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Impact of Surface Water Conditions on Preservative Leaching and Aquatic Toxicity from Treated Wood Products

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New alternative wood preservatives contain higher levels of copper (Cu) which can promote aquatic toxicity in natural water systems. Earlier work focused on evaluating toxicity using laboratory generated leaching solutions. In this study, the impact on preservative leaching and aquatic toxicity from treated wood products was evaluated using natural surface waters including waters from two rivers, three lakes, two wetlands, and one seawater, in addition to synthetic moderate hard water and deionized water. Blocks of wood treated with Cu based alternatives such as alkaline copper quaternary (ACQ) and copper boron azole (CBA), along with chromated copper arsenate (CCA)-treated wood, were leached under quiescent conditions, and total Cu, labile Cu, and heavy metal toxicity were measured. Results show that ACQ- and CBA-treated wood leach approximately 10 and 20 times more total Cu relative to CCA-treated wood and that the presence of organic and inorganic ligands in natural waters lowered the labile fraction of Cu relative to that from laboratory generated leaching solutions. Aquatic toxicity was found to correlate with the labile Cu fraction, and hence, the aquatic toxicity of the treated wood leachates was lower in natural waters in comparison to laboratory leaching solutions. The results of the present study suggest that studies designed to evaluate the impacts of treated wood should therefore consider the role of complexation in reducing the labile Cu fraction and its potential role in decreasing toxicity.

Introduction

As of January 2004, wood treated with chromated copper arsenate (CCA) was no longer manufactured for most residential uses. This phase out was prompted by risk assessments which indicated an elevated human health risk from arsenic (As) which could be ingested during direct contact with the wood (*1*−*4*). The primary active ingredients in most of the As-free alternatives formulations include copper (Cu) and an organic co-biocide, among which alkaline copper quaternary (ACQ) and copper boron azole (CBA) are the most popular wood preservatives in current use for the residential market. These Cu-based alternatives have been reported to leach several times more Cu (greater concentrations as well as higher percent leaching) than CCA-treated wood, and the aquatic toxicity measured was found to correlate with total Cu concentrations (*5*−*6*). In addition to the greater quantities of Cu in Cu-based alternatives relative to CCA, the enhanced leaching of Cu from these alternatives may also be due to the absence of Cr, which partly oxidizes the lignocelluloses material to provide binding sites for Cu in CCA-treated wood (*7*).

Although Cu can adversely impact aquatic organisms (*8*), several physical and chemical phenomena limit its toxicity. Free (hydrated) Cu^{2+} ions present in natural waters tend to complex with inorganic and organic ligands such as CO_3^{2-}, OH^-, and humic and fulvic acids (*9*−*11*) rendering Cu much less bioavailable to aquatic organisms and, as a result, less toxic (*8*, *12*−*13*). The chemical characteristics of the solution in contact with treated wood can thus significantly impact the bioavailability and aquatic toxicity of the copper leached (*8*, *14*).

Although free Cu^{2+} is considered the most toxic form of Cu (*15*), several studies have reported that other forms of Cu such as $CuOH^+$, $CuCO_3^0$, and $CuCO_3^0OH^-$ (the relative abundance of these forms depends largely on solution pH) are also likely to contribute to Cu toxicity (*13*, *16*−*19*). Labile Cu (the loosely bound Cu, which includes complexes such as $CuOH^+$, $CuCO_3^0$, and $CuCO_3^0OH^-$) converts in solution to free Cu^{2+} when a water sample is slightly acidified. Labile Cu, which can be measured by lowering solution pH and measuring Cu^{2+} with an ion selective electrode (ISE), has been shown in a few studies to correlate with aquatic toxicity (*13*, *20*).

In the present study, the impact of surface water conditions on preservative leaching and aquatic toxicity from treated wood products was evaluated. This work differs from earlier studies in that labile forms of Cu were measured in addition to measurements of total Cu. Also of significance, the current study utilized natural waters collected in the field, whereas earlier studies only utilized aqueous solutions generated in the laboratory. Heavy metal aquatic toxicity of leachate samples was assessed using the MetPLATE assay, and the toxicity was compared with the total and labile Cu concentration measured in these samples.

Materials and Methods

Collection of Wood Samples. Samples of southern yellow pine (SYP) treated with CCA, ACQ, and CBA were prepared using treated lumber purchased from home improvement stores in Gainesville, Florida. Untreated SYP wood samples were also included in the study as controls. Blocks of approximately 80 g (with dimensions as 7−8 cm length, 3.5−4.5 cm width, and 3.8 cm height with average surface area 140−150 cm^2) were obtained by cutting pieces of treated dimensional lumber (several 2.5 m lengths of 8.8 cm width by 3.8 cm height) using a power saw. For each wood type, a separate blade was used to cut the wood sample. Sawdust samples were collected for each treated wood type for subsequent total Cu measurements.

