry has converted to alternative wood preservatives, a majority of which do not contain arsenic or chromium.

In this research, the relative leachability of preservative chemicals from CCA-treated wood and four different arsenic-free preservatives was examined. Basic descriptions of each wood preservative are provided in the online Supporting Information section available with the web version of this article. While a variety of leaching tests have been performed on CCA-treated wood (8–13), fewer leaching tests have been conducted on wood treated with alternatives to CCA (see Solo-Gabriele et al. (14) for a compilation of industry-reported data). Additionally, side-by-side comparisons of leaching characteristics of preservative-treated wood products are very limited. Because of differences in preservative leaching properties that result from varying wood types, treatment conditions, and leaching test methodologies, comparing leaching results from different studies can prove difficult. Eighteen-hour batch leaching tests were performed. Such tests are often one of the first steps conducted to evaluate the leachability and potential migration of chemicals from soils and wastes (15), and in some cases are directly incorporated into regulations.

The leached chemical concentrations from the treated wood products tested were used along with relevant regulatory limits and risk-based target concentrations to assess potential impacts on waste disposal systems (e.g., landfills) and soil underlying and surrounding treated wood structures. Batch leaching test results may also provide a preliminary estimate of the relative impact of leached chemicals from treated wood products used in aquatic applications (e.g., piers, docks, bulkheads). Chemical leaching data alone, however, may not always be reflective of true aquatic risks (16). Water quality standards are developed using assumptions regarding an element's form and bioavailability, assumptions that may not be valid in a given environment. The risk presented by a mixture of chemicals in solution may be different than for the individual species alone. Bioassays can provide added insight that chemical measurements alone do not provide. To further examine the potential relative impact of the different wood preservative systems on aquatic environments, three aquatic toxicity assays were conducted on the leachate samples. The relative leaching concentrations and aquatic toxicities reported here provide needed input for broader risk or life-cycle assessments involving an evaluation of different treated wood products.

Materials and Methods

Sample Preparation. Treated wood samples were generated from a uniform stock of untreated southern yellow pine to minimize variability that can result from the treatment of different wood types. Eight 5-m (16-ft) lengths of 3.8 by 8.8 cm (1.5 by 3.5 in.) untreated dimensional lumber were purchased from a Miami, FL lumberyard. To reduce possible

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TABLE 1. Measured Preservative Retention Values of Treated Wood Samples Tested

chemical	preservative retention value (kg/m ³)					
	CCA-1	CCA-2	ACQ	CBA	CC	CDDC
CuO	0.66	0.80	2.5	1.8	3.0	2.8
CrO ₃	1.7	2.1				
As ₂ O ₅	1.4	1.6				
H ₃ BO ₃				1.5		
DDAC			1.5			
tebuconazole				0.064		
citric acid					1.3	
SDDC						6.7
total measured preservative	3.76	4.5	4.0	3.36	4.3	2.8 ^a
total target preservative	4.0	4.0	4.0	3.26	4.0	2.0 ^a

^a As CuO.

variability among boards, only pieces where wood grains were oriented horizontally and with 1.6 growth rings per cm (4 per inch) were selected. Each board was cut into eight 0.6-m (2 ft) lengths. Bundles of eight pieces were created, with each piece coming from a different board and location on the board (see Townsend et al. (17) for more details).

Four bundles were sent to chemical manufacturing facilities for treatment (CCA-Type C, CBA-Type A, CC, and ACQ-Type D). The nominal composition of the various wood preservatives types are described in the Supporting Information section. An additional bundle was sent to a wood treatment facility for CCA-Type C treatment. Thus, two samples of CCA-treated wood were evaluated in this study (hereafter referred to as CCA-1 and CCA-2). A remaining bundle was saved for testing untreated wood. The only wood preservative not obtained in this fashion was CDDC. Shortly after the research started, the CDDC manufacturing facility closed. Previous samples of CDDC-treated wood provided by the manufacturer were thus used. The samples used for the leaching analysis were cut into small blocks (2.5 by 5 by 10 cm) using a mill saw and then ground to particles less than 3 mm in diameter using a Fritsch Pulverisette 19 mill. The objective of size reduction was to meet size reduction requirements used in standard waste leaching procedures (18) (<0.95 cm) and to create a homogeneous sample so that relative chemical leaching could be compared.

Sample Preservative Retention. Following standard practice of the U.S. wood preservation industry, preservative retention values (RV) were measured by drilling the outer 1.5 cm of a representative wood sample, collecting the shavings, and sending them offsite to Timber Products Inspection (Conyers, GA) for analyses. Copper was later reanalyzed by four separate laboratories (see Townsend et al. (17) for details). The RV measured on the outer 1.5 cm of wood may slightly overestimate the RV of the wood as a whole (assuming inner regions of the wood received lower chemical penetration). Table 1 summarizes the RV measured for individual preservative components and the RV corresponding to the total preservative content. Table 1 also presents the targeted RV; measured RV were within 15% of the target RV (17). The RV targeted in this study corresponded to above ground use. Higher RV are applied for in-ground and aquatic uses.

Extraction Fluids. The TCLP (EPA Method 1311) extraction solution was prepared by mixing appropriate volumes of glacial acetic acid (CH₃COOH) and 1 N sodium hydroxide (NaOH) and diluting to 2-L using deionized (DI) water (solution pH of 4.93 ± 0.05). A 100-g, size-reduced, representative wood sample was placed into a 2.2-L Teflon-lined glass container. Two liters of the TCLP extraction fluid was added and the mixture was rotated for 18 ± 2 h. After rotation, the leachate was filtered through a 0.7-μm glass fiber filter and aliquots were placed in high-density polyethylene

(HDPE) containers (preserved to a pH of less than 2 for metals analysis) and in amber glass containers (without preservation for organic compound analysis) (18).

