

Long-Term Soil Accumulation of Chromium, Copper, and Arsenic Adjacent to Preservative-Treated Wood

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Chromated copper arsenate (CCA) treated wood has been used extensively in outdoor applications, ranging from fence posts to decking and wood foundations. CCA treatment provides long-term protection for wood because chemical reactions that take place during treatment fix the preservative elements in the wood. However, varying amounts of CCA have been reported to leach from the wood (Lebow 1996). The Environmental Protection Agency (EPA) and CCA producers recently reached an agreement to limit future use of CCA for some types of applications. One area of concern is the long-term accumulation of leached CCA in soil adjacent to treated wood structures. A study of CCA concentrations in soil beneath residential decks reported substantially elevated levels of copper, chromium, and arsenic (Stilwell and Gorny 1997). However, this finding conflicted with other studies that reported much lower concentrations of leached CCA components in soil adjacent to forest boardwalks (Comfort 1993, Lebow et al. 2000). The conflicting nature of these findings demonstrates the difficulty of interpreting soil measurements adjacent to in-service structures. The original treatment may be unknown, and there may be little historical data to indicate whether the site was previously exposed to contamination from construction debris or other non-leaching sources. In complicated structures such as decks, it may also be difficult to determine the surface area of the structure that is contributing to soil accumulations in any specific area. One way to overcome these obstacles is to sample soil adjacent to test specimens in exposure sites. The USDA Forest Service, Forest Products Laboratory uses such specimens to evaluate the long-term efficacy of wood preservatives. Treated wooden stakes are buried to one-half their length at exposure sites in Wisconsin and Mississippi. Treatment conditions and original preservative concentration are known for each stake, as are site history and conditions. The spacing of the stakes, and their simple geometry, make it possible to assume that the soil levels are attributable to a specific volume of wood. In this paper, we report soil levels of arsenic, copper, and chromium adjacent to stakes treated with CCA and exposed at test sites in Wisconsin and Mississippi for 22 years. The effects of site location and preservative concentration are discussed.

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MATERIALS AND METHODS

Soil samples were removed adjacent to stakes placed at a test site in the Harrison Experimental Forest near Gulfport, Mississippi, and a test site near Madison, Wisconsin. The Mississippi test site is a pine woodland receiving an average of 1,580 mm of rainfall per year, with soil texture characterized as loamy sand. The Wisconsin site is grassland, averaging 780 mm of precipitation per year, with several months of below-freezing temperatures. The soil at the Wisconsin site is characterized as clay loam.

The preservative-treated stakes evaluated in this study were Southern Pine sapwood with dimensions of 38 by 89 by 457 mm. The stakes were pressure-treated with a CCA Type-C solution, which is the formulation that has been used for commercial pressure treatments for over 20 years. CCA-C is composed of 47.5% CrO_3 , 18.5% CuO , and 34% As_2O_5 . Solutions of 0.5%, 1.0%, and 1.5% CCA were prepared to obtain retentions of 3.2, 6.4, and 9.6 kg/m^3 , respectively, within the treated wood. Each stake was weighed immediately before and after treatment to determine preservative uptake. The stakes for both exposure sites were treated together to remove any variability that might be associated with the treatment process. Following treatment the stakes were allowed to air dry and were then buried, upright, to a depth of 200 mm in soil at the test sites. The stakes were randomly placed in rows, with 600 mm spacing between stakes within rows and 900 mm spacing between rows.

Soil samples were removed adjacent to five replicate stakes for each CCA treatment level. Soil cores were removed in a pattern intended to create a three-dimensional profile of preservative levels adjacent to the stakes (Figure 1). Cores were removed to a depth of 600 mm at distances of 50 and 150 mm from one wide and one narrow face of each stake. The core was removed from the sampler in 100-mm sections, which were placed individually in polyethylene containers. After each core was removed, the probe was scrubbed and rinsed with distilled water. Control soil cores were removed to a depth of 600 mm from undisturbed areas adjacent to each test site. Control samples were removed from eight locations adjacent to the Mississippi plot and six locations adjacent to the Wisconsin plot.

The soil samples were air-dried to uniform moisture content in a room maintained at 27°C and 30% relative humidity. The dried samples were then passed through a 2-mm screen and the larger material was discarded. The remaining sample was ground using a ceramic mortar and pestle and extracted using a microwave-assisted version of EPA Method 3050B, which is intended for determination of arsenic and heavy metals in sediments and soils (EPA 1995). Copper and chromium concentrations in the resulting extract were determined by flame atomization atomic absorption spectroscopy; graphite furnace atomization was used for arsenic analysis. In all cases, appropriate laboratory standards and blanks were analyzed.

