

RELEASE OF COPPER, CHROMIUM, AND ARSENIC FROM TREATED SOUTHERN PINE EXPOSED IN SEAWATER AND FRESHWATER

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ABSTRACT

The use of chromated copper arsenate (CCA-C) treated wood in marine construction has drawn criticism from environmentalists because of the high levels of chemical concentration in the wood and the potential for harm to aquatic life. These criticisms have been difficult to address because of the lack of, or conflicting, information on the release of chemical elements of CCA-C into seawater. In this study, sections of lumber and piling were treated with CCA-C to retention levels of 20 or 40 kg/m³ and immersed for 15 months in deionized water and dilutions of an artificial seawater solution. The leaching solutions were periodically collected and analyzed for the concentration of released copper, chromium, and arsenic. Seawater had a mixed effect on leaching of the elements of CCA-C. The steady-state release rate of copper was much greater in seawater than in deionized water. In contrast, the steady-state release rate of arsenic was somewhat greater in deionized water than in seawater. The rate of chromium release was consistently much less than that of copper and arsenic and did not appear to be affected by seawater. Release rates of copper and arsenic were somewhat less from the wood treated to 20 kg/m³ than from the wood treated to 40 kg/m³, but retention had little effect on the rate of chromium release. Release rates per unit surface area were consistently greater from piling than from lumber, especially for arsenic. Long-term release of CCA-C elements was estimated from steady-state release rates that occurred after 10 to 15 months of leaching.

Chromated copper arsenate (CCA-C) is the most commonly used preservative in the United States to protect wood products from attack by decay fungi, insects, and marine borers. CCA-C provides long-term protection because the copper, chromium, and arsenic undergo chemical reactions within the wood that make these elements resistant to leaching. However, some release (i.e., leaching) of copper, chromium, and arsenic does occur after the treated wood is placed in service. There are concerns that toxic elements leached from CCA-C-treated wood might harm adjacent plants or animals.

These concerns have been particularly acute when CCA-C-treated wood is used in marine construction. CCA-C-treated lumber and piling intended for use in seawater are treated with several times more preservative (24 to 40 kg/m³) than is CCA-C-treated wood used in other

applications (1). In addition, preservative components leached into water have the potential for greater mobility and exposure to sensitive organisms than do preservative components leached into soil (17). These concerns led researchers to perform a series of studies investigating the toxicity of leached CCA-C components toward marine organisms (30-32). The authors reported that elevated concentrations of copper were detected in sediments and crabs near treated wood, and they used laboratory studies to demonstrate that high concentrations of leachate from CCA-C-treated wood were toxic to a variety of marine organisms. However, a subsequent laboratory study reported that concentrations of CCA-C leachate in sediments adjacent to marine piling were relatively low, and results from this study showed that these sediments had no adverse impact on the marine amphipod *Ampelisca abdita* (3). It is apparent that the potential environmental impact of CCA-C-treated wood is highly dependent on the rate at which the toxic components are released, but efforts to estimate the rate of CCA release in seawater have produced a range of results(2,3,5,11,13,16,19,33).

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The majority of studies have attempted to follow the retention of CCA components within the wood products or samples placed in seawater over time. Because of the variable distribution of preservative within the wood, even before leaching, it is difficult to precisely measure leaching with this approach. Arsenault (2) reported that a single CCA-A-treated piling, after 18 years of exposure in North Carolina waters, had no significant differences in CCA-A concentration or component ratios between the above-water zone, tidal zone, below-water zone, or below-mudline zone. In a more detailed study, southern pine posts were treated with CCA-C and exposed for 8 years in Key West, Fla. (11). Little change in overall CCA-C retention was detected, although a migration of copper to the outside of the posts appeared to occur over time.

Much greater release rates have been noted when samples of smaller dimensions are exposed in seawater. Extensive leaching of all three components was noted when 6- by 38- by 152-mm (0.25- by 1.5- by 6-in.) southern pine panels were treated with CCA-C and exposed for 78 months in Key West, Fla. (16). Panels treated to an initial retention of 19 kg/m³ (1.2 pcf) lost approximately 80 percent of the copper, 48 percent of the chromium, and 50 percent of the arsenic. Those panels treated to 40 kg/m³ (2.5 pcf) lost approximately 71 percent of the copper, 58 percent of the chromium, and 18 percent of the arsenic. In their work, Heggarty and Curran (13) treated 5- by 25- by 50-mm or 20- by 20- by 150-mm (0.2- by 1- by 20-in. or 0.8- by 0.8- by 6-in.) pine and beech sapwood blocks with CCA and exposed them in Irish coastal waters. The smaller blocks appeared to lose at least 50 percent of the CCA components after only 1 year, with the percentage of copper losses less than those of chromium or arsenic. An apparent redistribution to, or slower loss of preservative from the tracheids, rays and crossfield pits of pine was noted, and a portion of the copper appeared to migrate to the surface of the larger blocks (13). Significant CCA leaching and copper movement was also noted in 50- by 50- by 500-mm (6- by 6- by 20-in.) CCA-treated *Pinus patula* stakes exposed off the coast of South Africa for 2 years (28). Overall losses of both copper (25% to 40%) and arsenic (70%) were detected, but copper content in the outer 0.24 inch

(6 mm) of the blocks increased almost 40 percent compared with pre-exposure retention levels.

One might expect to obtain more precise estimates of CCA component release by analyzing the leaching solution rather than the wood. However, this approach does require control of water movement, thus "real world" leaching conditions can only be approximated. A recent laboratory test of CCA-C leaching from piling exposed in seawater appears to confirm that copper is the most leachable component. Researchers found that a total of approximately 529 mg of copper, 60 mg of arsenic, and little or no chromium was released from each square meter of pile surface after 28 days (3). A laboratory seawater study of CCA-C release from one face of a southern pine board, treated to only 4.8 kg/m³, reported losses of 1 µg/cm²/day for arsenic and copper, and 0.01 µg/cm²/day for chromium after 21 days (19). A subsequent laboratory evaluation of CCA-C leaching from one face of southern pine lumber treated to either 34 or 49 kg/m³ noted release rates of 0.17 to 0.95 µg/cm²/day for copper, 0.007 to 0.032 µg/cm²/day for chromium, and 0.045 to 0.14 µg/cm²/day for arsenic after 90 days (5).