Other leaching tests were performed in the same manner as the TCLP, with the exception of the leaching fluid. The synthetic precipitation leaching procedure (SPLP) (EPA Method 1312) contains nitric and sulfuric acid at a 40/60 weight ratio (solution pH of 4.2 ± 0.05) (18). The synthetic seawater extraction solution (pH = 8.5) was prepared by dissolving 0.5 cups of Instant Ocean in 3.8-L of deionized water; the resulting salinity of the solution was 3.2 psu. Water for the DI water extraction test was obtained using a Barnstead Model D4751 nanopure system; DI water pH ranged from 6 to 7. Every wood sample was leached in triplicate for every leaching fluid.

Leachate Analysis. Prior to analyzing the leachates for arsenic, boron, chromium, and copper, the leachates were digested using EPA Method 3010A (18). The method required the addition of nitric acid and hydrochloric acid to a representative 100-mL leachate sample. The samples were refluxed on a hot plate for up to 8 h with additional aliquots of nitric acid added as necessary. After digestion, the samples were filtered and diluted to 100 mL with DI water. Arsenic, chromium, and copper analysis was conducted using a Thermo Jarrel Ash Environ 60 inductively coupled plasma spectrometer with a detection limit of 0.03, 0.04, and 0.05 mg/L for the three metals, respectively. Boron was analyzed at a commercial laboratory using EPA method 200.7 (19). Blanks, blank spikes, and matrix spikes were included in these experiments for quality assurance and control purposes (18).

The DDAC analysis was adapted from a procedure developed by Chemical Specialties Inc. (Charlotte, NC) (20). An indicator solution was prepared by placing 0.03 g of methylene blue and 50 g of sodium sulfate in a 1-L volumetric flask and bringing to volume with 0.43 N sulfuric acid. Ten milliliters of leachate was added to a glass container along with 10 mL of DI water, 10 mL of chloroform, and 2 mL of the indicator solution. After shaking, the mixture partitioned into an aqueous phase and an organic phase (chloroform); the dye complexed with the DDAC turning the aqueous phase blue. The mixture was titrated with a 0.002 M sodium dodecyl sulfate (SDS) solution. The SDS solution was first standardized with a 0.002 M Hyamine 1622 solution. The SDS solution complexed with DDAC and displaced the dye into the chloroform layer. The titration endpoint was achieved when the chloroform layer turned blue.

The tebuconazole analysis followed a method adapted from an industry standard (Method 25-94) (20). The leachate samples in this study were first saturated with sodium chloride and extracted with 2 L of methylene chloride. The samples were then concentrated and analyzed using gas chromatography coupled with mass spectrometry (GC/MS) (Finnigan Trace 2000 GC/MS).

Citrate ions concentrations were measured using a Dionex Model DX500 ion chromatograph (IC) equipped with an anion IonPac AS11-HC exchange column. The IC manufacture's methodology was used (21). The citrate peak was found at a retention time of approximately 40 min.

The method for determining CDDC concentrations was adapted from AWA Method 25-94 (20). The method utilizes the fact that CDDC absorbs ultraviolet (UV) light at a wavelength of 435 nm. In this method, CDDC is extracted from treated wood using a methanol/chloroform azeotrope. A Hach DR4000 spectrophotometer was used to measure the absorbance of UV light by the leachate samples.

Calculation of Fraction of Preservative Leached. The fraction of preservative chemical leached from the wood samples (%), defined as *F* was calculated by dividing the mass of the chemical in the leachate by the mass of the chemical in the wood (using the RV measurements presented

earlier). The following equation was used to compute F :

$$F = \frac{C_L V_L}{RV \left(\frac{1}{\rho} \right) \left(\frac{MW_x}{MW_R} \right) M_w} * 100\% \quad (1)$$

C_L represents the concentration of chemical measured in the leachate (mg/L), V_L is the volume of leachate (L), RV is the retention value of the chemical constituent (kg chemical/m³ of wood), ρ is the density of the wood (assumed to be 513 kg/m³), M_w is the mass of wood used in the leaching test (mg), MW_x is the molecular weight of the chemical of interest (e.g., copper, arsenic), and MW_R is the molecular weight of the chemical reported in the RV analysis (e.g., CuO, As₂O₅).

Toxicity Assays. The wood leachates were tested using three bioassays (an invertebrate test, Microtox, and an algal assay) to assess their toxicity to freshwater and estuarine species. Only Microtox was subjected to the SW leachates since the invertebrate and algal assays utilized freshwater organisms. The invertebrate test was conducted in triplicate on each of the leachate samples, Microtox was performed in duplicate, and single analyses were run for the algal assay. Since three leachate samples were analyzed for every wood type, the average results of the individual leachate sample analyses were averaged and reported along with a standard deviation.

The invertebrate test was based upon the use of *Ceriodaphnia dubia* in compliance with published methods (22). In brief, a set of five serial dilutions for each wood leachate was prepared with moderately hard water (MHW). A 20-mL aliquot of each leachate or its dilution was transferred to triplicate 30-mL plastic cups. Ten neonates (<24 h old) were transferred to each test container. The assay was conducted for 48 h at 20 ± 2 °C with a 16:8 photoperiod (light:dark). At the completion of the exposure interval, the number of viable neonates was recorded. A negative control sample was also prepared each time the assay was performed and the neonate survival in the negative control sample was greater than 90% for each of the assays.