RESULTS AND DISCUSSION

The distribution of leached CCA elements in soil around the stakes was strongly affected by both horizontal and vertical proximity to the stake. The highest concentrations of arsenic, chromium, and copper were generally found in the soil removed at a distance of 5 cm laterally from the stakes (Tables 1 to 3). The highest median concentrations of arsenic, 32 mg/kg at the Wisconsin site and 55 mg/kg at the Mississippi site, were found in the upper 20 cm of soil. These levels were clearly elevated above levels found in the control samples. Median copper levels in the soil were not as elevated as arsenic levels, ranging from 35 mg/kg at the Wisconsin site to 25 mg/kg at the Mississippi site. Median chromium concentrations were much lower and often similar to those of the control samples. Samples removed at a distance of 15 cm horizontally from the specimens were much less likely to contain elevated concentrations of CCA components. The accumulation of CCA elements in close proximity to the stakes, with much lower levels at only slightly greater distances, suggests that the leached elements have low mobility in the soil. Various authors have reported that arsenic, chromium and copper can be adsorbed by a range of soil components, with organic matter playing an important role in adsorption of copper and chromium, and inorganic components such as iron and aluminum forming complexes with arsenic (Alloway 1990, Bergholm 1990, Elliott et al. 1986). Levels of accumulation in soil are a function of both the leaching rate of CCA components and their subsequent mobility in the soil. Past studies of CCA-treated specimens submerged in water or exposed to rainfall have indicated that the rate of leaching from the treated wood is greatest initially and then levels off to a more steady-state release rate that very gradually decreases over time (Lebow 1996). Eventually, the rate at which CCA components are leached into the soil adjacent to the stakes might fall below the rate at which the elements are leached out of the soil, and soil levels of leached components would begin to decline.

A comparison of the concentrations of leached components in the soil indicates no consistent effect of original treatment concentration on subsequent soil concentrations of chromium, copper, or arsenic. Although the lack of correlation with treatment retention may seem counterintuitive, it does correspond with a recent evaluation of leaching from decking specimens, which found that the rate of arsenic release can actually be greater at lower CCA retentions (Lebow et al. 2002). This effect appears to be caused by the higher proportion of chromium available to react with and “fix” the arsenic in wood when higher solution concentrations are used. The results of the study reported here suggest that within the range of CCA treatment retentions normally used in soil contact (6.4 to 9.6 kg/m³), the level of retention will have little effect on long-term soil concentrations near the wood.

Site differences did appear to affect the pattern of accumulation of CCA components in the soil (Tables 1 to 3). To minimize treatment and wood sourcing effects, specimens exposed at the Mississippi and Wisconsin sites were matched

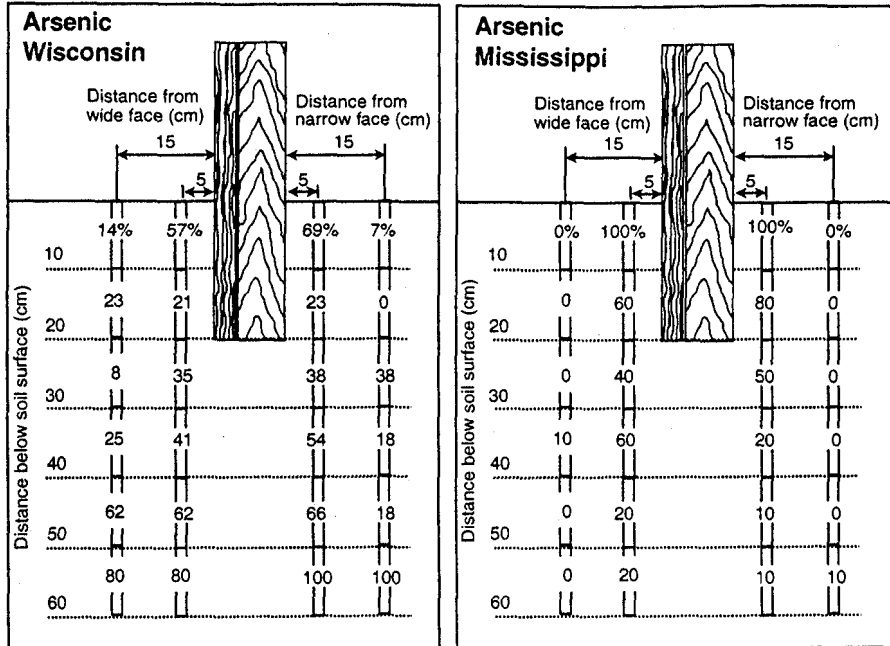


Figure 1. Percentage of samples in each sampling location that contained higher arsenic concentrations than did control samples at that site. Includes all preservative retentions.

