

# Effect of Copper to Quat Ratio on Fixation and Leaching of Preservative Components in Alkaline Copper Quat-Treated Wood

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## Abstract

This study investigates the effect of the relative proportion of copper oxide (CuO) to didecyl dimethyl ammonium carbonate (DDACb) in an alkaline copper quat (ACQ) formulation on the rate of copper fixation or stabilization and the resistance of treated wood to leaching of copper and quat (DDACb) for different ACQ retentions in wood. Red pine, jack pine, and black spruce samples were treated with ACQ at concentrations of 0.6, 1, and 1.5 percent with CuO to DDACb ratios of 2:1 (the usual ratio for ACQ-D), 1:1, and 1:2. Red pine samples posttreated at 50°C were evaluated for rate of fixation by the expressate method. Conditioned samples of the three species were evaluated for the leaching of copper, and DDACb (red pine). At similar ACQ retentions, a decrease in proportion of copper in the formulation resulted in a substantial reduction in the time required for copper fixation. There was a significant decrease in the amount of copper leached for all three species studied with reduction of proportion of copper in the ACQ formulation. Improved fixation time and reduced copper leaching resulted from the lower copper retentions in the samples with lower relative proportions of copper in the formulations. The reduction in leaching was higher for samples treated with concentrations of 1 and 1.5 percent ACQ. The formulation having a 1:1 CuO to DDACb ratio appears to be the most promising, considering the positive effects of reduced copper ratio on copper leaching and fixation time and the minimal effect on DDAC leaching.

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Since December 31, 2003, chromated copper arsenate (CCA)-treated wood products have been limited to nonresidential applications in the United States and Canada after CCA registrants submitted voluntary label change requests to the Environmental Protection Agency in the United States and the Pesticides Management Regulatory Agency in Canada (Lebow 2004). Several existing as well as new arsenic- and chromium-free waterborne preservatives, including alkaline copper quat (ACQ) and copper azole, were introduced as potential replacements for CCA for residential applications. Alternative preservatives typically use copper as an active ingredient because of its broad-spectrum fungicidal property and its low mammalian toxicity.

The commonly used copper monoethanolamine-based ACQ formulations contain copper compounds and a quaternary ammonium compound (quat) as a cobioicide, e.g., didecyl dimethyl ammonium chloride (DDAC) or benzalkyl ammonium chloride. Considerable research has

been done on the potential of quats as stand-alone wood preservatives for both aboveground and ground contact applications after initial research by Oertel (1965) and Richardson (1972) in which alkylammonium compounds were used for antisapstain applications. However, field stake tests showed that the quats were rapidly biodegraded in ground contact, which led to fortifying the quat with copper. The early formulations focused on having sufficient copper

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to protect the quat from biodegradation and tended to have a relatively low copper to quat ratio. For example, the first commercial formulation, ACQ Type A, was 1:1 copper oxide (CuO) to quat. These lower copper ratio preservatives appeared to have excellent efficacy (Richardson 1991). For commercial reasons, the industry finally settled on a 2:1 CuO to quat ratio (ACQ Types B, C, and D) and most manufacturers use amine or in some cases a combination of amine and ammonia solution as a solvent (American Wood Protection Association [AWPA] 2006a).

The new formulations have challenges related to poor copper fixation and long fixation times, especially for high retention treatments (Ung and Cooper 2005). Studies in southern pine treated with copper amine-based preservative show that up to 35 percent of copper can leach out depending on preservative loading and exposure conditions (Waldron et al. 2003). Even though copper has low mammalian toxicity, ionic copper can be toxic to many nontarget invertebrates and aquatic flora and fauna. Copper bioconcentration values range from 100× for benthic algae to 30,000× for phytoplankton. Marine mollusks concentrate copper by an average factor of 5,000 (Brooks 2004). In contrast, the quat component of the preservative is well fixed in wood but highly water soluble in the environment, with an octanol-water partition coefficient of zero, so the chances of bioaccumulation, bioconcentration, and biomagnifications of DDAC are very low (Henderson 1992). Improvement of copper leach resistance of preservative-treated wood during outdoor exposure is critical to minimize the environmental impact of such treated products.