The Microtox system is a commercially available test that quantifies changes in the bioluminescence of the marine bacterium *Vibrio fischeri*. The salinity of the wood leachates was adjusted to 2 psu with reagent grade sodium chloride. Four dilutions of each wood leachate were prepared with Microtox diluent, and each dilution was assayed in duplicate. A 15-min exposure interval was used for each assay.

The algal assay was based upon the use of a unicellular green algae *Rhaphidocelis subcapitata* (formerly *Selenastrum capricornutum*) (23). Five dilutions of each wood leachate were prepared in triplicate with algal assay media. To minimize the formation of metal complexes, the media was prepared minus ethylenediamine tetraacetate (EDTA), a trace nutrient in the algal media. A 50-mL aliquot of each leachate or its dilution was transferred to 125-mL sterile Erlenmeyer flasks. Each flask was inoculated with a 1-mL aliquot of algal cells (500 000 cells/mL). Algae were exposed for 96 h at 25 °C with constant illumination (400 ± 40 foot candles) and daily agitation. At the completion of the assay, the algal cells were quantified using a hemocytometer and a phase contrast microscope.

The toxicity results for each assay were expressed as the concentration of wood leachate (i.e., the percentage of leachate diluted with the appropriate diluent) that produced a 50% effect (EC₅₀). Graphical interpolation was used to determine the EC₅₀ values for the results of the Microtox and *R. subcapitata* assays. The EC₅₀ values for the *C. dubia* assays were determined using a US EPA data analysis software package. For presentation and discussion purposes, all EC₅₀ values were subsequently converted to toxicity units (1/EC₅₀), where higher TU values indicate increased toxicity.

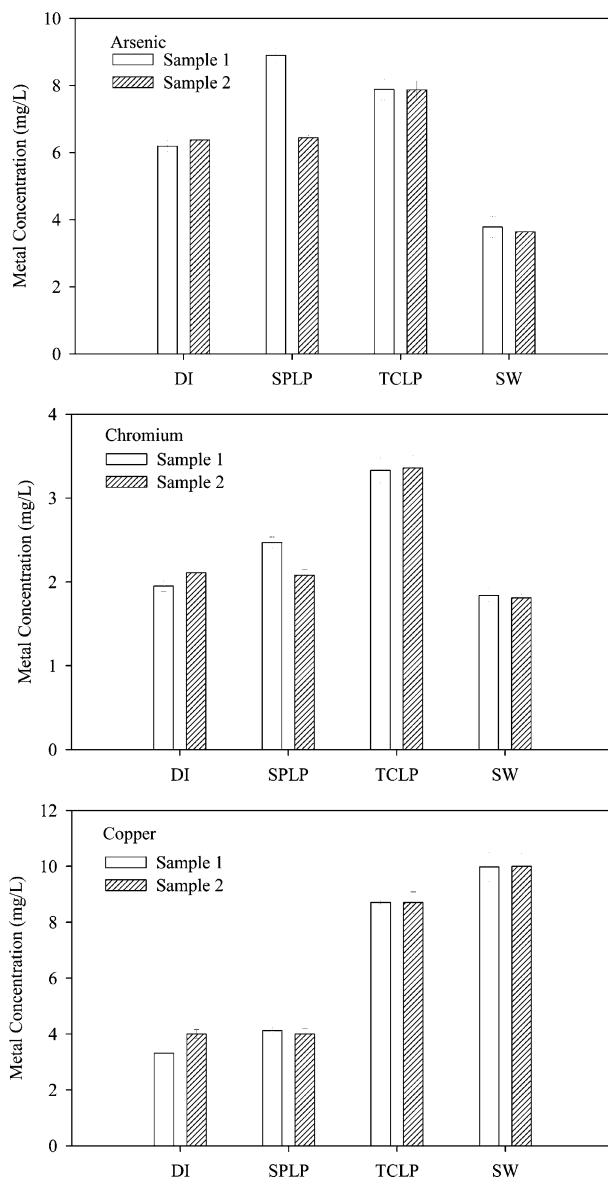


FIGURE 1. Average concentrations of As, Cr, and Cu leached from CCA-treated wood samples (error bars represent standard deviation of triplicate samples).

Results and Discussion

Preservative Concentrations in the Leachate. A total of 84 wood leachate samples were analyzed for the concentrations of their respective wood preservative components (seven wood product samples analyzed using four different leaching fluids, each in triplicate). The untreated wood sample leached below detection for all of the preservative compounds analyzed.

CCA-Treated Wood. The concentrations of arsenic, chromium, and copper measured in both CCA-treated wood leachate samples are presented in Figure 1. The error bars reflect the standard deviation of the triplicate leaching tests performed on each sample. For a majority of the elements and leaching fluids, the two CCA-treated wood samples leached similar concentrations. The concentrations of all three elements ranged from 2 to 10 mg/L. Previous leaching research on CCA-treated wood has shown that arsenic and copper leach more relative to chromium (11–13, 24). This was consistently observed in the data collected in the current study.