Assessment of CCA component release in seawater could be simplified by assuming that seawater and freshwater leaching rates are equivalent and that salinity has no effect on leaching. Salinity, which is often thought of as only salt (sodium chloride) content, is actually a measure of all dissolved solids, including species of sulfur, magnesium, calcium, and other elements (Table 1). Although

the assumption that salinity does not affect CCA-C leaching has not been well tested, past studies indicate that some components in seawater have the potential to alter the rate of CCA-C leaching. Sodium chloride content, perhaps the most obvious difference between fresh and seawater, does appear to have an effect on leaching of CCA components. Leaching of chromium and arsenic from pine sapwood blocks was increased when sodium chloride was added to distilled water to create salinities from 0 to 70 parts per thousand (ppt), although losses leveled off at about 50 ppt (14). After 40 weeks at a salinity of 34 ppt, typical for seawater, arsenic leaching increased by 25 percent and chromium leaching by 45 percent compared with that in deionized water. The trend for copper leaching was less clear, because leaching was inhibited at low salinities, then increased when salt concentrations reached 35 ppt (14). Because sodium chloride concentrations in seawater are typically less than 30 ppt, this finding suggests that seawater will have minimal effect on copper leaching. However, Plackett (24) measured copper losses from CCA-C-treated sawdust leached in solutions that contained either calcium chloride, calcium nitrate, magnesium nitrate, or a 1:1 mixture of di-potassium hydrogen orthophosphate and potassium di-hydrogen ortho-phosphate. All solutions caused increasing copper leaching with increasing ionic strength, and even at a low concentration (0.06 M), losses were several times those caused by deionized water. Among the solutions tested, the phosphate ions caused the most copper leaching at high concentra-

TABLE 1. — Major ion composition of Instant Ocean synthetic sea salt^a

Ion		Total weight	Ionic concentration at 34 ppt salinity
		(%)	(mg/L)
Chloride	Cl ⁻	47.470	18,740
Sodium	Na ⁺	26.280	10,454
Sulfate	SO ₄ ²⁻	6.602	2,631
Magnesium	Mg ²⁺	3.230	1,256
Calcium	Ca ²⁺	1.013	400
Potassium	K ⁺	1.015	401
Bicarbonate	HCO ₃ ⁻	0.491	194
Boron	B	0.015	6.0
Strontium	Sr ²⁺	0.001	7.5
Solids total		86.11	34,089.50
Water	H ₂ O	13.88	
Total		99.99	

^a Adapted from TAF-REV.-10-23-91. Aquarium Systems, 8141 Tyler Boulevard, Mentor, Ohio.

TABLE 2.—Average CCA-C retention of nonleached samples.

Method of determining retention	Piling specimens		Lumber specimens	
	Low retention	High retention	Low retention	High retention
	----- (kg/m ³) (pcf) -----			
Assay ^a	19.1 (1.19)	41.9 (2.62)	16.0 (1.00)	33.5 (2.09)
Uptake	18.5 (1.16)	34.2 (2.14)	19.2 (1.20)	41.4 (2.59)

^a Assay zone 0 to 15 mm (0 to 0.6 in.) for lumber, 0 to 20 mm (0 to 0.8 in.) for piling.

TABLE 3.—Experimental design.

Specimen types: 2
Lumber: Cut from 12 boards; 4 specimens (each from a different board) placed in each bucket.
Piling: Cut from 3 pilings; 3 specimens (each from a different piling) placed in each bucket.
Target retentions: 2
20 and 40 kg/m ³
Leaching solutions: 3
Deionized water, 23 ppt seawater (40 kg/m ³ retention only), and 34 ppt seawater.
Leaching intervals: 7 (months)
0.03, 0.3, 1, 3, 6, 10, and 15
Replicates: 3
Three replicates (buckets) for each specimen-type-retention-leaching solution combination.

tions, and calcium chloride appeared to have the most effect on low to moderate concentrations. The effects of these inorganic ions on leaching of arsenic and chromium were not evaluated.

The only previously reported comparison of CCA-C leaching in freshwater (distilled) and seawater was performed using a 2-week leaching on 19-mm (3/4-in.) cubes treated to either 16, 19, or 40 kg/m³ (33). Seawater was obtained from the Bay of Mexico; salinity was not reported. The authors reported that total chromium release was 2 to 3 times greater in seawater than in freshwater, and arsenic release was slightly lower in seawater. Copper release was greater in seawater at the 16 kg/m³ retention, equivalent in both solutions at the 19 kg/m³ retention, and greater in distilled water at the 40 kg/m³ retention. No explanation was offered for the conflicting effects of retention and seawater on copper release. A more recent study compared CCA-C leaching of a single sample treated with 49.1 kg/m³ and leached in 26-ppt seawater to that of a single sample treated to 39.6 kg/m³ and leached in 13-ppt seawater (5). Although the lack of replication prevented definitive conclusions, it appeared that copper and arsenic release rates were greater in the 13-ppt seawater, and chromium release was slightly greater at the 26-ppt salinity, after 90 days of leaching.

It is evident that a wide range of release rates have been reported for CCA-C components in seawater. It is also unclear if and how CCA-C leaching differs in seawater and freshwater. This paper describes a study that addresses those concerns.

MATERIALS AND METHODS

PRESERVATIVE TREATMENT

Three de-barked southern pine posts, 1.52 m (5 ft.) in length and 390 to 460 mm (15 to 18 in.) in circumference, and 12 southern pine sapwood boards, 2.44 m (8 ft.) in length by 89 mm (3.5 in.) wide by 38 mm (1.5 in.) thick were equilibrated to approximately 12 percent moisture content in a room maintained at 23°C (74°F) and 65 percent relative humidity. Each post was cut to obtain 20 specimens 7.6 mm (3 in.) in length, for a total of 60 post specimens. Of these, 45 specimens were reserved for leaching trials, and the remaining specimens were used to determine preservative retention after treatment. Each board was cut to obtain 9 clear specimens 102 mm (4 in.) in length, for a total of 108 lumber specimens. Of these, 60 specimens were reserved for leaching trials, and the remaining specimens were used to determine preservative retention after treatment. Prior to treatment, each post and lumber specimen was end-sealed with two coats of a neoprene rubber sealant.