Rapid copper-wood ion exchange complexation reactions occur with carboxylic and phenolic groups of wood components (Cooper 1991, Jin and Preston 1993, Ruddick 1996, Kamdem and Zhang 2000, Staccioli et al. 2000, Zhang and Kamdem 2000). Slower precipitation reactions fix additional copper in wood. Fixation of copper in the wood after treatment with copper amine-based preservatives varies with the wood species, posttreatment temperature and relative humidity, and formulation parameters such as copper sources, type of amine, amine to copper molar ratio, and pH of the copper amine solution (Zhang and Kamdem 1999, Jiang and Ruddick 2000, Lucas and Ruddick 2002, Ung and Cooper 2005). The amount of copper available for leaching from treated wood increases with copper retention (Tascioglu et al. 2005, Ung and Cooper 2005). Quaternary ammonium salts also undergo electrostatic interaction and cation exchange with dissociated (anionic) carboxylic groups and phenolic hydroxyls in the wood (Loubinoux and Malek 1992, Doyle and Ruddick 1994). Hence fixation of quaternary ammonium salts mainly depends on the number of anionic sites in wood (Loubinoux et al. 1992, Loubinoux and Malek 1992). Since the number of these reaction sites is limited, copper and quaternary ammonium compounds will compete for the same reaction sites in the wood. This raises the question of which ACQ ingredient competes more effectively to secure the anionic sites in the wood. Tascioglu et al. (2005) confirmed that the quat components in the formulation stabilize or fix faster than the copper component. A higher mass to charge ratio of quat (about 300) compared with copper (32) supports the rapid fixation of quat in wood. Higher copper leaching at higher copper retention and the faster stabilization of quat compared with copper suggest that leaching of copper might be reduced without affecting the preservative efficacy at a

given total ACQ retention by lowering the copper to quat ratio in the formulation.

In this study we investigate the feasibility of reducing copper leaching and increasing the rate of fixation of copper in ACQ-treated wood by reducing the relative proportion of copper (as oxide) to quat in the formulation.

## Materials and Methods

Defect-free boards of red pine (*Pinus resinosa* Ait.) sapwood, jack pine (*Pinus banksiana* Lamb.) heartwood, and black spruce (*Picea mariana* (Mill.) BSP) heartwood were selected and processed to 19-mm cubes and conditioned to an average moisture content of about 8 percent. For each species, component ratio and solution concentration, 22 blocks were treated to provide 8 blocks for monitoring rate of fixation, 2 blocks for measuring quat content before leaching, and 12 blocks (two replicate sets of six blocks) for leaching studies.

The ACQ treating solution was prepared using didecyl dimethyl ammonium carbonate (DDACb) quat stock solution of 50 percent DDACb and copper amine stock solution with 9 percent elemental copper. Solutions were mixed with water to provide CuO to DDACb ratios of 2:1, 1:1, and 1:2 at ACQ solution concentrations of 0.6, 1, and 1.5 percent. All solutions had a pH of about 8.8. Samples were pressure treated with ACQ solution in a retort using an initial vacuum of -84.6 KPa relative to gauge (25 in. mercury) for 20 minutes followed by application of pressure of 1,034 KPa (150 psi) for 60 minutes. Weights of the samples before and after treatment were used to calculate solution retention. Samples were wrapped in plastic immediately after treatment to prevent moisture loss and conditioned at 50°C, and those for leaching evaluation were conditioned for 3 weeks to facilitate fixation of active ingredients. For fixation monitoring, red pine samples were removed from the conditioning oven at different intervals and placed in a press; the expressate was analyzed for copper using x-ray fluorescence spectroscopy (XRF; Oxford Lab-X3000) to monitor fixation. Fixed samples were subjected to laboratory leaching according to the AWPA-E11-06 (AWPA 2006c) method. Leachate samples collected at different time intervals were analyzed for copper using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Perkin Elmer Optima 3000 DV with an auto sampler AS90). ICP-AES was operated at a power level of 1,300 W. Gas flows for plasma, auxiliary, and nebulizer in the ICP-AES were set at 15, 0.5, and 0.8 L/min, respectively, while sample inflow was maintained at 1 mL/min. Leached and unleached blocks of ACQ-treated red pine were ground, and two aggregate samples from each condition were extracted following the procedure AWPA-A16-93 for the extraction of quaternary ammonium compounds from treated samples (AWPA 2006b). The extracts were analyzed for DDACb using ion chromatography, using Dionex model DX600 with an autosampler AS40. Analysis was conducted with suppressed conductivity using 11 percent 0.2 N H<sub>2</sub>SO<sub>4</sub>/80 percent acetonitrile/9 percent deionized water as the mobile phase. DDACb was analyzed for red pine samples only because of poor solution uptake in jack pine and black spruce heartwood samples. Cumulative losses of copper and quat were expressed as percent loss or loss per unit area (mg/m<sup>2</sup>). Tukey's multiple comparison test was conducted to compare the means.

Table 1.—ACQ treating solution and retention.