One factor impacting metal leachability from treated wood is solution pH (11, 13, 24), with metal leachability tending to increase as the pH decreases. The initial pH conditions of the different leaching fluids were 4.93 for TCLP, 4.2 for SPLP, 6 to 7 for DI, and 8.5 for SW. The solution pH that the sample is exposed to during the extraction depends not only on the initial pH, but also on the degree to which the extraction solution is buffered and the acidity or alkalinity of the material being leached. The pH measurements in leachates from the SPLP and DI extraction tests were similar at approximately 4.5. The TCLP, a buffered solution, exhibited a slightly higher final pH (approximately 5), while the final SW pH was the highest (approximately 6.5).

Another factor affecting metal leachability is the ability of the solution to complex with the metals. Warner and Solomon (11) as well as Cooper (13) observed increased metal leaching, especially copper, from CCA-treated wood when citric acid was used to control pH. Citrate complexation resulted in enhanced metal leaching. Similar rationale accounts for the enhanced copper leaching in the TCLP relative to the SPLP or DI; copper complexes with acetate. The higher leachability of copper in seawater was attributed to presence of ligands (Cl^- , Br^-), which are capable of forming stable soluble copper complexes and high concentrations of divalent cations (e.g., Mg^{2+} , Ca^{2+}) (25).

Arsenic-Free Preservatives. The concentrations of preservative compounds leached from the arsenic-free treated wood samples are presented in Figure 2. Copper concentrations ranged from 7 to 117 mg/L, with the greatest copper concentrations being leached from the CC-treated wood (55–117 mg/L) and the least being leached from the CDDC-treated wood (6.8–11 mg/L). Both ACQ and CBA—the two preservative types poised to replace CCA—leached similar copper concentrations (26–79 mg/L). As was the case with CCA, copper leached more in the TCLP and SW solutions when compared to the SPLP and DI solutions. One exception to this was the relatively low leachability of copper from CC-treated wood in the SW solution. The CC SW sample had the highest pH measured of the SW leachates, a possible cause for less copper leaching. The citrate ion released into solution in the seawater, reducing the degree of copper complexation taking place. Boron leached similar amounts in the ACQ- and CBA-treated wood samples; concentrations did not vary noticeably with leaching fluid type.

The organics leached approximately the same for all leachate types with the exception of tebuconazole in SPLP and citric acid in TCLP. Citric acid is a weak organic acid (26) and it has the propensity to chelate copper. This was observed in previous CCA-treated wood leaching studies when California's waste extraction test (WET), which uses citric acid instead of acetic acid, leached very large concentrations of copper relative to other leaching fluids (24). A possible explanation for the lower citrate leaching in the TCLP was competition between citrate and acetate to complex with the copper, resulting in less citrate leaching into solution. No explanation was found for why tebuconazole leached more in SPLP other than experimental variability often associated with trace organic chemical analysis.

Comparison of Copper Leaching. The chemical common to all sample types was copper. Figure 3 presents a side-by-side comparison of copper leaching among the five treated wood types (two CCA samples were averaged). Figure 3a compares the concentrations of copper leached (mg/L). The lowest copper concentrations were encountered in the CCA and the CDDC leachates. The ACQ and CBA leachate copper concentrations were of similar magnitude for most leaching fluids, while the CC leachates in all cases showed the greatest copper concentrations. Figure 3a also illustrates the impact of the extraction solution on copper leaching. The greatest