Collection and Preparation of Leaching Fluid. Ten different leaching solutions were used in this study. These leaching solutions were collected from eight natural waters in Florida (Figure A-1, online supplemental section) and included two rivers (R1 and R2), three lakes (L1, L2 and L3),

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TABLE 1. Characteristics of Leaching Solutions Prior to Contact with Wood Samples

leaching solution	sample type	pH	TDS (mg/L)	alkalinity (mg/L as $CaCO_3$)	hardness (mg/L as $CaCO_3$)	chloride (mg/L)	TOC (mg/L)	COD (mg/L)	turbidity (NTU)	Cu (μg/L)
DI	deionized water	6.44	<10	<1	<1	<10	<10	<10	0.2	<4.0
MHW	moderate hard water	7.74	150	57	94	<10	26	23	0.2	<4.0
R1	river	6.39	90	17	25	26	32	41	0.94	<4.0
R2	river	7.98	820	59	116	36	41	47	1.78	<4.0
L1	lake	7.35	165	54	59	22	43	62	1.96	<4.0
L2	lake	7.24	160	107	90	<10	49	30	1.64	13.0
L3	lake	7.28	360	97	73	17	110	75	2.58	<4.0
W1	wetland	6.98	940	37	44	27	173	140	4.31	11.0
W2	wetland	6.59	185	27	12	<10	57	41	1.45	35.0
S1	seawater	8.14	39000	250	2080	>15000	21	960	0.29	<4.0

two wetlands (W1 and W2), and the Atlantic Ocean (S1). Deionized water (DI) and moderately hard water (MHW) were also used as leaching solutions for comparative purposes. Each leaching solution collected from the field was passed through a strainer (nylon 75 mesh) to remove sediments, weeds, and leaves as it was poured into a 20-L container. Sample containers were filled to maximum capacity to minimize head space. Upon collection, the water samples were transported immediately to the laboratory, and experiments were started within 24 h. The MHW leaching solution was prepared according to standard protocols (Method 600/4−90/027, *21*).

Laboratory Leaching Procedures. For each treated-wood leaching-fluid combination, tests were run in quadruplicate with the exception of the untreated wood blocks which were leached in duplicate for a total of 140 tests. Experimentation was adapted from the wood industry standard protocols (E-11 Standard, *22*) as evaluated in previous work (*5*, *23*). In brief, the methodology required the immersion of the sample block (80 g block in this experiment) for 24 h within 1.6 L of leaching solution, resulting in a liquid to solid ratio (*L*/*S*) of 20:1. The resulting leachate was split into two aliquots; one aliquot was preserved with nitric acid to a pH below 2.0 for metal analysis, and the second aliquot was collected in an amber glass bottle and kept unpreserved for labile Cu measurement and toxicity testing which was conducted within 24 h of sample collection.

Chemical and Toxicity Analysis. The sawdust generated from cutting block specimens was analyzed for its total Cu, Cr, As, and B content. This was accomplished by digesting 2-g subsamples in triplicate (Method 3050B, *24*) and analyzing the digested samples using inductively coupled plasma, atomic emission spectroscopy (ICP-AES, Thermo Electron Corporation, Trace Analyzer) using standard protocols (Method 6010B, *24*). The total Cu concentrations in the wooden blocks were 1330 ± 70 mg-Cu/kg for CCA, 2860 ± 85 mg-Cu/kg for ACQ, and 5420 ± 120 mg-Cu/kg for CBA-treated wood. Ar, Cr, and B content are presented in the Supporting Information (Table A-1).

The 10 leaching solutions used for experimentation were characterized for pH, total dissolved solids (TDS), alkalinity, hardness, chloride, total organic carbon (TOC), chemical oxygen demand (COD), and turbidity (in NTU). U.S. EPA methods (*24*) and other standard methods (*25*) were employed as applicable for the measurement of these water quality parameters. Cu, As, Cr, and B concentrations in the wood leachates were measured by first digesting the aqueous leachate samples as per standard protocols (Methods 3010A, *24*) and then analyzing the digestates by ICP-AES using the same methods described above. The detection limits for Cu, As, Cr, and B were 4, 12, 4, and 6 μg/L, respectively. The Cu concentrations are presented and discussed in this paper; concentrations of other elements are included in the Supporting Information. Statistical analyses were performed on the data set using "students t-test" and single factor ANOVA analysis as appropriate at 95% confidence limits.

Labile Cu was measured by lowering solution pH (to a pH = 4) and measuring Cu^{2+} with an ion specific electrode as presented in previous literature (*17*, *26*). Toxicity was measured using MetPLATE. MetPLATE is a heavy metal specific aquatic toxicity assay based on inhibition of β-galactosidase activity in an *E. coli* strain (*27*) and has been used for evaluating aquatic toxicity of treated wood leachate in previous studies (*5*, *28*). For this method, enzyme activity is quantified using a chromogenic substrate, chlorophenol-red β-galactopyranoside (CPRG). In the presence of an active enzyme from *E. coli*, CPRG is cleaved, changing the sample solution from yellow to red-purple. The extent of substrate conversion is quantified by measuring absorbance at 570 nm. The detailed stepwise procedure has been presented elsewhere (*29*). A negative control of moderately hard water and a positive control of 1 mg/L Cu as $CuSO_4$ were used with each set of analyses. In addition, for comparative purposes several dilutions of 1 mg/L Cu as $CuSO_4$ were evaluated for toxicity using the MetPLATE toxicity assay. The results of the tests were computed in units of effective concentration for 50% enzyme activity inhibition (EC_{50}) and in toxicity units (TU) which are derived as the inverse of EC_{50}. Higher EC_{50} values indicate lower toxicity whereas higher TU values indicated higher aquatic toxicity.