The specimens were pressure treated with CCA-C preservative solution conforming to American Wood Preserver's Association Standard P5-95 (1), using an initial vacuum of -85 kPa (25 in.Hg) for 30 minutes followed by 1 hour of pressure at 1,034 kPa (150 psi). Solution concentrations were adjusted to obtain retention levels of approximately 20 kg/m³ (1.25 pcf) and 40 kg/m³ (2.5 pcf) (Table 2). Specimens with the same target retention were treated in the same charge, but piling and lumber specimens were treated in separate charges. Retention of CCA-C was determined both by amount of uptake (weight gain) and by assaying the specimens reserved for this purpose. Samples for assay retention were removed from both wide faces of each lumber specimen to a depth of 15 mm (0.6 in.) from the wood surface. Samples were collected from a minimum of eight locations from the circumference of each piling specimen, and to a depth of 10 mm (0.8 in.) from the surface. As shown in Table 2, the average assay retention of the selected specimens was slightly greater than the average uptake retention for all piling specimens, and slightly less than the average uptake retention for the lumber specimens. Following treatment, the specimens were stacked under plastic for 1 week at 23°C (74°F), then air-dried for 2 weeks in a room maintained at 23°C (74°F) and 65 percent relative humidity. Following this conditioning, and immediately prior to leaching, the moisture content of both the lumber and piling specimens averaged 27 percent.

EXPERIMENTAL DESIGN

Three leaching solutions, two types of wood products, and two CCA-C retention levels were evaluated (Table 3). Three piling specimens, one cut from each of the original three pilings, were placed in each leaching container. Three replications of each leaching solution and CCA-C retention combination were used. Four lumber specimens, each cut from a different board, were placed in each container. With three replications, this allowed 1 specimen cut from each of the original 12 boards to be included in each leaching solution and CCA-C retention combination. Within each retention group and time period, differences in the mean release rate of copper, chromium, and arsenic in each type of leaching solution at each leaching interval were evaluated statistically as a completely random-

TABLE 4.—Mean rates of elemental copper, chromium, or arsenic release from lumber specimens leached in deionized water or seawater solutions.^a

CCA-C loading	Leaching solution	Leaching rate after the following months of leaching						
		0.03	0.3	1	3	6	10	15
		----- (µg/cm ² /day) -----						
Copper								
Low	Deionized	4.62 A	1.45 A	0.45 A	0.11 B	0.01 B	0.01 B	0.01 B
Low	Sea, 34 ppt	4.19 A	0.78 B	0.47 A	0.22 A	0.18 A	0.17 A	0.25 A
High	Deionized	3.52 A	1.22 A	0.43 A	0.08 C	0.05 C	0.03 C	0.02 C
High	Sea, 23 ppt	2.51 B	0.71 B	0.56 A	0.26 A	0.23 A	0.24 A	0.30 A
High	Sea, 34 ppt	2.66 B	0.65 B	0.44 A	0.18 B	0.14 B	0.16 B	0.21 B
Chromium								
Low	Deionized	1.10 A	0.22 A	0.07 A	0.02 A	0.004 A	0.003 A	0.004 A
Low	Sea, 34 ppt	0.74 A	0.29 A	0.21 A	0.01 B	0.002 B	0.004 A	0.003 A
High	Deionized	1.10 A	0.20 A	0.05 A	0.011 A	0.005 A	0.003 A	0.014 A
High	Sea, 23 ppt	0.61 B	0.05 B	0.01 B	0.007 B	0.005 A	0.003 A	0.004 A
High	Sea, 34 ppt	0.69 B	0.05 B	0.01 B	0.004 C	0.002 A	0.002 A	0.002 A
Arsenic								
Low	Deionized	0.94 A	0.34 A	0.21 A	0.16A	0.05 A	0.03 A	0.03 A
Low	Sea, 34 ppt	0.68 A	0.18A	0.11 A	0.03 B	0.01 B	0.01 A	0.01 A
High	Deionized	0.98 A	0.39 A	0.21 A	0.14A	0.05 A	0.04 A	0.08 A
High	Sea, 23 ppt	0.53 B	0.16 B	0.09 B	0.03 B	0.01 B	0.01 B	0.01 B
High	Sea, 34 ppt	0.60 B	0.13 B	0.10 B	0.03 B	0.02 B	0.01 B	0.01 B

^a Means within the same leaching time and CCA-C loading groups were compared statistically to determine if the type of solution had an effect on leaching. These means are significantly different ($\alpha = 0.05$ Fisher's LSD method) if they are not marked with the same letter.

TABLE 5.— Mean rates of elemental copper, chromium, or arsenic release from piling specimens leached in deionized water or seawater solutions.^a

CCA-C loading	Leaching solution	Leaching rate after the following months of leaching						
		0.03	0.3	1	3	6	10	15
		----- (µg/cm ² /day) -----						
Copper								
Low	Deionized	8.04 A	2.46 A	0.80 B	0.11 B	0.02 B	0.01 B	0.03 B
Low	Sea, 34 ppt	8.55 A	2.59 A	1.55 A	0.83 A	0.42 A	0.31 A	0.37 A
High	Deionized	9.15 A	3.58 A	0.90 C	0.17 B	0.04 C	0.02 C	0.04 B
High	Sea, 23 ppt	6.54 B	3.10 A	2.42 A	1.41 A	1.02 A	0.77 A	0.85 A
High	Sea, 34 ppt	6.24 B	2.10 B	1.56 B	0.90 A	0.64 B	0.52 B	0.69 A
Chromium								
Low	Deionized	1.27 A	0.29 A	0.10 A	0.03 A	0.010A	0.006 A	0.008 A
Low	Sea, 34 ppt	0.88 B	0.07 B	0.03 B	0.01 B	0.004 B	0.004 B	0.003 B
High	Deionized	1.47 A	0.30 A	0.08 A	0.03 A	0.008 B	0.004 A	0.006 A
High	Sea, 23 ppt	0.77 C	0.09 B	0.04 B	0.02 B	0.010 A	0.006 A	0.007 A
High	Sea, 34 ppt	1.00 B	0.06 B	0.03 B	0.01 B	0.004 B	0.004 A	0.005 A
Arsenic								
Low	Deionized	4.12 A	0.88 A	0.40 A	0.27 A	0.09 A	0.06 A	0.11 A
Low	Sea, 34 ppt	1.91 B	0.39 B	0.18 B	0.04 B	0.02 B	0.02 A	0.02 B
High	Deionized	6.95 A	1.08 A	0.62 A	0.46 A	0.17A	0.09 A	0.18 A
High	Sea, 23 ppt	4.59 B	1.10 A	0.63 A	0.18 B	0.11 A	0.08 A	0.08 B
High	Sea, 34 ppt	3.14 B	0.87 A	0.39 A	0.15 B	0.06 A	0.05 A	0.07 B

^a Means within the same leaching time and CCA-C loading groups were compared statistically to determine if the type of solution had an effect on leaching. These means are significantly different ($\alpha = 0.05$ Fisher's LSD method) if they are not marked with the same letter.

ized experimental design (piling) or as a randomized block design (lumber).