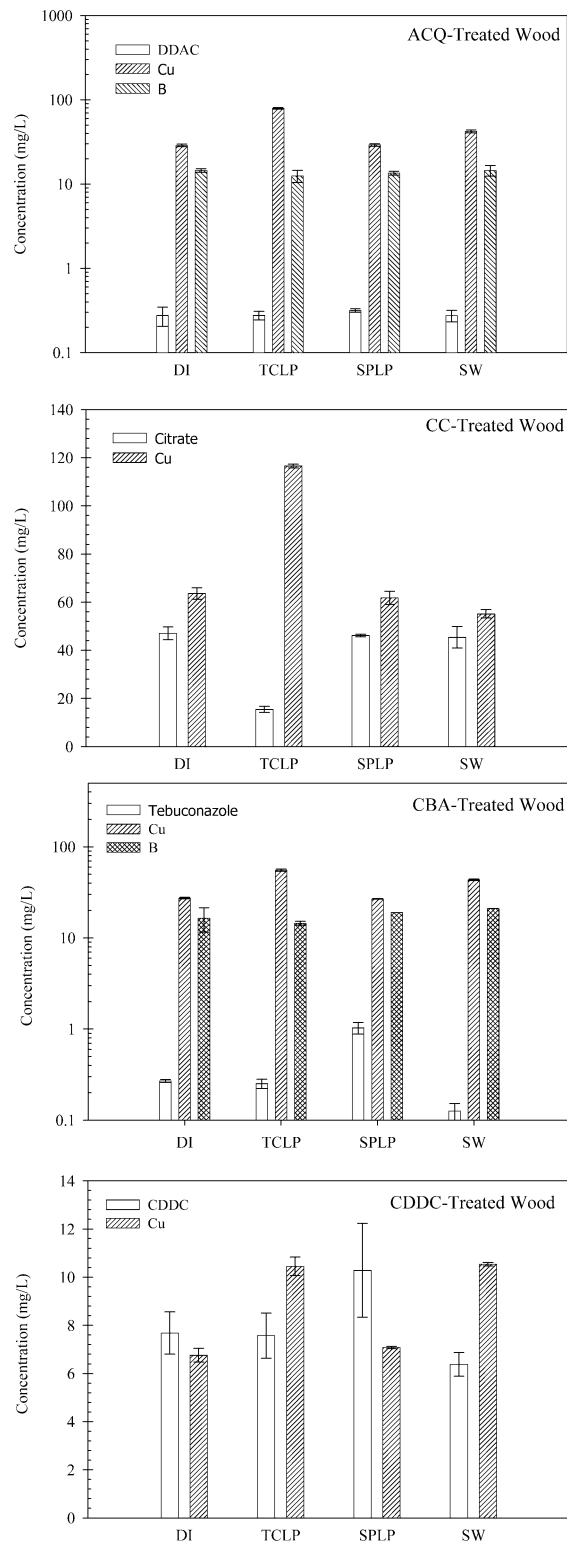


FIGURE 2. Average concentrations of preservative compounds leached from arsenic free-treated wood samples (error bars represent standard deviation of triplicate samples).

copper concentrations occur using the TCLP (as a result of complexation with acetate) and the lowest concentrations were measured using the SPLP and DI, both of which leach approximately the same amount. Copper leaching in the SPLP and DI tests was controlled by pH conditions, which were similar in both tests. The SW tests extracted copper in a similar magnitude as TCLP for the CCA and CDDC samples.

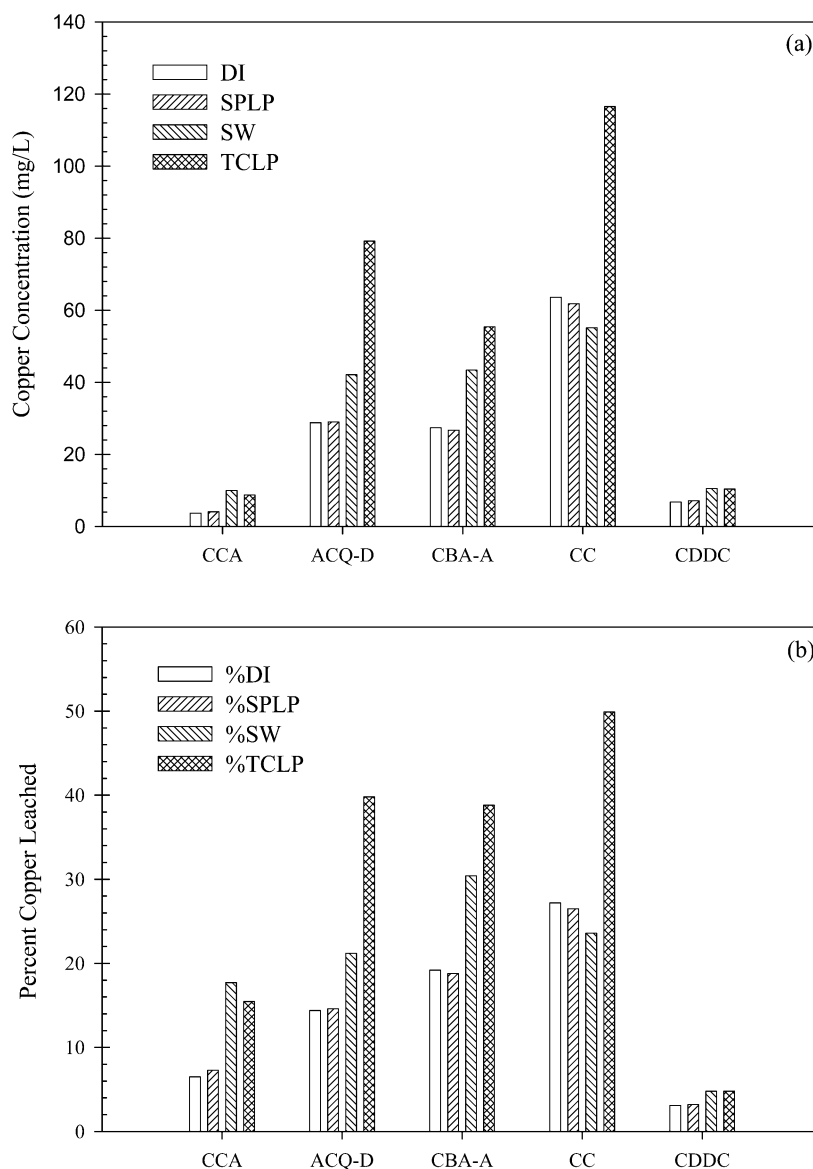


FIGURE 3. Comparison of copper leaching from treated wood.

Copper is present in greater amounts in ACQ-, CBA-, CC-, and CDDC-treated wood, and thus copper would be expected to leach in greater concentrations. As a means of normalizing the leaching data for the initial copper present, Figure 3b compares the percentage of copper leached from the original samples. CDDC leached a smaller fraction of copper than CCA. CDDC-treated wood contains roughly 3 times more copper than the CCA-treated wood samples tested, but less of the overall copper leaches, resulting in the similar leachate concentrations presented in Figure 3a. When the fraction of copper leaching from CCA is compared to that from ACQ-, CBA-, and CC-treated wood, CCA leaches less. The ACQ-, CBA-, and CC-treated wood samples contain more copper than CCA-treated wood initially and they also leach a greater fraction of the initial copper in the wood. One of the advantages of CCA is the fixation of the preservative elements to the wood fibers as a result of the reduction of Cr(VI) to Cr(III) in the treatment process. The same degree of copper fixation does not appear to occur for the arsenic-free chemicals, with the exception of CDDC. Since the CDDC treated wood sample evaluated here did not originate from the same stock of wood as the other samples, other differences may also have played a role.