Results and Discussion

Characterization of Leaching Fluids. Leaching solutions prior to contact with the wood blocks were characterized by pH values in the neutral range (6.39−8.14) (Table 1). Comparatively higher concentrations of various parameters (such as pH, TDS, chloride, COD) were measured for S1 water as compared to other water samples, with the lowest concentrations measured in the DI and MHW leaching solutions. Copper concentrations were below the detection limit of the ICP-AES in more than half of the leaching solutions with the exception of L2, W1, and W2.

Total Leached Copper Concentration. Cu was leached from all three treated wood types (Figure 1) as opposed to untreated wood leachates which were characterized by Cu concentrations that were below the detection limit in all cases. Ar, Cr, and B leaching with different leaching solutions are presented in Supporting Information (Figures A-2 and A-3). In general, higher Cu concentrations were observed in the CBA wood leachate (12.4 ± 2.1 mg/L to 18.5 ± 3.2 mg/L) followed by ACQ (3.3 ± 0.75 mg/L to 5.8 ± 0.14 mg/L) and CCA (0.42 ± 0.14 mg/L to 0.82 ± 0.19 mg/L). The relative quantities of Cu leached are largely influenced by the relative concentrations of Cu in the wood, as the Cu concentration in the CBA-, ACQ-, and CCA-treated wood matrices was 5420 ± 120, 2860 ± 85, and 1330 ± 70 mg/kg, respectively. This could also be due to a limited number of relatively strong

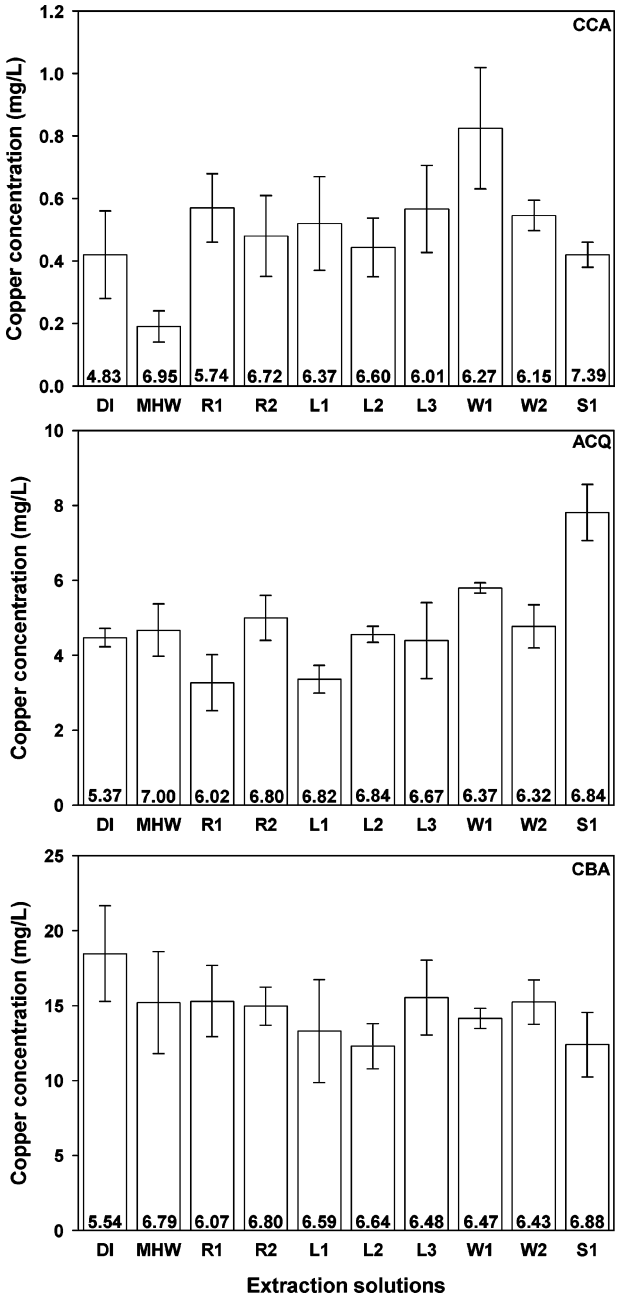

FIGURE 1. Total copper Leached from CCA (top)-, ACQ (middle)-, and CBA (bottom)-treated wood products in different leaching solutions (error bars represent standard deviation of four replicates, the final pH of the extraction solutions is presented within the bars).

binding sites in wood (e.g., acidic and phenolic sites), and a larger number of weaker binding sites (e.g., hydroxyl groups in carbohydrates). As a result, a limited amount of copper could be strongly bound to the wood, and an excess of copper will only be weakly bound and thus can be more easily leached. Within a particular wood type, more Cu was found in leaching solutions characterized by higher levels of alkalinity and TOC in most cases.