Ratio (CuO:DDACb)	ACQ (%)	Retention (kg/m <sup>3</sup> )								
		Red pine			Jack pine			Spruce		
		ACQ	CuO	DDACb	ACQ	CuO	DDACb	ACQ	CuO	DDACb
2:1	0.6	4.6	3.1	1.5	2.1	1.4	0.7	3.2	2.1	1.1
	1.0	8.2	5.5	2.7	3.0	2.0	1.0	4.4	2.9	1.5
	1.5	11.4	7.6	3.8	3.8	2.6	1.3	5.9	4.0	2.0
1:1	0.6	4.4	2.2	2.2	2.3	1.2	1.2	3.2	1.6	1.6
	1.0	6.8	3.4	3.4	3.6	1.8	1.8	5.0	2.5	2.5
	1.5	10.2	5.1	5.1	5.1	2.6	2.6	7.5	3.8	3.8
1:2	0.6	4.3	1.4	2.9	2.7	0.9	1.8	2.9	1.0	2.0
	1.0	6.7	2.2	4.5	4.4	1.5	2.9	5.0	1.7	3.3
	1.5	10.3	3.4	6.9	5.7	1.9	3.8	7.3	2.4	4.9

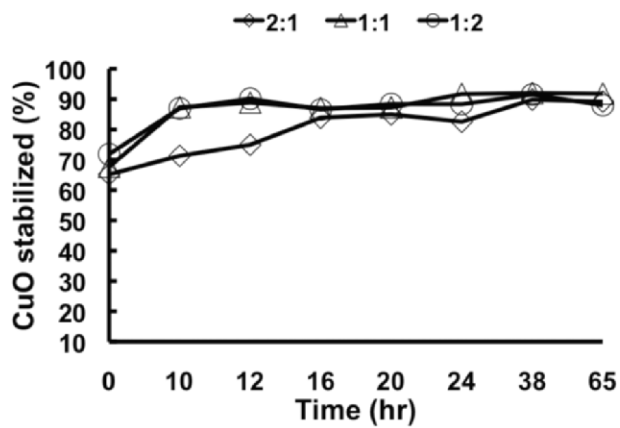
### Results and Discussion

Concentrations of ACQ solution used for treating red pine, jack pine, and black spruce samples and the corresponding ACQ, CuO, and DDACb retentions, estimated based on solution uptake, are summarized in Table 1. Jack pine and black spruce had low preservative absorption compared with red pine. For example, 0.6 percent ACQ solution resulted in ACQ retentions ranging from 4.3 to 4.6 kg/m<sup>3</sup>, 2.1 to 2.7 kg/m<sup>3</sup>, and 2.9 to 3.2 kg/m<sup>3</sup> for red pine, jack pine, and black spruce, respectively.

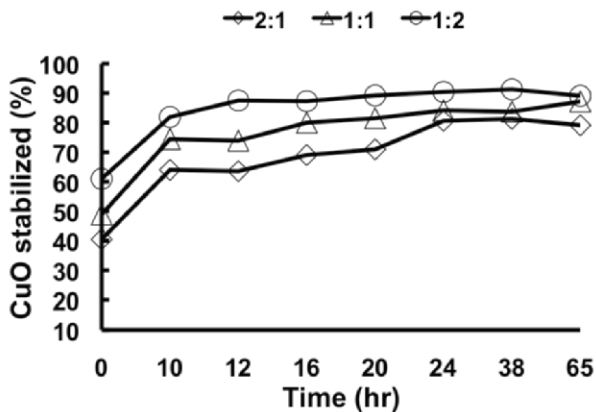
Rates of CuO fixation in red pine samples during posttreatment conditioning at 50°C are summarized in Figure 1. About 65 percent of the copper was adsorbed immediately after treatment for samples treated with 0.6 percent ACQ with a CuO to DDACb ratio of 2:1 (retention was 3.1 kg/m<sup>3</sup> CuO and 1.5 kg/m<sup>3</sup> DDACb), compared with about 68 percent for the 1:1 formulation (retention was 2.2 kg/m<sup>3</sup> CuO and 2.2 kg/m<sup>3</sup> DDACb) and 72 percent for the 1:2 formulation (retention was 1.4 kg/m<sup>3</sup> CuO and 2.9 kg/m<sup>3</sup> DDACb). Copper was fixed immediately after treatment by ion exchange, and the relative amount was lower for samples treated with higher ACQ concentrations due to the limited exchange capacity of the wood. Copper fixation immediately after the treatment was about 40 and 18 percent for the samples treated with 1 percent ACQ (retention was 5.5 kg/m<sup>3</sup> CuO and 2.7 kg/m<sup>3</sup> DDACb) and 1.5 percent ACQ (retention was 7.6 kg/m<sup>3</sup> CuO and 3.8 kg/m<sup>3</sup> DDACb) with a CuO to DDACb ratio of 2:1. Considerable improvement in fixation immediately after the treatment was observed with a reduction of CuO to DDACb to 1:2, resulting in 61 and 42 percent CuO adsorbed soon after the treatment for ACQ concentrations of 1 percent (retention was 2.2 kg/m<sup>3</sup> CuO and 4.5 kg/m<sup>3</sup> DDACb) and 1.5 percent (retention was 3.4 kg/m<sup>3</sup> CuO and 6.9 kg/m<sup>3</sup> DDACb), respectively (Fig. 1). These results show that with the reduction in relative proportion of copper in the formulation, the available ion exchange sites can initially bind a higher proportion of copper. This results in rapid fixation of copper immediately after treatment because of the lower copper retention in the treated samples. Following this initial rapid ion exchange absorption, copper fixation in samples treated with ACQ with a CuO to DDACb ratio of 2:1 occurs at a slower rate compared with the formulation with a ratio of 1:2 especially for the samples treated with higher ACQ concentrations. For samples treated with 1.5 percent ACQ having a CuO to DDACb ratio of 2:1 (retention was 7.6 kg/m<sup>3</sup> CuO and 3.8 kg/m<sup>3</sup> DDACb) 12