Evaluating the Fraction of Preservative Leached. The fractions of preservative chemicals leached from the wood

TABLE 2. Fraction of Preservative Compounds Leached from the Treated Wood Samples

sample	metal/organic co-biocide	% leached			
		DI	TCLP	SPLP	SW
CCA	Cr	2–2.1	3.3–3.4	2.1–2.5	1.8
	As	6.9–7.1	7.8–8.7	6.4–9.9	3.6–4.2
	Cu	6.5	14–17	6.4–8.1	16–19
ACQ	Cu	14	40	15	21
	DDAC	0.19	0.19	0.22	0.19
CBA	Cu	19	39	19	30
	B	64	56	74	82
	tebuconazole	4.4	4.2	17.2	2.1
CC	Cu	27	50	26	24
	citrate	38	12	37	36
CDDC	Cu	3.1	4.8	3.2	4.8
	SDDC	1.2	1.2	1.6	0.97

were calculated and are presented in Table 2. While data on arsenic, chromium, and copper leaching from CCA-treated wood have been published by several investigators, public domain leaching data for the other wood preservatives evaluated are less common. The greatest sources of data on these preservatives are industry reports. A summary of

preservative leaching and depletion data from industry reports was compiled by Solo-Gabriele et al. (14). The industry leaching data were generated using AWP Standard Method E11-97 (20). Method E-11 involves leaching small blocks of preserved wood by submerging them in 300 mL of DI water. The water is changed periodically over 2-weeks, the component concentrations are measured, and the cumulative preservative leached is calculated. The concentration of preservative chemicals measured in a leachate sample will vary according to the particular leaching procedure employed. Factors such as particle size, leaching time, and liquid-to-solid ratio have a great impact on leachate concentrations (24, 27). Comparing the fraction of chemical leached rather than the chemical concentration in the leachate helps minimize differences occurring because of varying liquid-to-solid ratios. Copper and chromium for the most part leached at greater fractions in this study compared to those in the literature. The fractions of arsenic leached from the leachates are similar to the literature values of 6–10% arsenic.

The total metal leached from CCA-treated wood (copper plus chromium plus arsenic) ranged from a low of 14% for the DI and SPLP extraction fluids to a high of 27% for the TCLP extraction fluid. This range of concentrations is approximately the same range as the fraction of copper leached from ACQ and CBA (14–40%). While a greater fraction of copper leaches from ACQ- and CBA-treated wood, a relatively large fraction of the arsenic leaches from the CCA-treated wood. Since ACQ and CBA are the two chemicals replacing CCA to the greatest extent, the data suggest the new treated wood products on the market will tend to leach similar amounts of metals/metalloids as CCA-treated wood, but that the arsenic and chromium have been replaced by copper. The fraction of copper leached from CC-treated wood was greater than the sum of the metals leached from CCA-treated wood. CDDC-treated wood leaches a smaller fraction of the initial metals present compared to CCA-treated wood and the other copper containing preservatives. CDDC is not currently being used as a wood preservative in North America, but the leaching results suggest that its use might be worth exploring if copper leaching is a concern.

More than 50% of the boron leached from the CBA-treated wood. Borate-treated wood has been known to leach large amounts of boron, and traditionally its use has been limited to conditions where leaching is not expected (in interior building construction for example). DDAC leached from ACQ-treated wood (0.19–0.22%) at a lower fraction than reported in the industry literature (4%). The tebuconazole leached from CBA-treated wood at levels that were somewhat lower than industry-reported data except in SPLP (17%), while citrate and SDDC leached at levels consistent with industry-reported data. Chemical leaching concentrations are greatly influenced by conditions of the leaching test, and the leaching tests performed here were not the same as used by the wood treating industry.

Comparison of Toxicity. The results of the three assays (Figure 4) show that all of the samples analyzed exhibited varying degrees of toxicity. The measured treated wood toxicity was greater than that of untreated wood alone. While the toxicity results for untreated wood are not presented, they exhibited some toxicity. The average TU values for the invertebrate assay ranged from 0.046 (DI) to 0.029 (SPLP), for the algal assay the values ranged from 0.16 (TCLP) to 0.016 (DI), and for Microtox the average TU values for the untreated wood leachates ranged from 0.037 (DI) to 0.023 (SPLP). Since the untreated wood samples did not leach arsenic, copper, or chromium above the detection limit, the measured toxicity of the wood samples is therefore assumed to be a result of other chemicals naturally present in the wood. Manganese, for example, has been found to leach from southern yellow pine in previous experiments involving