For CCA-treated wood, significant differences ($p < 0.01$) were observed in the leachate Cu concentrations from different natural waters for CCA-treated wood (e.g., lake vs river vs seawater). Significant difference were also observed for individual means of CCA DI and CCA MHW leachates ($p = 0.034$) as well as for the means of CCA W1 and CCA W2 leachates ($p = 0.068$). For the CCA-treated wood leachates, the lowest concentration of Cu (0.20 ± 0.05 mg/L) was measured in the leachate produced with MHW as the leaching fluid. This observation may be due to the relatively high pH of MHW and the relatively low organic levels as measured by TOC and COD. The importance of pH has been documented by Townsend et al. (*30*) who found that CCA-treated wood sawdust leaches more Cu at lower pH values. For the seawater sample, S1, pH alone cannot be used to explain the relatively high quantities of Cu leached. The chemistry of the seawater sample is very different and characterized by high salt content, relatively high COD, and a relatively high and near-neutral pH (final pH = 7.39). The salts in the seawater sample, in particular, Cl^- and Br^- ligands, are capable of forming stable soluble Cu complexes (*31*), which likely contributed to the amounts observed. Although the final pH was slightly higher (pH = 6.27) for W1 CCA leachate compared to W2 CCA leachate (pH = 6.15), higher Cu concentration in W1 CCA leachate was observed, which could possibly be due to comparatively high organic matter (TOC = 173 mg/L for W1 compared to 57 mg/L for W2). The Cu leaching from CCA-treated wood blocks appears to be influenced by the presence of inorganic and organic ligands and the final pH of the leaching solution.

For ACQ-treated wood, Cu concentration was highest in the seawater (S1) leachate. For the other natural water types, no statistical significant difference was observed between the lake and the river water leachates. The individual means, of ACQ W1 and ACQ W2 leachates, were statistically different ($p = 0.041$). The final pH values of the leachate from different leaching solutions were in the range of 5.37 (DI water) to 7.00 (MHW). A trend of lower concentration with increasing pH was observed in most cases with the presence of organic matter also playing a role in a few observations (e.g., W2 vs W1). Statistically similar concentrations in ACQ leachate from DI and MHW waters can be attributed to the formation of Cu $(CO_3)_2^{2-}$ and $CuOH^+$ around pH = 7 bringing more Cu in solution (*31*).

For CBA-treated wood, the Cu concentrations were not statistically different between water types and between individual samples within a water type. The highest Cu concentration (18.5 ± 3.2 mg/L) on average was observed in the DI leachate of CBA-treated wood, and the lowest (12.3 ± 1.5 mg/L) was observed in the lake water (L2). This followed the pH trend with more leaching occurring at lower pH.

For CCA-treated wood, the percent Cu leached was 0.3−1.5% for the different leaching solutions. For the ACQ- and CBA-treated wood blocks, the percent leached for Cu varied from 2.2 to 6.7% and 4.4 to 7.7%, respectively, for different leaching solutions used in this study. The measurements from the current study are consistent but slightly lower than those measured previously (*6*, *23*). The percent leached may have been higher (4.9−6.5% for CCA and 8.9−9.2% for CBA) as measured by Kennedy and Collins (*23*) because a longer exposure period was used (14 days) compared to the exposure period used in the current study (1 day). Stook et al. (*6*) conducted a similar set of experiments with the exception of sample size (sawdust versus block), leaching solution types (synthetic versus natural), and mixing conditions (aggressive versus quiescent). The values observed in Stook et al. (6.4−19% for CCA, 14−40% for ACQ, 19−39% for CBA) were higher likely because of the differences in experimental conditions, in particular with respect to the smaller sample size (*30*).

Labile Copper Concentrations in Treated Wood Leachate. For all three wood types, the highest labile Cu concentration was measured in the treated wood DI leachate (Figure 2). The labile Cu concentration could not be measured in the seawater treated wood leachates due to interference from chloride while using the Cu-specific electrode. DI water leachate had 8%, 5%, and 3% labile Cu for CCA, ACQ, and CBA samples, respectively. The majority of the labile Cu in the DI water leachate was complexed, possibly with the