hours of posttreatment at 50°C resulted in only 49 percent of fixed CuO compared with 76 percent for ACQ with a 1:2 ratio (retention is 3.4 kg/m<sup>3</sup> CuO and 6.9 kg/m<sup>3</sup> DDACb). Furthermore, the extent of copper fixation was higher for the formulations with lower proportions of copper, especially for the 1:2 formulations because of the lower copper retention in the treated samples (Fig. 1).

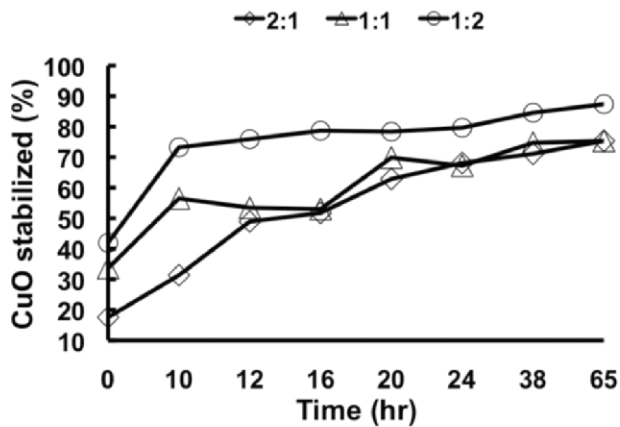
The percent copper leached and amounts leached per unit area (mg/m<sup>2</sup>) after 2 weeks of laboratory leaching are shown in Figures 2 and 3, respectively. The percentage of available copper leached by the different formulations (Fig. 2) was generally not greatly affected by the formulation, although in red pine the 1:2 formulation had a significantly higher percentage of copper leaching than the 2:1 and 1:1 formulations for the lowest retention treatment (Fig. 2a). In red pine and jack pine, there was a significantly higher percentage of copper leaching for the highest copper to quat ratio at the highest retention (Figs. 2a and 2b). When leaching was expressed as absolute leaching amounts (mg/m<sup>2</sup>) for red pine (Fig. 3a), analysis of variance showed that the amount of copper leached per unit area increased significantly with increasing treating solution concentration for all three CuO to DDACb ratios. For a CuO to DDACb ratio of 2:1, the average copper leaching increased from 490 mg/m<sup>2</sup> for red pine samples treated with 0.6 percent ACQ (retention was 3.1 kg/m<sup>3</sup> CuO and 1.5 kg/m<sup>3</sup> DDACb) to 990 and 2,450 mg/m<sup>2</sup>, respectively, for samples treated with 1 percent ACQ (retention was 5.5 kg/m<sup>3</sup> CuO and 2.7 kg/m<sup>3</sup> DDACb) and 1.5 percent ACQ (retention was 7.6 kg/m<sup>3</sup> CuO and 3.8 kg/m<sup>3</sup> DDACb). A similar pattern of increase in copper leaching with an increase in treating solution concentration was observed for jack pine and black spruce (Figs. 3b and 3c) in agreement with Ung and Cooper (2005) and Tascioglu et al. (2005). Reducing the ratio of CuO to quat significantly reduced copper leaching at all concentrations because of the lower copper retention in the samples. For red pine samples treated with 0.6 percent ACQ, reduction of the CuO to DDACb ratio from 2:1 to 1:1 and 1:2 (retention was 3.1 kg/m<sup>3</sup> CuO and 1.5 kg/m<sup>3</sup> DDACb, 2.2 kg/m<sup>3</sup> CuO and 2.2 kg/m<sup>3</sup> DDACb, 1.4 kg/m<sup>3</sup> CuO and 2.9 kg/m<sup>3</sup> DDACb, respectively) resulted in only a slight decrease in leaching from 490 to 420 and 365 mg/m<sup>2</sup>, respectively (the two smaller values are not significantly different; Fig. 3a). Copper leaching from red pine treated with 1 percent ACQ decreased from 990 to 735 and 465 mg/m<sup>2</sup>, respectively (all significantly different) with a decrease in relative proportion of copper in ACQ from 2:1 to 1:1 and 1:2 (retention was 5.5 kg/m<sup>3</sup> CuO and 2.7 kg/m<sup>3</sup> DDACb,