LEACHING CONDITIONS

Specimens were leached in solutions of deionized water or seawater adjusted to salinities of 23 or 34 ppt. The 34-ppt dilution was chosen to represent “full

strength” seawater, as might be found in the open ocean. The 23-ppt dilution represented brackish water, such as in an estuary. The seawater solutions were prepared from Instant Ocean, a commercial synthetic sea salt that contains the major ions typically found in seawater (Table 1) (6).

The specimens were placed in 7.6-L (2-gal.) polyethylene containers with polyethylene spacers placed on top of the specimens to force them to remain submerged when the lids to the containers were closed. Sufficient leaching solution (approximately 2,800 g for piling and 2,100 g for lumber) was weighed into

each container to cover the specimens during agitation. The lids were loosely fitting with the intention of allowing air exchange while retarding evaporation. Slight evaporation (< 2.5% of solution, measured by container weight loss) occurred during the longer leaching periods, and measurements of CCA-C release were adjusted accordingly. Fresh water was not added, because salinity increases as a result of evaporation were less than 1 ppt.

The filled containers were placed on a suspended platform and slowly rocked by raising and lowering one end of the platform. The specimens were agitated in this manner for 12 hours per day, using alternating 3-hour on/off cycles. The leaching solution was drained, collected,

and replaced with fresh solution after 1 day, 10 days, 1 month, 3 months, 6 months, 10 months, and 15 months.

ANALYTICAL METHODS

Copper, arsenic, and chromium concentrations in the treated wood and leaching solutions were determined with a Perkin Elmer 5100PC Atomic Absorption Spectrometer (ASS) equipped with a Zeeman Furnace Module. Leaching solutions were analyzed by either graphite furnace or flame atomization, as appropriate. Wood samples were digested in a mixture of hydrogen peroxide and nitric acid using a CEM MD6-2000 Microwave Digester (AWPA Method A7-93). Copper, chromium, and arsenic concentrations in the resulting solution were then determined by flame atomization.

RESULTS AND DISCUSSION

EFFECT OF SALINITY, RETENTION, AND DIMENSION ON RELEASE RATE

Copper. -The effect of salinity on the rate of copper release changed over time. For the first month, leaching of copper in deionized water was greater than or equal to the rate of release in either seawater solution (Fig. 1). However, during the remaining months, copper release in the seawater solutions was significantly greater than the release in deionized water (Tables 4 and 5). When leaching rates stabilized, after 10 to 15 months, the rate of copper release in seawater was 8 to 25 times greater than that in deionized water. This trend was apparent for both CCA-C retention levels and for both lumber and piling. The lower initial copper release in the seawater solutions may have reflected the time required for seawater components to diffuse into the wood. The lumber and piling samples were not vacuum or pressure impregnated with leaching solution, as is often done in accelerated leaching trials.

The trend of equivalent or greater initial release of copper in deionized water followed by much greater long-term release in seawater may also be a function of the different forms of copper fixation products in the wood. During the initial stage of leaching, when the release of copper was high in all solutions, a variety of forms of copper are being removed from the wood. These might include copper bound to water-soluble extractives, copper adsorbed to particulate matter, and copper precipitated within the wood structure. Any suspended particulate or colloidal forms of copper are likely to be at least as mobile or more mobile in deionized water than in seawater. Calcium in seawater has been noted to coagulate and precipitate about 40 percent of suspended riverborne copper flowing into seawater, potentially reducing copper levels in the water column (27). As leaching continues, the contribution of such colloids to the overall copper release probably declines, because these components would be relatively mobile and more readily leached than other types of copper fixation products. Over the long term, leaching of more conventionally fixed copper, such as that fixed by ion-exchange reactions with the wood, would become a greater proportion of the copper release. Several authors have noted the importance of ion-exchange reactions as a mechanism

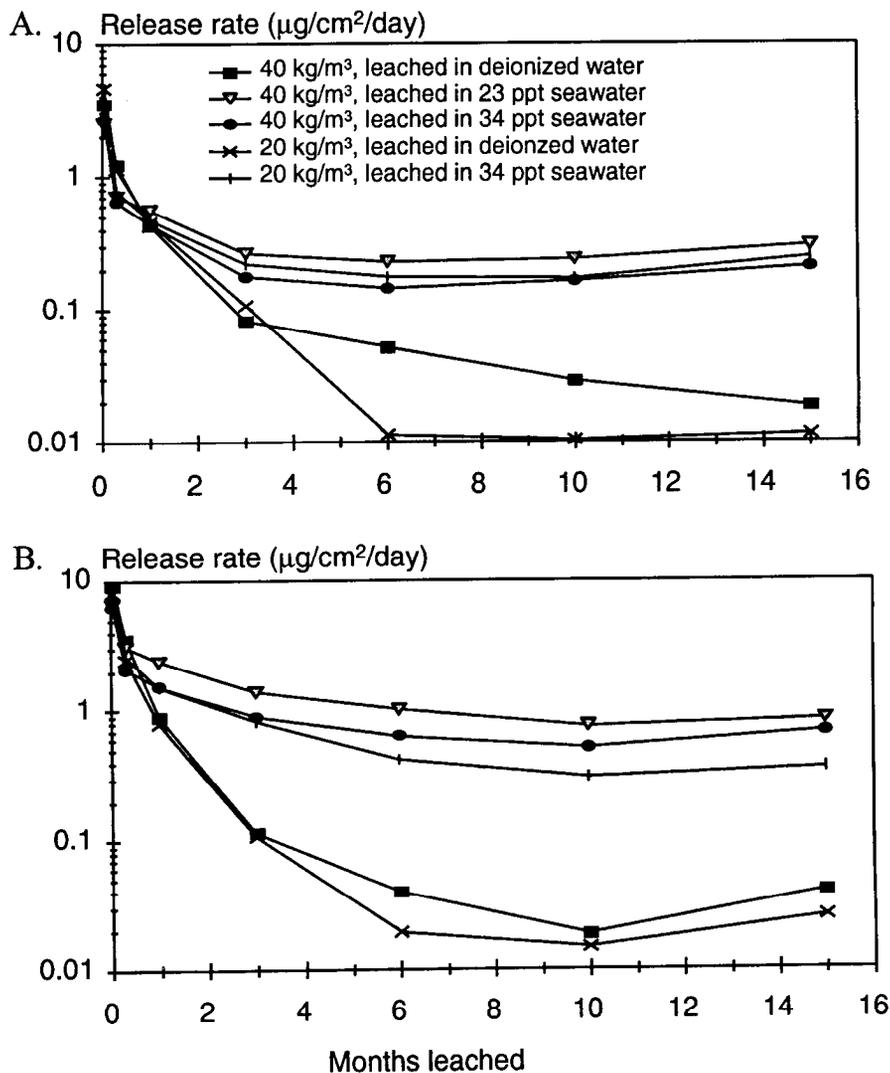


Figure — 1. Rate of copper release from CCA-treated lumber (A) and piling (B) sections during immersion in seawater or deionized water.