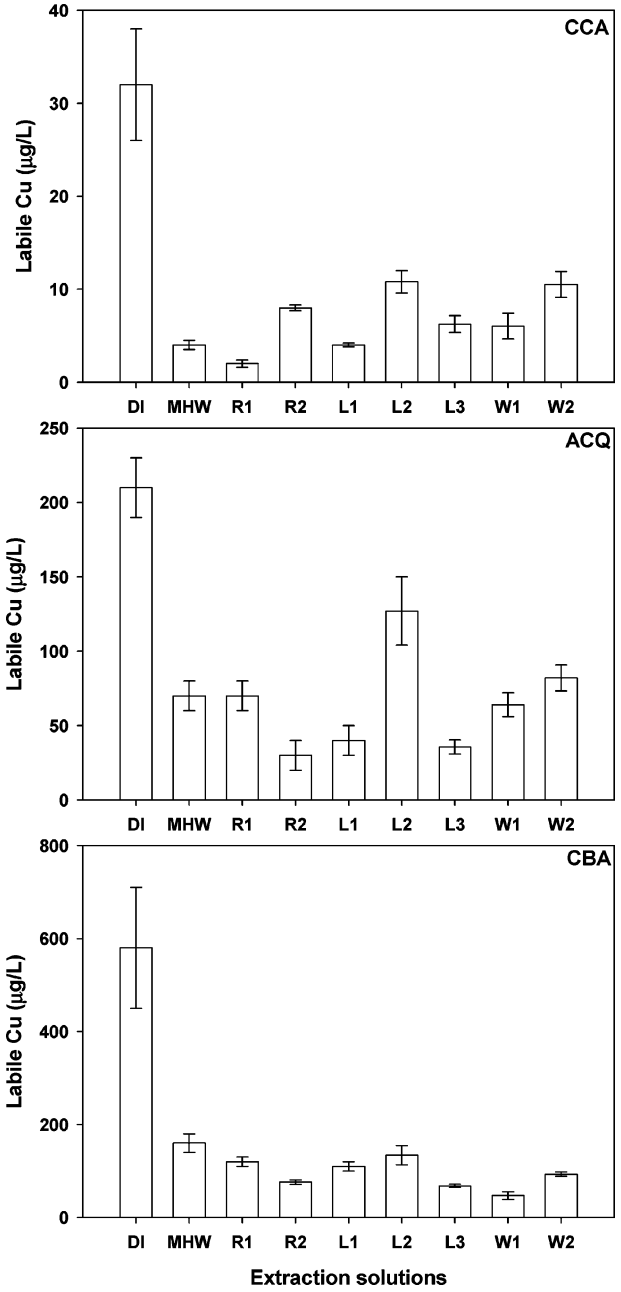

FIGURE 2. Labile copper concentration in the treated wood leachate (error bars represent standard deviation of four replicates).

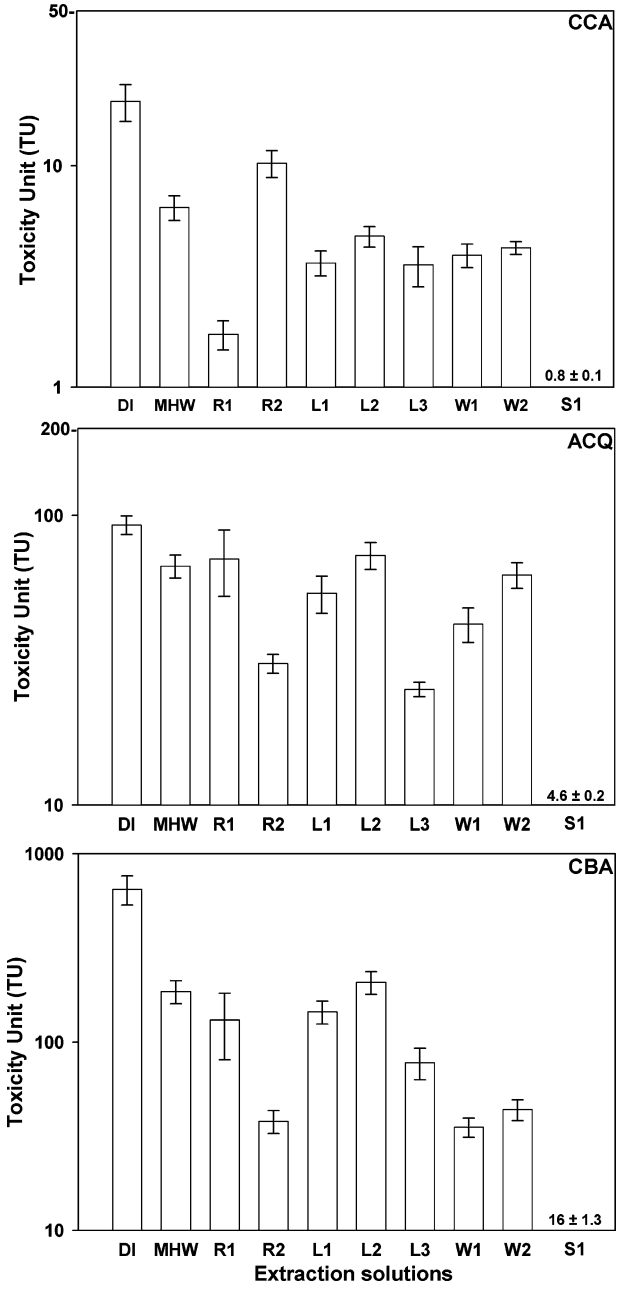

FIGURE 3. MetPLATE toxicity of treated wood leachates as a function of leaching solution (error bars represent standard deviation of four replicates).