(a)



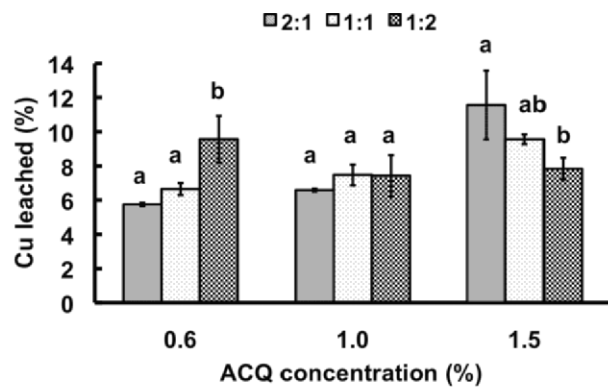
(b)



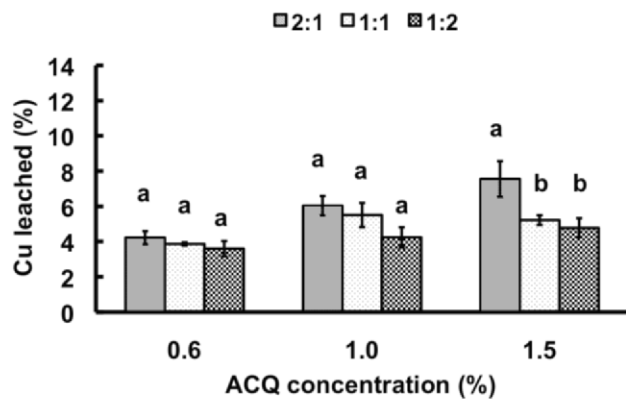
(c)

Figure 1.—Percentage of copper fixed over time in red pine treated with ACQ having different CuO to DDACb ratios: (a) 0.6 percent ACQ, (b) 1 percent ACQ, (c) 1.5 percent ACQ.

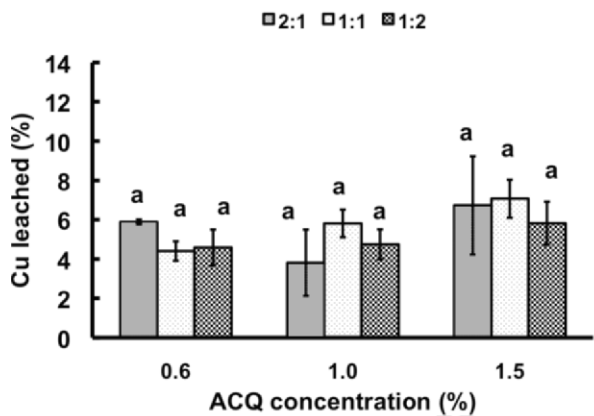
3.4 kg/m<sup>3</sup> CuO and 3.4 kg/m<sup>3</sup> DDACb, 2.2 kg/m<sup>3</sup> CuO and 4.5 kg/m<sup>3</sup> DDACb, respectively). For samples treated with 1.5 percent ACQ, the decrease in copper leaching was from 2,450 to 1,400 and 750 mg/m<sup>2</sup> (all significantly different) with a decrease in the proportion of copper in ACQ from 2:1 to 1:1 and 1:2 (retention was 7.6 kg/m<sup>3</sup> CuO and 3.8 kg/m<sup>3</sup> DDACb, 5.1 kg/m<sup>3</sup> CuO and 5.1 kg/m<sup>3</sup> DDACb, 3.4 kg/m<sup>3</sup> CuO and 6.9 kg/m<sup>3</sup> DDACb, respectively). Comparable



(a)



(b)



(c)

Figure 2.—Copper leached (%) from samples treated with ACQ having different CuO to DDACb ratios: (a) red pine, (b) jack pine, (c) black spruce. (Note: for each ACQ concentration level, mean bars with the same letters are not significantly different at 95% level of confidence.)

results were observed in jack pine and black spruce (Figs. 3b and 3c), although the leaching amounts were lower and not all differences were statistically significant. For all three species studied, the 1:1 formulation had an average of 20, 25, and 45 percent lower copper leaching (mg/m<sup>2</sup>) compared with the 2:1 formulation for ACQ concentrations of 0.6, 1, and 1.5 percent, respectively. Further reduction in the ratio of CuO to DDACb to 1:2 resulted in an average reduction in copper leaching compared with the 2:1