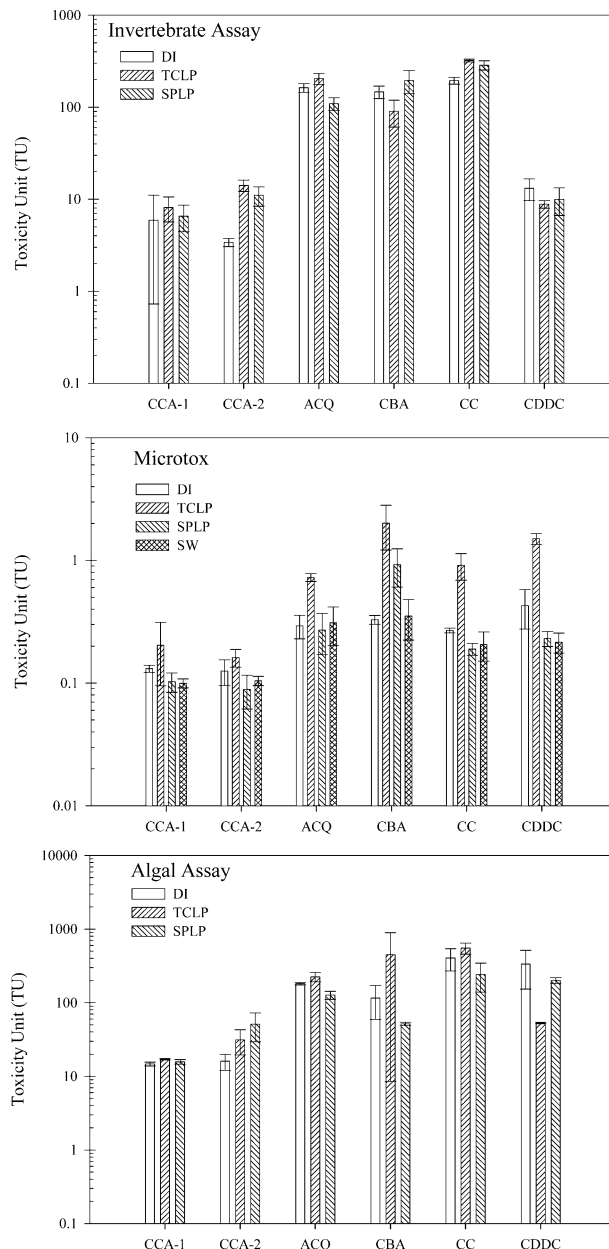


FIGURE 4. Toxicity of treated wood leachates as function of extraction fluid for three different assays (error bars represent standard deviation of triplicate samples).

untreated construction wood; previous researchers have measured manganese toxicity using aquatic bioassays (28). The specific cause of the untreated wood leachate toxicity, however, was not examined.

When comparing the relative toxicity of the treated wood leachates, a clear distinction is noted between the two leachates produced from CCA-treated wood and those produced by leaching the arsenic-free wood samples, with the CCA-treated wood samples being less toxic. The CCA-treated wood leachates exhibited TU values ranging from 3.1 to 14 using the invertebrate assay, while the ACQ, CBA, CDDC, and CC samples exhibited TU values ranging from 54.1 to 2000. The toxicity measured by the algal assay ranged from 15 to 46 TU for CCA-treated wood leachates, while the arsenic-free treated wood leachate samples ranged between 53 and 500 TU. CDDC exhibited the lowest toxicity among the arsenic-free samples in the invertebrate assay relative to ACQ, CC, and CBA. The difference was less pronounced using Microtox, with the CCA-treated wood leachates ranging from

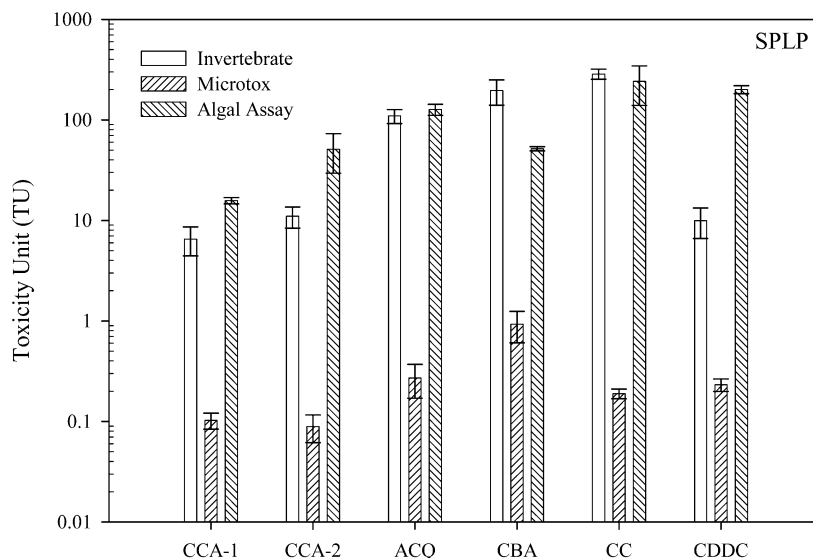


FIGURE 5. Comparison of toxicity assay results for SPLP leachates (error bars represent standard deviation of triplicate samples).

0.1 to 0.2 TU and the arsenic-free treated wood leachates ranging from 0.2 to 1.7 TU. The toxicity of CDDC observed in the algal assay and Microtox was statistically the same as that for the other arsenic-free preservatives. Figure 5 presents all three toxicity assays on one plot for one extraction fluid (SPLP).

The three assays displayed varying degrees of sensitivity as observed by comparing the TU values among the different assays in Figure 4. The TU values are much greater in the invertebrate and algal assays relative to Microtox. This is better illustrated in Figure 5 where the results of all three assays are plotted side by side for only the SPLP leachates. The algal assay was somewhat more sensitive than the invertebrate assay in the CCA- and CDDC-treated wood leachates; the results were similar for the ACQ- and CC-treated wood leachates, and the invertebrate assay was more sensitive than the algal assay for the CBA-treated wood leachates. In all cases, the algal and invertebrate assays were more sensitive than Microtox. The relative sensitivity of the tests are consistent with other experiments where the three different methods were compared on the same samples (18).