dissolved organic carbon (DOC) leached out from the wood blocks. Van der Sloot et al. (*32*) showed that DOC leaches out from various treated wood products with higher DOC leaching at higher pH. The study also reported that nearly 90% of the Cu leached was bound to DOC in the neutral pH range as compared to less than 10% for solutions having pH less than 5.0. For the natural waters in the current study, the percent labile Cu (of the total Cu measured) was found to vary from 0.3 to 2.4% for CCA, 0.5 to 2.5% for ACQ, and 0.14 to 2.1% for CBA, respectively. This proportion was similar to those observed by Ndungu et al. (*33*) who found that about 3% of total dissolved Cu was labile in Cu-contaminated natural water samples in the San Francisco Bay area. When comparing the labile Cu concentrations with the leaching solution water quality parameters as observed in the present study, the labile Cu concentration in the leachate sample was found to be inversely proportional to the TOC and alkalinity concentrations in the leaching solutions. The R^2 values between labile Cu concentrations and TOC in leaching solutions were 0.83, 0.72, and 0.98, respectively, for CCA, ACQ, and CBA. Similarly, for labile Cu and the alkalinity of the leaching solutions, R^2 values were 0.89, 0.73, and 0.95, respectively, for CCA, ACQ, and CBA leachates (Figure A-4 in Supporting Information). This indicates that with higher TOC and alkalinity of the water, a lower fraction of total Cu would be in the form of labile Cu.

Aquatic Toxicity of Treated Wood Leachate. Leachates from untreated southern yellow pine were found to be nontoxic to the MetPLATE test bacteria. The treated wood leachates all showed some degree of toxicity using MetPLATE (Figure 3). Lower toxicity was observed with S1 samples for each wood type (0.8 ± 0.1 TU for S1-CCA; 4.63 ± 0.15 for S1-ACQ; and 15.9 ± 1.34 for S1-CBA) compared with the other leachates. In general, among the other nine leachates for each wood treatment, toxicity followed the pattern CBA > ACQ > CCA (Figure 3). For all three treated wood leachates, the highest toxicity was observed from the DI leachate (CCA,

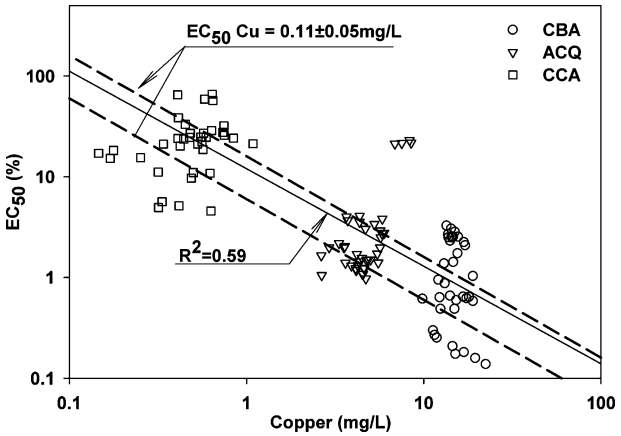

FIGURE 4. Total copper concentrations (mg/L) vs toxicity EC_{50} for treated wood leachates. (The dotted lines indicate the range of toxicity predicted due to total Cu alone.)

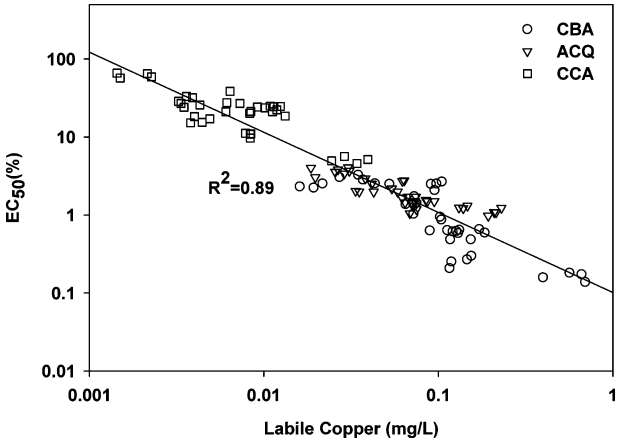

FIGURE 5. Labile copper concentrations (mg/L) vs toxicity EC_{50} for treated wood leachates.

19.5 TU ± 3.7; ACQ, 92.8 TU ± 6.8; CBA, 649 TU ± 114). This coincides with the relatively high labile copper concentrations associated with DI water. The highest toxicity from ACQ-treated wood leachate (with DI water) was almost 5 times greater than the toxicity observed with CCA-treated wood leachate (with DI water). This is not unexpected as copper (EC_{50} of 0.11 mg-Cu^{+2}/L) is highly toxic to the *E. coli* within the MetPLATE kit. These test microbes are less sensitive to chromium (EC_{50} of 6.9 mg-Cr^{+3}/L) and not sensitive to arsenic (*27*). Since ACQ-treated wood contains more Cu than CCA and the percentage leached from ACQ is also higher than that from CCA (*5*), the increased toxicity associated with ACQ-treated wood is likely due to the increase in Cu leaching. Along similar lines, the toxicity from CBA-DI leachate was more than 6 times that of ACQ. Again, this increase in toxicity is likely due to greater Cu leaching from CBA-treated wood.