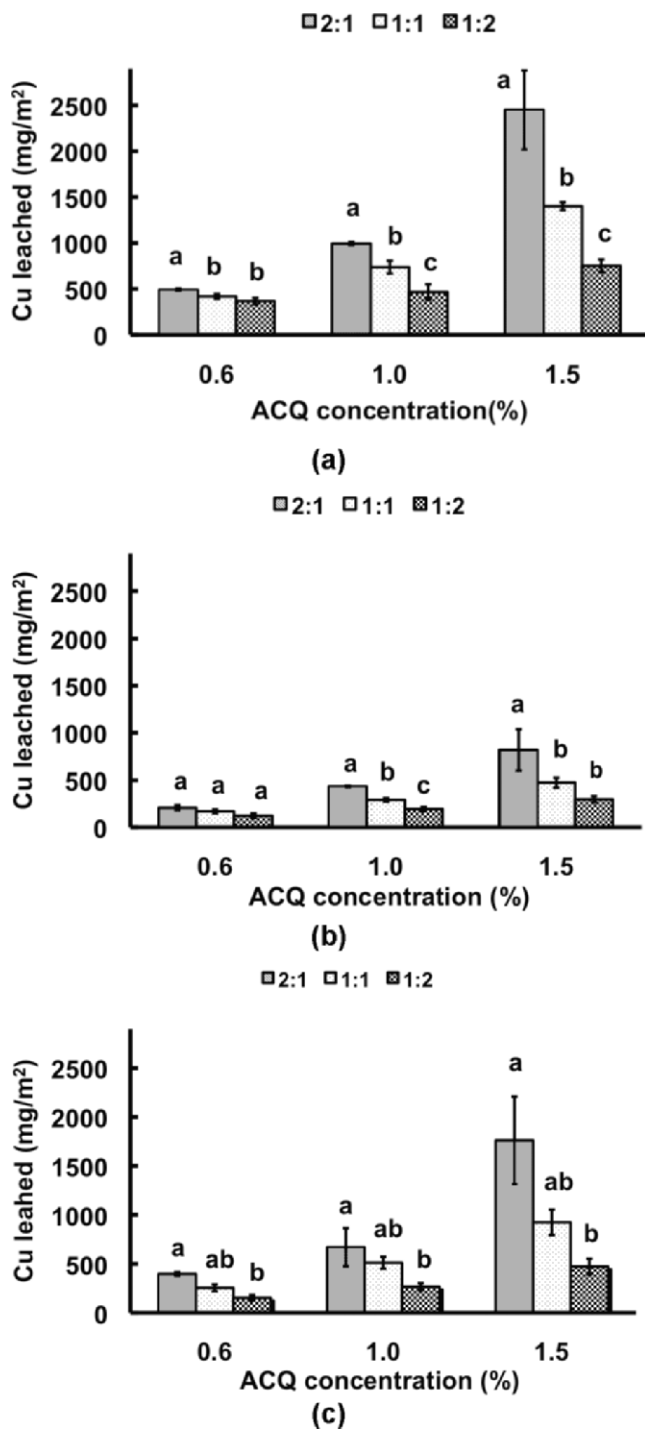


Figure 3.—Copper leached ( $\text{g}/\text{m}^2$ ) from samples treated with ACQ having different CuO to DDACb ratios: (a) red pine, (b) jack pine, (c) black spruce. (Note: for each ACQ concentration level, mean bars with the same letters are not significantly different at 95% level of confidence.)

formulation of 40, 55, and 70 percent for the samples treated with 0.6, 1, and 1.5 percent ACQ, respectively.

Results showed that in the case of a sample having comparable copper retention increase in relative proportion to DDACb retention is not significantly affecting the amount of copper leached or the amount of copper retained in the leached samples. For example, the 1:1, 0.6 percent