sets from the same pressure treatment charges. Consequently, differences in levels of leached components in the soil are attributable to site differences such as climate and soil characteristics. At the Mississippi site, samples with elevated CCA levels tended to be tightly clustered in the upper 20 cm of soil and immediately adjacent to the stake. At the Wisconsin site, elevated CCA concentrations were found at greater depths in the soil and at a greater lateral distance from the stake. This trend was especially apparent for arsenic, as shown in Figure 1. At the Mississippi site, elevated arsenic concentrations were rarely found at a distance of 15 cm laterally from the stakes. This agrees with earlier work with older CCA formulations (DeGroot et al. 1979), which reported that samples removed 15 cm laterally from the stakes contained only background concentrations of CCA components. At the Wisconsin site, arsenic concentrations were somewhat lower than those at the Mississippi site, but arsenic was distributed over a larger area; most frequently, elevated samples were found at the 50- to 60-cm soil depth. It might be expected that greater leaching would occur in Mississippi because of the greater annual rainfall and absence of freezing temperatures. However, the reason for the greater soil mobility of leached arsenic at the Wisconsin site is less clear. A greater understanding of the effect of site characteristics on leaching and soil mobility of arsenic is needed.

Table 1. Median concentration of copper in soil adjacent to CCA-treated specimens exposed for 22 years near Madison, Wisconsin, and Gulfport, Mississippi

CCA in wood (kg/m ³)	Horizontal distance from stake (cm)	Median concentration of copper (mg/kg) at various vertical distances from soil surface (an) ^a							
		0-10	10-20	20-30	30-40	40-50	50-60		
Wisconsin site									
3.2	Wide face	5	26 (9)	21 (16)	20 (4)	29 (4)	27 (17)	—	
		15	19 (12)	19 (18)	20 (6)	30 (14)	18 (31)	35 (2)	
	Narrow face	5	24 (6)	17 (15)	22 (7)	25 (3)	34 (14)	35 (3)	
		15	19 (2)	21 (6)	24 (7)	31 (9)	30 (4)	34 (1)	
6.4	Wide face	5	27 (9)	22 (2)	25 (9)	27 (6)	29 (11)	31 (7)	
		15	21 (9)	18 (7)	24 (6)	24 (12)	31 (9)	30 (26)	
	Narrow face	5	30 (13)	18 (8)	23 (7)	33 (50)	33 (13)	30 (11)	
		15	17 (14)	18 (3)	25 (6)	31 (5)	33 (11)	31 (4)	
9.6	Wide face	5	25 (15)	20 (9)	22 (8)	24 (9)	24 (1)	20 (1)	
		15	16 (5)	19 (48)	20 (10)	25 (10)	20 (13)	—	
	Narrow face	5	23 (70)	18 (7)	20 (15)	22 (7)	28 (2)	25 (6)	
		15	19 (8)	17 (4)	21 (6)	25 (4)	31 (17)	20 (1)	
—	Control area		14 (3)	14 (3)	15 (6)	16 (6)	20 (8)	18 (11)	
Mississippi site									
6.4	Wide face	5	20 (26)	16 (22)	9 (4)	8 (8)	7 (3)	8 (2)	
		15	10 (4)	5 (1)	9 (1)	6 (2)	10 (1)	11 (3)	
	Narrow face	5	14 (8)	25 (9)	8 (4)	10 (5)	9 (5)	6 (2)	
		15	9 (3)	7 (2)	7 (3)	10 (3)	10 (4)	5 (1)	
9.6	Wide face	5	16 (14)	21 (28)	9 (4)	9 (4)	8 (3)	9 (4)	
		15	10 (4)	5 (1)	10 (3)	7 (4)	11 (3)	8 (4)	
	Narrow face	5	8 (17)	16 (30)	12 (9)	10 (6)	9 (3)	9 (3)	
		15	8 (2)	7 (1)	8 (2)	9 (2)	12 (2)	8 (7)	
—	Control area		5 (1)	6 (1)	7 (2)	7 (2)	7 (2)	7 (2)	

^aNumbers in parentheses represent interquartile range.

Table 2. Median concentration of chromium in soil adjacent to CCA-treated specimens exposed for 22 years near Madison, Wisconsin, and Gulfport, Mississippi