Comparison of Aquatic Toxicity with Leached Copper Concentration. Since copper was suspected to be the primary toxicant to the MetPLATE bacteria, the EC_{50} values measured for all leachate samples were plotted as a function of their corresponding total copper concentration (Figure 4) and labile copper concentration (Figure 5). In general, an increase in toxicity was observed with an increase in Cu concentrations in most of the leachates. The EC_{50} value obtained for Cu was 0.11 ± 0.05 mg/L. Using this toxicity value for Cu, the toxicity was predicted using the different Cu concentrations as per the following equation (adapted from Stook et al. (*5*)).

$$\%\ EC_{50,predicted} = \frac{EC_{50,Cu}\ \text{measured in mg/L}}{\text{concentration of Cu in mg/L}} \times 100 \quad (1)$$

Dashed lines created using the EC_{50} values obtained from eq 1 represent the range of toxicity expected to occur solely as a result of dissolved total copper (Cu^{+2}). The correlation coefficient between EC_{50} (%) data and leached Cu concentration was found to be 0.59, when performing a linear regression for the entire data set. The correlation was higher ($R^2 = 0.89$) when comparing labile Cu concentrations versus toxicity (Figure 5). This observation is consistent with the inverse correlation between aquatic toxicity and the TOC and alkalinity levels of the leaching solutions.

Implications. Total Cu concentrations in the leachates produced with various surface waters followed the trend CBA > ACQ > CCA. The larger quantities of Cu leached from the Cu-based alternatives were a combination of two factors: the larger amount of copper present in the wood matrix and the higher percentage of Cu lost. The larger percentage of copper lost may be due to the differences in copper fixation (or binding) to the wood matrix. CCA-treated wood contains chromium which serves as a fixing agent promoting low solubility complexes with the wood matrix. The Cu-based alternatives do not have chromium, and so the lack of this fixing agent may contribute to the enhanced leaching of the Cu present in these alternatives.

The labile Cu concentration was generally found to follow the trend of higher concentrations in the copper alternatives versus that in CCA (CBA > ACQ > CCA). Toxicity values measured in different leachates followed a similar trend with higher correlations observed when toxicity was compared to labile copper concentrations. Labile Cu concentration was found to correlate with the water chemistry of the leaching solutions, with lower toxicity measured in natural waters as compared to the toxicity measured in DI and MHW. Thus, aquatic toxicity of the leachates from treated wood is impacted by the presence of inorganic and organic ligands in the natural waters. Studies designed to evaluate the impact of treated wood should hence include measurements of labile copper. Furthermore, results from the current study were based upon an 80 g treated wood block immersed in 1600 mL of solution. In real scenarios, it is likely that the proportion of wood to water would be different. Risk assessments that utilize the results from the current study should also consider dilution and mixing under natural conditions.

Acknowledgments

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Supporting Information Available

Table showing total arsenic, chromium, and boron concentrations. Four figures showing the sampling locations, arsenic and chromium concentrations, boron concentration, and labile copper. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Roberts, S.; Ochoa, H. Letter report from the University of Florida Center for Environmental & Human Toxicology to J. Ruddell, Division of Waste Management, Florida Department of Environmental Protection, regarding potential human health risks posed by arsenic in CCA-treated wood, April 10, 2001.

(2) Dang, W.; Chen, J.; Mottl, N.; Phillips, L.; Wood, P.; McCarthy, S.; Lee, R.; Helmke, M.; Nelson, M.; Coon, K. A probabilistic risk assessment for children who contact CCA-treated Playsets and