for copper fixation in CCA-treated wood (7,10,12,25). It is known that seawater cations such as Ca^{2+} and Mg^{2+} compete with metals for ion-exchange sites on organic matter (27). Although copper may form stronger complexes with organics than does Ca^{2+} or Mg^{2+} , the high concentration of these ions in seawater can decrease copper complexation with organic ligands (4). Thus, the displacement of ion-exchange fixed copper by seawater cations may at least partially explain the higher long-term release rate in the seawater solutions. The rate of copper release appeared somewhat greater for the 23-ppt seawater solution than the 34-ppt seawater solution. This difference was statistically significant ($\alpha = 0.05$) after 3, 6, 10, and 15 months for the lumber specimens (Table 4) and after 1, 6, and 10 months for the piling (Table 5).

CCA-C retention also had a slight effect on the rate of copper release from the samples. For the first 3 months, release of copper from the samples treated to 20 kg/m^3 was equivalent to that released from the piling and lumber treated to 40 kg/m^3 . The high rate of release of leachable forms of copper during the early stages of the trial may have masked any retention differences, because as the test continued, release from the 20- kg/m^3 specimens began to decrease below that

of the higher retention level. This trend was apparent for both seawater and deionized water leaching solutions and for both piling and lumber. One exception was the 34-ppt seawater leaching of copper from the lumber specimens. In this group, release of copper was similar for both retention levels throughout the study.

The rate of copper release, per unit surface area, was generally greater for piling than lumber. This result might be expected, because although the lumber and piling were treated with equivalent amounts of CCA-C per unit volume, the piling samples had approximately twice as much preservative per unit surface area. In addition, the true piling surface area was probably underestimated by simply measuring circumference and calculating the surface area, because these round specimens developed small checks during pre-treatment drying. Others have also noted that the amount of CCA-C released, per unit surface area, tends to be greater from round-stock than dimension lumber (29).

Chromium. — In comparison to copper, chromium release rates were much lower and relatively insensitive to the seawater concentration of the leaching solutions. For both the lumber and piling, leaching was initially slightly (although

not always significantly) greater in deionized water than either seawater solution. The relatively low initial release rate in seawater may have been caused by precipitation of chromium in colloidal form, as was discussed for copper. Others have noted that chromium is likely to form complexes with polyflavanoid tannin extractives (23,26), and these complexes may have been precipitated by seawater metals but remained soluble in the deionized water leachate. However, unlike the copper release, little consistent difference in chromium release between the leaching solutions emerged during the later stages of leaching. In the one trend that did emerge, for the piling treated to the lower retention, the rate of leaching was consistently greater in deionized water than in seawater. It appears that the bulk of chromium fixation products, which have been theorized to include chromium complexed with various wood components as well as CrAsO_4 , and $\text{Cr}(\text{OH})_3$ (9,10,20-22), are not susceptible to mobilization by seawater components.

CCA-C retention (20 kg/m^3 or 40 kg/m^3) had little consistent effect on the rate of chromium release from either lumber or piling, regardless of the seawater concentration of the leaching solution. The rate of chromium release from the 20 kg/m^3 retention lumber leached in

TABLE 6. — Comparison of release rates found in our study with those reported in other studies.

	Baldwin et al. 1996 (3)			Our study		
	Piling treated to 40 kg/m^3			Piling treated to 40 kg/m^3		
	Total release, 28 days in 31 ppt seawater			Total release, 30 days in 34 ppt seawater		
	($\mu\text{g/cm}^2$)			($\mu\text{g/cm}^2$)		
Copper	53.0			53.3		
Chromium	not elevated			2.0		
Arsenic	5.6			1.9		
	Merkle et al. 1993 (19)			Our study		
	Lumber treated to 4.8 kg/m^3			Lumber treated to 20 kg/m^3		
	Release rate, 11 days in 40 ppt seawater			Release rate, 10 days in 34 ppt seawater		
	($\mu\text{g/cm}^2/\text{day}$)			($\mu\text{g/cm}^2/\text{day}$)		
Copper	1.3			0.8		
Chromium	0.014			0.3		
Arsenic	1.0			0.2		
	Breslin and Adler-Ivanbrook 1998 (5)				Our study	
	Lumber treated to 34 to 49 kg/m^3				Lumber treated to 40 kg/m^3	
	Release rate in 26 ppt seawater				Release rate in 34 ppt seawater	
	($\mu\text{g/cm}^2/\text{day}$) (max. to min.)				($\mu\text{g/cm}^2/\text{day}$) (max. to min.)	
	12 hours	35 days	90 days	24 hours	30 days	90 days
Copper	5.7 to 16.5	0.7 to 1.3	0.17 to 0.95	2.6 to 2.8	0.42 to 0.47	0.14 to 0.21
Chromium	0.31 to 0.37	0.04 to 0.10	0.007 to 0.032	0.62 to 0.57	0.007 to 0.01	0.003 to 0.005
Arsenic	0.13 to 1.65	0.075 to 0.20	0.045 to 0.14	0.57 to 0.61	0.09 to 0.11	0.024 to 0.031