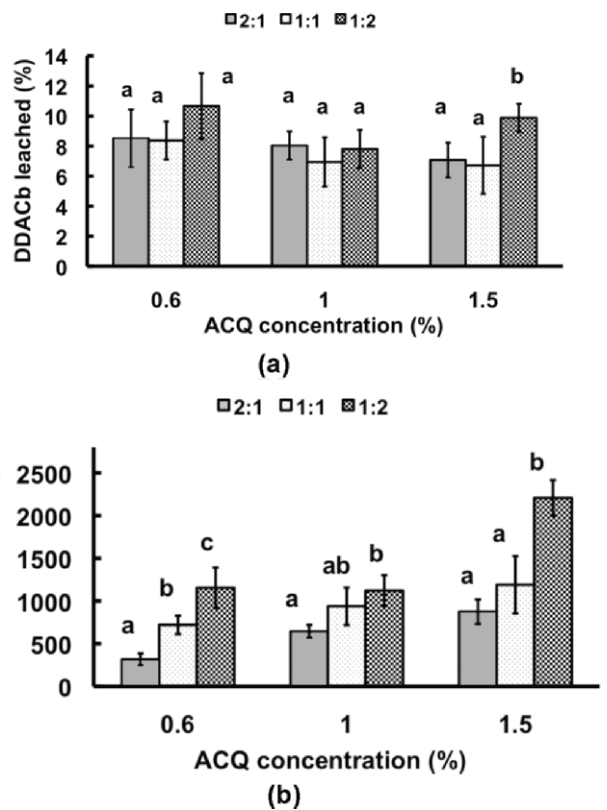


Figure 4.—DDACb leached from red pine treated with ACQ having different CuO to DDACb ratios: (a) in %, (b) in  $\text{g}/\text{m}^2$ . (Note: for each ACQ concentration level, mean bars with the same letters are not significantly different at the 95% level of confidence.)

ACQ and the 1:2, 1.0 percent ACQ treatments had similar CuO retentions ( $2.2 \text{ kg}/\text{m}^3$ ) although the latter had DDACb retention that was twice as high ( $4.5 \text{ vs. } 2.2 \text{ kg}/\text{m}^3$ ); however, the average amounts of copper leached were 6.6 percent ( $420 \text{ mg}/\text{m}^2$ ) from the lower DDACb formulation and 7.4 percent ( $465 \text{ mg}/\text{m}^2$ ) from the higher DDACb formulation (differences not statistically significant). Similarly, the 1:1, 1.0 percent ACQ and the 1:2, 1.5 percent ACQ treatments both resulted in  $3.4 \text{ kg}/\text{m}^3$  CuO retention and a DDACb retention of  $3.4 \text{ kg}/\text{m}^3$  and  $6.9 \text{ kg}/\text{m}^3$ , respectively; the average amount of copper leached after 3 weeks of fixation was 7.5 percent ( $735 \text{ mg}/\text{m}^2$ ) and 7.8 percent ( $750 \text{ mg}/\text{m}^2$ ), respectively, and was not significantly different. This indicates that the initial copper ion exchange sites may have been decreased by higher quat in the formulation but ultimately the amounts of copper fixed and the amounts of copper leached were not affected.

Leaching amounts of DDACb from the red pine samples, expressed as a percentage or the amount leached per unit area, are summarized in Figure 4. The leaching losses of DDACb when expressed as a percentage of the amount initially present (Fig. 4a) were between 6 to 10 percent for all formulation concentrations and ratios of CuO to DDACb. However, the absolute losses ( $\text{mg}/\text{m}^2$ ) were higher for the 1:2 ratio as compared with the 2:1 and 1:1 ratios (Fig. 4b). For 0.6 percent ACQ samples, DDACb leaching averaged 315, 720, and  $1,155 \text{ mg}/\text{m}^2$ , respectively, from red pine samples treated with ACQ at a CuO to DDACb ratio of 2:1,

1:1, and 1:2 (retention was 3.1 kg/m<sup>3</sup> CuO and 1.5 kg/m<sup>3</sup> DDACb, 2.2 kg/m<sup>3</sup> CuO and 2.2 kg/m<sup>3</sup> DDACb, 1.4 kg/m<sup>3</sup> CuO and 2.9 kg/m<sup>3</sup> DDACb, respectively). For 1 percent ACQ samples, the average DDACb leaching was, respectively, 645, 935, and 1,120 mg/m<sup>2</sup> (retention was 5.5 kg/m<sup>3</sup> CuO and 2.7 kg/m<sup>3</sup> DDACb, 3.4 kg/m<sup>3</sup> CuO and 3.4 kg/m<sup>3</sup> DDACb, 2.2 kg/m<sup>3</sup> CuO and 4.5 kg/m<sup>3</sup> DDACb, respectively). Greater quat leaching was observed for samples treated with 1.5 percent ACQ; red pine samples leached 875, 1,190, and 2,200 mg/m<sup>2</sup>, respectively, for ratios of 2:1, 1:1, and 1:2 (retention was 7.6 kg/m<sup>3</sup> CuO and 3.8 kg/m<sup>3</sup> DDACb, 5.1 kg/m<sup>3</sup> CuO and 5.1 kg/m<sup>3</sup> DDACb, 3.4 kg/m<sup>3</sup> CuO and 6.9 kg/m<sup>3</sup> DDACb, respectively). For the samples treated with the lowest ACQ concentration (0.6%), the amount of DDACb leaching was significantly higher (Fig. 4b) for 1:1 and 1:2 ratio samples compared with 2:1 CuO to DDACb samples. At higher ACQ concentrations (1% and 1.5%), an increase in the relative proportion of quat in the formulation to 1:1 CuO to DDACb did not result in a significant increase in the amount of quat leached (Fig. 4b) compared with the 2:1 formulation. However, a further increase in the relative proportion of quat in the formulation to 1:2 CuO to DDACb resulted in significantly higher (Fig. 4b) quat leaching compared with the 2:1 formulation.