Decks; U.S. Environmental Protection Agency, Office of Pesticide Programs: Washington, DC, 2003.
(3) Khan, B.; Solo-Gabriele, H.; Dubey, B.; Townsend, T.; Cai, Y. Arsenic speciation of solvent-extracted leachate from new and weathered CCA-treated wood. *Environ. Sci. Technol.* **2004**, *38* (17), 4527−4534.
(4) Hemond, H.; Solo-Gabriele, H. Children's exposure to arsenic from CCA-treated wooden decks and playground structures. *Risk Anal.* **2004**, *24* (1), 51−64.
(5) Stook, K.; Dubey, B.; Ward, M.; Townsend, T.; Bitton, G.; Solo-Gabriele, H. Heavy metal toxicity of pressure treated wood leachates with MetPLATE. *Bull. Environ. Contam. Toxicol.* **2004**, *73* (6), 987−994.
(6) Stook, K.; Tolaymat, T.; Ward, M.; Dubey, B.; Townsend, T.; Solo-Gabriele, H.; Bitton, G. Relative leaching and aquatic toxicity of pressure-treated wood products using batch leaching tests. *Environ. Sci. Technol.* **2005**, *39* (1), 155−163.
(7) Schultz, T.; Nicholas, D. A brief overview of non-arsenical wood preservative systems, Wood deterioration and preservation. *Adv. Changing World* **2003**, *845*, 420−432.
(8) Flemming, C.; Trevors, J. Copper toxicity and chemistry in the environment: a review. *Water, Air, Soil Pollut.* **1989**, *44*, 143−158.
(9) Newell, A.; Sanders, J. Relative copper binding capacity of dissolved organic compounds in a coastal-plain estuary. *Environ. Sci. Technol.* **1986**, *20* (8), 817−821.
(10) Donat, J.; Lao, K.; Bruland, K. Speciation of dissolved copper and nickel in South San Francisco bay: a multi method approach. *Anal. Chim. Acta* **1994**, *284*, 547−571.
(11) Chow, C.; Kolev, S.; Davey, D.; Mulcahy, D. Determination of copper in natural waters by batch and oscillating flow injection stripping potentiometry. *Anal. Chim. Acta* **1996**, 79−87.
(12) Ma, H.; Kim, S.; Cha, D.; Allen, H. Effects of kinetics of complexation by humic acid on toxicity of copper to *ceriodaphnia dubia*. *Environ. Toxicol. Chem.* **1999**, *18*, 828−837.
(13) Devez, A.; Gomez, E.; Gilbin, R.; Elbaz-Poulicher, F.; Persin, F.; Andrieux, P.; Casellas, C. Assessment of copper bioavailability and toxicity in vineyard runoff waters by DPASV and algal bioassay. *Sci. Total Environ.* **2005**, *348*, 82−92.
(14) Tao, S.; Liang, T. Long-term monitoring of bioavailable copper in the aquatic environment using a resin-filled dialysis membrane. *Bull. Environ. Contam. Toxicol.* **1997**, *58*, 712−719.
(15) Brand, L.; Sunda, W.; Guillard, R. Reduction of marine phytoplankton reproduction rates by copper and cadmium. *J. Exp. Mar. Biol. Ecol.* **1986**, *96*, 225−250.
(16) Brown, P.; Markich, S. Evaluation of the free ion activity model of metal-organism interaction:extension of conceptual model. *Aquat. Toxicol.* **2000**, *51* (2), 177−194.
(17) Eriksen, R.; Mackey, D.; Dam, R.; Nowak, B. Copper speciation and toxicity in Macquarie harbour, Tasmania: an investigation using a copper ion selective electrode. *Mar. Chem.* **2001**, *74*, 99−113.
(18) Lorenzo, J.; Nieto, O.; Beiras, R. Effect of humic acid on speciation and toxicity of copper to Paracentus lividus larvae in seawater. *Aquat. Toxicol.* **2002**, *58*, 27−41.
(19) Hauri, J.; Horne, A. Reduction in labile copper in the 7-day *Ceriodaphnia dubia* toxicity test due to the interaction with zooplankton food. *Chemosphere* **2004**, *56*, 717−723.
(20) Deaver, E.; Rodgers, J. Measuring bioavailable copper using anode stripping voltammetry. *Environ. Toxicol. Chem.* **1996**, *15*, 1925−1930.
(21) U.S. Environmental Protection Agency. *Methods for measuring the acute toxicity of effluents in receiving waters to freshwater and marine organisms*, 4th edition; EPA/600/4-90/027; Washington, DC, 1991.
(22) AWPA. *E11-97 Standard method of determining the leachability of wood preservative*; American Wood Preservers' Association Standards; American Wood Preservers' Association: Selma, AL, 2005.
(23) Kennedy, M.; Collins, P. *Leaching of preservative components from pine decking treated with CCA and copper azole, and interaction of leachates with soils*; International Research Group on Wood Protection IRG/WP 01-50171; Stockholm, Sweden, 2001.
(24) U.S. Environmental Protection Agency. *Test methods for evaluating solid waste, SW846*, 3rd ed.; Office of Solid Waste and Emergency Response: Washington, DC, 2003.
(25) APHA, AWWA, WEF. *Standard methods for the examination of water and wastewater*, 19th ed.; 1995.
(26) Wiese, C.; Schwedt, G. Strategy for copper speciation in white wine by differential pulse anodic stripping voltammetry, potentiometry with an ion-selective electrode and kinetic photometric determination. *Fresenius J. Anal. Chem.* **1997**, *358*, 718−722.
(27) Bitton, G.; Jung, K.; Koopman, B. Evaluation of a microplate assay specific for heavy metal toxicity. *Arch. Environ. Contam. Toxicol.* **1994**, *27*, 25−28.
(28) Dubey, B.; Townsend, T.; Solo-Gabriele, H.; Bitton, G. *Comparison of Temporal Changes in Metal Leaching and Aquatic Toxicity from Wood Treated with CCA and Alternative Preservatives*; Proceedings, IRG/WP 05-50236; International Research Group on Wood Protection: Stockholm, Sweden, 2005.
(29) Dubey, B. Comparison of Environmental Impacts of Wood Treated with Chromated Copper Arsenate (CCA) and Three As-Free Preservatives. Ph.D. Dissertation, University of Florida, Gainesville, FL, 2005.
(30) Townsend, T.; Tolaymat, T.; Solo-Gabriele, H.; Dubey, B.; Stook, K.; Wadanambi, L. Leaching of CCA treated wood: implications for waste disposal. *J. Hazard. Mater.* **2004**, *B114*, 75−91.
(31) Stumm, W.; Morgan, J. *Aquatic chemistry: chemical equilibria and rates in natural waters*, 3rd ed.; Wiley & Sons: New York, 1996.
(32) van der Sloot, H.; van Zomeran, A.; Meeussen, J. Assessment of leaching behaviour of preserved wood in view of the test method selection and development of environmental acceptance criteria. Presented at Environmental Risk Assessment, Petten, The Netherlands, October 22, 2004.
(33) Ndungo, K.; Hurst, M.; Bruland, K. Comparison of copper speciation in estuarine water measured using analytical voltammetry and supported liquid membrane techniques. *Environ. Sci. Technol.* **2005**, *39*, 3166−3175.

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