CCA in wood (kg/m ³)	Horizontal distance from stake (cm)	Median concentration of chromium (mg/kg) at various vertical distances from soil surface (cm) ^a								
		0-10	10-20	20-30	30-40	40-50	50-60			
Wisconsin site										
3.2	Wide face	5	9 (4)	10 (12)	10 (3)	14 (8)	13 (2)	—		
		15	9 (8)	8 (10)	12 (5)	11 (14)	8 (11)	16 (1)		
	Narrow face	5	13 (8)	6 (8)	11 (5)	10 (4)	15 (10)	14 (5)		
		15	8 (5)	8 (13)	14 (11)	14 (7)	15 (5)	13 (1)		
6.4	Wide face	5	9 (3)	10 (5)	10 (5)	11 (4)	10 (5)	12 (5)		
		15	10 (8)	10 (3)	11 (7)	11 (6)	12 (8)	9 (9)		
	Narrow face	5	9 (9)	9 (7)	9 (4)	13 (14)	14 (2)	13 (6)		
		15	9 (5)	10 (8)	12 (5)	13 (5)	15 (6)	13 (4)		
9.6	Wide face	5	10 (10)	9 (2)	10 (5)	12 (4)	14 (5)	9 (1)		
		15	10 (4)	12 (12)	12 (3)	14 (3)	12 (1)	—		
	Narrow face	5	14 (26)	12 (5)	15 (6)	8 (3)	14 (3)	9 (1)		
		15	10 (4)	11 (7)	12 (2)	12 (2)	14 (6)	9 (1)		
—	Control area	16 (4)	14 (2)	15 (3)	16 (6)	15 (4)	17 (6)			
Mississippi site										
6.4	Wide face	5	8 (5)	6 (6)	6 (5)	5 (3)	6 (6)	6 (3)		
		15	7 (4)	5 (1)	8 (3)	11 (7)	6 (2)	9 (10)		
	Narrow face	5	7 (1)	8 (6)	15 (13)	16 (2)	5 (2)	5 (2)		
		15	5 (2)	4 (3)	3 (5)	7 (3)	10 (3)	5 (1)		
9.6	Wide face	5	7 (3)	6 (4)	4 (5)	4 (5)	6 (4)	8 (5)		
		15	6 (6)	5 (1)	12 (8)	8 (12)	8 (3)	16 (13)		
	Narrow face	5	6 (2)	6 (4)	13 (9)	16 (5)	4 (3)	5 (4)		
		15	4 (3)	7 (5)	5 (3)	6 (2)	11 (2)	8 (11)		
—	Control area	4 (2)	4 (3)	6 (2)	5 (4)	5 (4)	7 (6)			

^aNumbers in parentheses represent interquartile range.

Table 3. Median concentration of arsenic in soil adjacent to CCA-treated specimens exposed for 22 years near Madison, Wisconsin, and Gulfport, Mississippi

CCA in wood (kg/m ³)	Horizontal distance from stake (cm)	Median concentration of arsenic (mg/kg) at various vertical distances from soil surface (cm) ^a						
		0-10	10-20	20-30	30-40	40-50	50-60	
		Wisconsin site						
3.2	Wide face	5	3 (22)	18 (24)	14 (8)	13 (20)	10 (9)	—
		15	6 (13)	8 (8)	12 (4)	14 (10)	19 (2)	20 (2)
	Narrow face	5	32 (33)	11 (18)	12 (2)	16 (8)	16 (15)	19 (3)
		15	5 (10)	8 (10)	12 (4)	7 (13)	14 (5)	17 (2)
6.4	Wide face	5	19 (31)	10 (12)	13 (7)	13 (4)	12 (10)	18 (4)
		15	7 (14)	9 (13)	9 (12)	14 (6)	18 (6)	17 (12)
	Narrow face	5	21 (27)	9 (10)	15 (9)	15 (84)	17 (7)	17 (3)
		15	9 (7)	9 (4)	12 (9)	14 (9)	13 (17)	15 (4)
9.6	Wide face	5	22 (24)	9 (12)	16 (7)	19 (1)	21 (1)	17 (1)
		15	9 (9)	6 (80)	13 (3)	14 (10)	11 (1)	—
	Narrow face	5	23 (146)	9 (11)	18 (9)	18 (9)	10 (20)	18 (3)
		15	2 (2)	12 (5)	15 (11)	13 (3)	15 (5)	15 (1)
—	Control area		7 (2)	8 (2)	9 (6)	11 (2)	12 (4)	12 (7)
		Mississippi site						
6.4	Wide face	5	43 (87)	19 (46)	4 (21)	7 (22)	4 (1)	4 (1)
		15	3 (3)	1 (1)	2 (1)	2 (1)	3 (1)	3 (1)
	Narrow face	5	16 (36)	55 (66)	4 (14)	1 (6)	4 (1)	3 (2)
		15	3 (2)	2 (1)	2 (1)	3 (1)	3 (1)	3 (1)
9.6	Wide face	5	20 (37)	22 (52)	5 (34)	6 (11)	4 (2)	5 (3)
		15	3 (2)	2 (1)	3 (1)	3 (2)	3 (1)	3 (1)
	Narrow face	5	24 (21)	49 (60)	11 (11)	1 (5)	4 (3)	4 (2)
		15	3 (2)	2 (1)	2 (1)	3 (1)	3 (1)	3 (4)
—	Control area		1 (1)	1 (1)	2 (1)	3 (1)	3 (2)	2 (2)

^a Numbers in parentheses represent interquartile range.

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