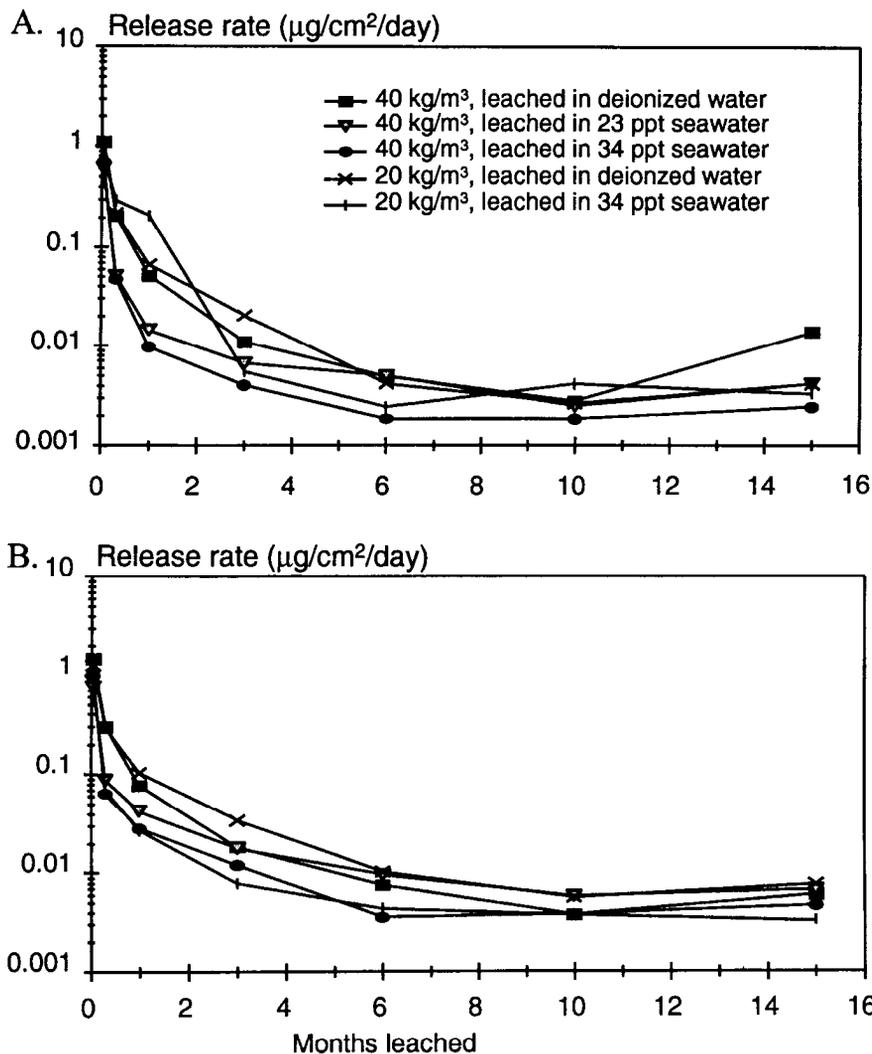


Figure 2. — Rate of chromium release from CCA-treated lumber (A) and piling (B) sections during immersion in seawater or deionized water.

34-ppt seawater was well above that of the 40 kg/m^3 retention leached in 34-ppt seawater after 1 month, but this appears to be an anomaly. Past studies have reported both increased and decreased chromium leaching rates with increasing retention (15,18,33). The rate of chromium release from both retention levels was quite low compared with copper and arsenic, especially over the long term.

The rate of chromium release from the lumber specimens tended to be slightly lower than for the piling, although this trend was not nearly so evident for chromium as for copper and arsenic. Again, this effect may be a result of the greater retention-to-surface area ratio for the piling.

Artenic. — Arsenic release tended to be greater in the deionized water than either seawater solution, although this trend was not as apparent for piling treated to the 40 kg/m^3 retention. For lumber treated to the 40 kg/m^3 retention, the release of arsenic was significantly greater in deionized water than either seawater solution at every sampling time (Table 4). Unlike chromium, the greater release in deionized water did not appear to decrease over time. It appears that the seawater may help to immobilize arsenic fixation products. It is possible that the lower pH of the deionized water (6.2 to 6.8 for deionized water compared to 7.8 to 8.2 for the seawater solutions) increased leaching, although other studies have reported that pH does not signifi-

cantly affect leaching of CCA-C components until the leaching solution decreases to about pH 4 (8). It has also been reported that the presence of metal cations (such as Na^+ , Mg^{2+} , K^+ and Ca^{2+} in seawater) could result in the immobilization of soluble arsenic through the precipitation of metal arsenates (4).

The effect of retention on the rate of arsenic release differed for piling and lumber. Arsenic release from piling was consistently less at the lower retention (20 kg/m^3) in both freshwater and seawater. However, this trend was not evident in the lumber sections, where retention had little consistent effect on arsenic release. Release of arsenic was much greater from the piling than from the lumber at both retention levels. Although this difference in leaching between piling and lumber was noted to some extent for copper and chromium, the effect was quite marked for arsenic. Only the rate of arsenic leaching from the 20 kg/m^3 retention in 34-ppt seawater was similar for lumber and piling.

EFFECT OF USING A CLOSED-SYSTEM LEACHING APPARATUS

The release and movement of copper, chromium, and arsenic from CCA-C-treated wood into a leaching medium is complex, but is dependent on factors such as chemical reaction rates, solubility, particle size, and diffusion of the leaching solution into and out of the porous structure of the wood. It is also reasonable to expect that the concentration of released components in the leaching solution within the wood is much greater than that in the surrounding environment, and that this gradient drives the outward diffusion of released components. Like many previous leaching studies (3,5,19), this study employed a closed-system leaching apparatus to allow accurate measurement of the volume of leaching solution contacting the wood and subsequent calculation of the concentration of leached chemical elements. However, with this type of system, leached CCA-C components accumulate in the leaching solution. Such accumulation flattens the gradient between copper, chromium, and arsenic concentrations in the solution within the wood and the solution in the container, and could potentially retard further diffusion of CCA-C components from the wood. The effect of accumulation of the chemical elements of CCA-C in the leachate is likely to be negligible in latter stages of the test, but would be

greatest during the initial stages of leaching, when the rate of release is greatest. Some release may then be delayed until the leaching solution is replaced, and a sharper gradient is again established between the inside and the outside of the wood. The likely effect of this phenomenon would be to slow the apparent rate of the initial release and possibly to obscure initial differences in release caused by differences in the leaching solutions (as was noted for copper). These concerns were the reason for more frequent changes of the leaching solution during the initial stages of the study.