Implications. The TCLP and SPLP were both developed by the U.S. EPA for characterizing wastes and contaminated soils. The TCLP was developed as a regulatory method to determine whether a solid waste is a toxicity characteristic (TC) hazardous waste. It was designed to simulate the leaching expected to occur in a municipal solid waste (MSW) landfill under the acid-forming conditions that occur during early stages of anaerobic waste decomposition. Of the chemicals examined in this study, arsenic and chromium are the only two that have TC threshold concentrations (5 mg/L for each metal). Arsenic concentrations in the CCA-treated wood leachates exceeded the TC limit for arsenic; chromium concentrations did not exceed its respective TC limit. Similar results were observed previously (24, 27). Arsenic leaching above the TC limit would normally result in discarded treated wood to be classified as a TC hazardous waste. CCA-treated wood has, however, been excluded from the definition of hazardous waste at the U.S. federal level, though not all states have adopted this exclusion.

Since copper is not on the TC list (nor are any of the other compounds contained in the arsenic-free preservatives), discarded ACQ-, CBA-, CC-, and CDDC-treated wood would not be U.S. hazardous wastes, but copper can cause a solid waste to be TC hazardous waste in California. While California's waste extraction test (WET) was not performed as part of this research, copper concentrations measured

with the TCLP were greater than the soluble threshold limit concentration (STLC; 25 mg of Cu/L) for the ACQ-, CBA-, and CC-treated wood tested here, indicating that when discarded these materials would be a California TC hazardous waste for copper (WET routinely extracts greater concentrations than TCLP, 29). The total concentrations of copper in all four arsenic-free preservatives exceeded California's total threshold limit concentration (TTLC; 2500 mg of Cu/kg), again indicating that these wood products would require management as a hazardous waste unless otherwise exempted.

The TCLP may also potentially be used to evaluate the impact of co-disposed wastes on lined landfill leachate quality. The TCLP results suggest that all of the treated wood types evaluated might result in elevated leachate concentrations if disposed in large enough amounts (CCA for arsenic, chromium, and copper and the alternatives for copper). The TCLP cannot, however, account for all of the physical, chemical, and biological processes occurring within a landfill. Hopper et al. (29), for example, found oxyanions to leach more in MSW landfill leachate than the TCLP. In simulated construction and demolition (C&D) debris landfills (30), arsenic and chromium are much more mobile than copper. Thus, while the TCLP results indicate that all three metals might represent a concern at unlined landfills, data from other studies suggest that copper may be removed in the landfill system.

Treated wood in many cases will be disposed in unlined C&D debris landfills. One method for assessing the impact on groundwater underneath an unlined landfill is to compare leaching test results (usually SPLP for C&D debris landfills) to groundwater criteria. As and Cr have primary drinking water standards (which are often adopted as groundwater standards) of 0.05 and 0.1 mg/L, respectively, and copper has a secondary drinking water standard of 1.0 mg/L. The arsenic standard, in future years, will be 0.01 mg/L. The preservative concentrations in all of the leachates exceed these water quality criteria; arsenic certainly exceeds by the greatest magnitude. Again, many factors beyond what can be accounted for using the SPLP will impact actual concentrations in the groundwater. So, while the results are not definitive with respect to groundwater contamination, they do suggest that the disposal of the copper-based alternatives versus CCA-treated wood is advantageous from the standpoint of potential impact on groundwater.

Leaching test results are also used to assess the impact of land applied wastes. An issue of concern in some parts of the United States is the inclusion of treated wood in landscape

mulch. Using similar logic as discussed above for unlined landfills, CCA-treated wood would appear to pose the greatest risk with respect to water contamination compared to the newer chemicals. The leaching results can also be extended for a rough assessment of the relative potential impact of treated wood structures leaching and contaminating soil. If the amount of preservative compound leached during an SPLP were added to 1 m³ of typical soil, the resulting arsenic concentration for CCA-treated wood would be approximately 75 mg/kg, while the resulting copper concentration for ACQ- and CBA-treated wood would be approximately 300 mg/kg. When these estimations are compared to soil cleanup target levels in Florida (0.8 mg/kg for arsenic and 110 mg/kg for copper), As from CCA-treated wood would exceed by a factor of 94, while Cu from ACQ and CBA would exceed by a factor of 2.7. While the soil concentrations estimated were calculated simply for comparison purposes, the concentrations do fall within the range measured under CCA-treated structures (5, 31).

The above discussion indicates that on the basis of the leaching results obtained in this study, the major replacements for CCA will have a positive benefit with respect to landfill disposal issues and in-service soil contamination. CCA-treated wood appears to present less of a risk to aquatic ecosystems, however, when compared to the copper-based alternatives because of the smaller amount of copper that leaches. Additional work is needed to determine if the relatively smaller amount of aquatic toxicant leaching from CCA-treated wood is acceptable or whether the higher release rates of the copper-based preservative truly pose an impact. Leaching in aquatic water bodies would be accompanied by very large degrees of dilution in most cases. When copper leaches from a treated wood product such as a submerged pile, several physiochemical factors can modify its bioavailability and, hence, its toxicity in aquatic systems (25, 32–34). Additional research is needed examining the fate of wood preservative chemicals in natural waters and the impact of water chemistry on preservative bioavailability. Monitoring of aquatic impacts in actual water bodies where alternative treated wood products have been in use would be valuable.

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Supporting Information Available

Background material on waterborne wood preservatives. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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