In summary, decreasing the relative proportion of copper to DDACb in the formulation from 2:1 to 1:1 or 1:2 considerably reduces the time required for the fixation of copper and decreases the amount of copper leaching by lowering the copper retention in the treated wood. An increase in relative proportion of DDACb in the formulation to a 1:1 ratio does not appear to contribute to additional DDACb leaching from the ACQ-treated wood at higher ACQ concentrations, confirming its rapid fixation and the relatively high capacity of wood to bind quats (Preston et al. 1987). Reduction in copper leaching and improved copper fixation at a given ACQ retention, as a result of reduction in relative proportion of copper in the formulation, suggests a possible reformulation to tackle the challenges of poor copper fixation and long fixation times associated with ACQ-treated wood; however, the efficacy of such reformulations will be a consideration. DDACb used in ACQ formulation is a dialkyl-type, quaternary ammonium compound, which is a very effective biocide. Considerable research has been done in the past to use dialkyl quaternaries such as DDAC as stand-alone preservatives. Laboratory soil block tests by Butcher et al. (1977) showed that 0.25 to 0.5 percent DDAC, which corresponds to an active retention of 1.6 to 3.2 kg/m<sup>3</sup>, could protect pine samples against brown-rot fungi *Gloeophyllum trabeum* and *Poria placenta* and white rot fungus *Fomes gilvus*. McNamara (1984) reported similar biological performance for DDAC- and CCA-treated wood. Retention of active ingredients in the red pine samples, treated with ACQ and having different CuO to DDACb ratios, after leaching is summarized in Table 2. The DDACb retentions left after intensive accelerated leaching of the samples treated with ACQ having CuO to quat ratio of 1:1 and 1:2 are above the minimum toxic threshold reported by Butcher et al. (1977). The presence of copper as a cobioicide in the ACQ formulation will also aid in the biological efficacy of the formulation and ACQ formulations having a CuO to DDACb ratio of 1:1 and 1:2 are expected to have good biological efficacy. This is supported by Richardson (1991), who reported comparable performance for CCA and

Table 2.—Retention of ACQ active ingredients in red pine after leaching.

Ratio (CuO:DDACb)	ACQ (%)	ACQ leaching (%)		Retention after leaching (kg/m <sup>3</sup> )	
		Cu	DDACb	CuO	DDACb
2:1	0.6	5.7	8.5	2.9	1.4
	1.0	6.6	8.0	5.1	2.5
	1.5	11.6	7.1	6.7	3.5
1:1	0.6	6.6	8.4	2.0	2.0
	1.0	7.5	6.9	3.1	3.1
	1.5	9.6	6.7	4.6	4.8
1:2	0.6	9.6	10.7	1.3	2.6
	1.0	7.4	7.8	2.1	4.1
	1.5	7.8	9.9	3.2	6.2

ammoniacal copper quat with a CuO to DDAC ratio of 1:1, which led to the introduction of this formulation as ACQ-A in the AWP standards. However, the long-term biological efficacy of such alternative formulations will have to be confirmed by field testing.

## Conclusions

A decrease in the relative proportion of copper in the ACQ formulation from a CuO to DDACb ratio of 2:1 to 1:1 and 1:2 results in lower copper retention in the treated samples, substantially decreasing the amount of copper leached per unit area for the three species studied, based on laboratory leaching experiments using small specimens. The reduction in the leaching was higher for samples treated with concentrations of 1 and 1.5 percent ACQ compared with the sample treated with 0.6 percent ACQ. For samples treated with 1.5 percent ACQ, the reduction in the ratio of CuO to DDACb to 1:2 resulted in up to 70 percent reduction in copper leaching compared with the leaching observed for the formulation with 2:1 ratio because of the lowest copper retention in the 1:2 formulation. However, the proportional leaching of DDACb was higher for the 1:2 ratio because of the higher DDACb retention. Considerable reduction in the time required for the fixation of copper was observed as a result of lowering the relative proportion of copper in the ACQ formulation because of the lower copper retention. The CuO to DDACb formulation with 1:1 ratio appears to be the most promising, considering the positive effects of reduced copper ratio on copper leaching and fixation time and the minimal effect on DDACb leaching.

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