ESTIMATION OF IN-SERVICE RELEASE

It is difficult to predict or assess the potential environmental impacts of marine construction projects using CCA-C-treated wood without data that can be used to estimate the release of preservative components from the wood. One objective of this study was to provide these data. Comparisons with past studies are difficult because of differences in CCA-C retention levels, specimen dimensions, and exposure periods. Previous authors have reported on release rates from piling for up to 28 days (3), from lumber for up to 21 days (19), or from lumber for up to 90 days (5) (Table 6). As shown in Table 6, the release rates for piling reported in our study agree closely with those noted by Baldwin et al. (3) after 28 days. Release rates for lumber reported by Merkle et al. (19) after 11 days and Breslin and Adler-Ivanbrook (5) are slightly greater than those found in our study. Release rates noted by Merkle et al. (19) appear high for arsenic, considering the low retention levels of the samples used in that study. Lower CCA retention levels have been reported to increase the proportion of leachable arsenic, possibly because a lower proportion of chromium is available to react with the arsenic (2,33). In general, the release rates detected in our study fall within the range of results presented in previous studies, especially when one considers that these previous studies were sampled only during the initial stages of leaching, when the release rate rapidly decreases. From our study, it appears that a longer exposure, at least 6 to 10 months, is needed to determine the more stable, long-term release rate for lumber and piling treated to high marine retention levels. Because the initial release rate data generated in our

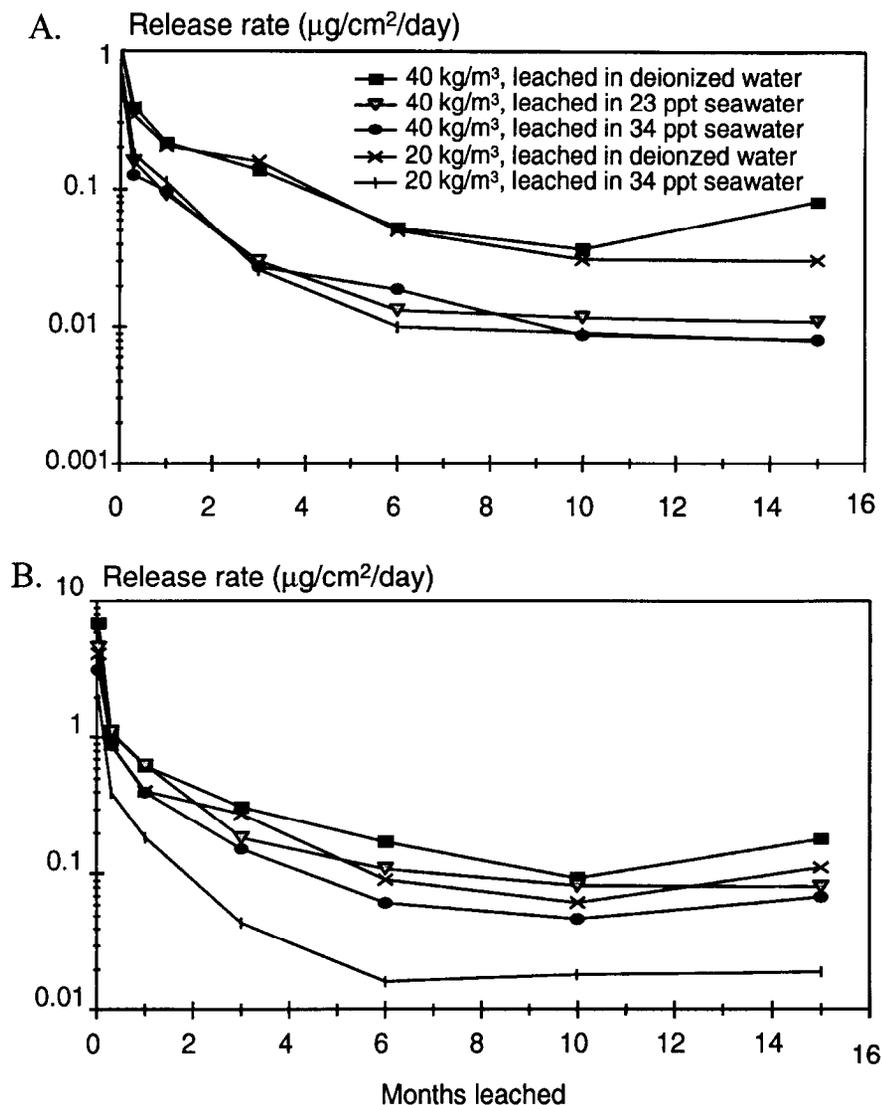


Figure 3. — Rate of arsenic release from CCA-treated lumber (A) and piling (B) sections during immersion in seawater or deionized water.

study agree closely with that of Baldwin et al. (3), and because our study was conducted for a longer duration than previous studies, it appears reasonable to use these data to estimate long-term release of CCA-C components in service.

The rate of release of CCA-C components from the wood can be divided into two zones. During the first 6 months, a rapid release of the most easily mobilized fixation products occurs. Following this initial rapid release, the leach rate plateaus at a much lower level, which reflects the much lower solubility or mobility of the remaining fixation products (Figs. 1 through 3). This lower level release rate can be used to estimate long-term leaching, but the contribution of the

initial rapid release zone to overall leaching cannot be completely ignored. One way to overcome this problem is to calculate long-term release based on the lower release rate at 10 to 15 months, then add in the cumulative leaching contribution for the first 6 months. This model can be expressed as:

$$y = B_{LT} \Delta t_m + B_I$$

where:

$$y = \text{amount released } (\mu\text{g}/\text{cm}^2) \text{ after a time } m \text{ (in months)}$$

$$B_I = \sum B_i \Delta t_i = \text{initial release}$$

$$B_i = \text{release rate over a given time interval } (\mu\text{g}/\text{cm}^2)$$

$$\Delta t_i = \text{time interval (months)}$$

B_{LT} = long-term release rate (10 and 15 month rates in our study)
 Δt_m = total time interval of estimate (months), minus initial release time (6 months)

$\hat{\sigma}_L^2$ = variance in long-term release rate (Table 8)
 $\hat{\sigma}_{IL}$ = covariance, initial, and long-term release rates (Table 8)
 m = number of months in service
 $\hat{\sigma}_e^2$ = variance of bucket from its rate trend

Assuming a random regression coefficient model, the parameters B_{LT} and B_I were estimated and are shown in Table 7.

The estimate of variability, or standard deviation, of long-term release, based on data generated in our study, can be calculated as:

Standard deviation for any period of m months =

$$[\hat{\sigma}_I^2 + (m - 6)^2 \hat{\sigma}_L^2 + 2(m - 6) \hat{\sigma}_{IL} + \hat{\sigma}_e^2]^{1/2}$$

where:

$\hat{\sigma}_I^2$ = variance in initial release during first 6 months (Table 8)

Using the model just described, the estimated 10-year release of copper, chromium, and arsenic was calculated (Table 7). Several trends are notable when the release of CCA-C components is viewed over a longer time, such as 10 years. First, the increased leaching of copper in seawater becomes more dramatic because of the greater long-term release rate. The slower release of arsenic in seawater is also more apparent, as is the greater release of copper and arsenic from piling than from lumber. Even after 10 years, estimated chromium release is

quite low and appears largely unaffected by the salinity of the leaching solution. It is also apparent that the first 6 months of release can make a large contribution to the long-term total release. In some cases, such as copper leaching in deionized water, the release that occurs during the first 6 months would account for approximately 40 percent of the 10-year total. In contrast, release of copper during the first 6 months in seawater would account for only a small percent of the 10-year total. As shown in Table 8, much of the error in estimating long-term release is also associated with the first 6 months of leaching when release rates are rapidly decreasing. Variability in release during initial stages is likely to be even greater for commercial charges, which will have differences in retention, surface cleanliness, and post-treatment conditioning.

TABLE 7. — Release of CCA components in the first 6 months, long-term release rate, and estimated release after 10 years in service.^a

CCA level	Leaching solution	Release in first 6 months			Long-term release rate			Estimated release after 10 years			Estimated depletion after 10 years		
		B_I			B_{LT}			$B_{LT} \Delta t_m + B_I$					
		Cu	Cr	As	Cu	Cr	As	Cu	Cr	As	Cu	Cr	As
Lumber													
		(μg/cm ²)			(μg/cm ² /month)			(μg/cm ²)			(%)		
Low	Deionized	31	6	22	0.3	0.1	0.9	69 (7)	18 (1)	127 (35)	3	< 1	3
Low	Sea, 34 ppt	48	8	7	6.4	0.1	0.3	777 (30)	21 (8)	36 (9)	27	< 1	1
High	Deionized	33	5	21	0.7	0.3	1.9	111 (58)	36 (38)	234 (24)	2	< 1	2.5
High	Sea, 23 ppt	55	2	7	8.2	0.1	0.3	994 (114)	14 (2)	45 (4)	16	< 1	< 1
High	Sea, 34/00	40	2	7	5.6	0.1	0.3	684 (106)	9 (2)	36 (4)	11	< 1	< 1
Piling													
Low	Deionized	54	9	44	0.6	0.2	2.7	126 (17)	33 (4)	350 (59)	2	< 1	4
Low	Sea, 34 ppt	149	3	13	10.3	0.1	0.6	1322 (216)	15 (0)	77 (19)	21	< 1	1
High	Deionized	73	8	78	0.9	0.2	4.1	176 (- -)	25 (- -)	524 (- -)	2	< 1	3
High	Sea, 23 ppt	258	4	48	24.4	0.2	2.4	3043 (296)	26 (4)	325 (10)	26	< 1	2
High	Sea, 34 ppt	164	3	33	18.6	0.1	1.8	2284 (336)	18 (1)	235 (48)	21	< 1	1

^a Numbers in parentheses represent one standard deviation from the mean.

TABLE 8. — Variance of initial, long-term, and overall release rates.

CCA level	Leaching solution	Variance of initial (6 month) release ($\hat{\sigma}_I^2$)			Variance of long-term release ($\hat{\sigma}_L^2$)			Covariance, initial, and long-term release ($\hat{\sigma}_{IL}$)			Variance of bucket from its rate trend ($\hat{\sigma}_e^2$)		
		Cu	Cr	As	Cu	Cr	As	Cu	Cr	As	Cu	Cr	As
Lumber													
		(μg/cm ²) ²			(μg/cm ²) ²			(μg/cm ²) ²			(μg/cm ²) ²		
Low	Deionized	7.5	0.1	1.0	0.003	0.000	0.095	0.008	0.001	0.045	0.007	0.005	0.048
Low	Sea, 34 ppt	20.0	117.6	6.5	0.000	0.001	0.005	3.703	-0.338	0.044	14.912	0.013	0.015
High	Deionized	6.7	0.0	31.3	0.252	0.113	0.086	0.157	-0.153	-2.579	0.603	0.976	10.718
High	Sea, 23 ppt	79.4	0.2	0.4	0.796	0.000	0.002	11.108	0.002	-0.010	11.939	0.009	0.004
High	Sea, 34/00	16.1	0.1	0.2	0.785	0.000	0.001	4.779	0.003	0.015	5.749	0.002	0.013
Piling													
Low	Deionized	25.1	2.2	20.3	0.014	0.001	0.207	0.410	0.042	3.468	0.417	0.014	7.965
Low	Sea, 34 ppt	476.3	0.3	3.7	2.956	0.000	0.022	33.216	-0.004	0.305	8.371	0.002	0.062
High	Deionized	--	--	--	--	--	--	--	--	--	--	--	--
High	Sea, 23 ppt	607.8	0.4	8.0	5.944	0.001	0.004	41.707	0.019	0.143	27.923	0.005	0.068
High	Sea, 34 ppt	305.6	0.2	147.9	7.482	0.000	0.089	65.280	0.003	4.498	112.194	0.004	2.561

Note that after 10 years only a very small percentage of the chromium and arsenic is estimated to be depleted from the wood (Table 7). Depletion of copper in seawater would be greater, ranging from 11 to 26 percent. This suggests that the long-term release rate of copper will begin to decline due to loss of copper from the wood, and that the long-term release rate used for copper in Table 7 will result in overestimates of copper release over very long exposures.

CONCLUSIONS

Seawater has a mixed effect on leaching of CCA-C components. The most dramatic effect is the much higher steady-state release rate of copper in seawater than in deionized water. In contrast, the steady-state release rate of arsenic was somewhat greater in deionized water than in seawater. The rate of chromium release was consistently much lower than that of copper and arsenic and did not appear to be affected by the salinity. Release rates of copper and arsenic were somewhat lower from wood treated to 20 kg/m³ than from wood treated to 40 kg/m³, but retention had little effect on the rate of chromium release. Release rates, per unit surface area, were consistently greater from piling than from lumber, especially for arsenic. Long-term release of CCA-C components can be estimated from steady-state release rates that occur after 6 to 10 months of leaching. In some cases, however, the amount of leaching that occurs in the first 6 months represents a large fraction of long-term leaching, and an estimate of release during this early period must be included.

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