



Migration of Preservatives from Pressure-Treated Wood

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This chapter describes the potential pathways for the movement of preservatives from wood into surrounding environments and some of the factors, such as water temperature, pH, salinity, and preservative retention, affecting these losses. Methods for assessing the migration of wood preservatives to surface waters and rainwater runoff will be described and compared. The chapter ends with a discussion of preservative loss rates measured in immersion and rainwater runoff studies. Definitions of the terms used in this chapter are provided at the end.

7.1 PROTOCOLS FOR MEASURING PRESERVATIVE COMPONENT LOSS FROM COMMODITIES IMMersed IN AQUATIC ENVIRONMENTS

7.1.1 What should be measured?

In general, and in particular for marine piling, it is only the outside shell of the wood that is initially preserved. The dynamic state of preservatives within the wood cells results in continued migration of the mobile components of the preservative in all directions within the wood. This results in a redistribution of the preservative within the wood's interior, as well as migration to the outside environment. The initially high concentrations of preservative in the outer layers of wood thus decline as active ingredients migrate to other locations within and outside of the wood. This means that any determination of preservative loss rates based on retention assays at some depth beneath the wood's surface is flawed because this method overestimates the losses of preservative to the environment. Additionally, the high natural variation in preservative distribution in wood renders this approach inaccurate. Meaningful assessments of environmental losses to surface

or rainwater can only be achieved by measuring the concentrations of active ingredients in the receiving media.

Furthermore, the composition of complex mixtures, such as creosote, changes during the treating process; it is not appropriate to assess environmental response based on the neat product. Creosote is a byproduct of the coking of coal and it contains hundreds of compounds.

Polycyclic aromatic hydrocarbons (PAH) are the compounds generally considered to be of concern in the environment; creosote contains a broad suite of these, ranging in molecular weight from naphthalene to benzo[g,h,i]perylene. The two-ring, low molecular weight compounds have higher water solubility and volatility than do the intermediate- and high-molecular-weight compounds. Goyette and Brooks (1998) determined the PAH composition in raw creosote oil, in piling treated according to WWPI/CITW (1996) Best Management Practices (BMP), in surface sheens found during construction, and in sediments over a period of 535 d following construction. Naphthalene, the most soluble of the PAH, comprised 24% of the raw oil, but only 10% of the PAH in expressate from the BMP piling. The remaining 14% of the naphthalene was lost during the treating process, which involved final steaming of the wood at high temperature under vacuum. The higher molecular weight compounds are hydrophobic and they comprise the bulk of the PAH found in the treated wood. This was emphasized in the report of Kang et al. (2005) who did not detect high molecular weight compounds down current from creosote-treated lumber in their dynamic immersion studies. It is the suite of PAH (in the case of creosote) remaining in the wood after treatment that must be evaluated to understand environmental responses to the product.

7.1.2 The nature of wood

Wood has a complex structure that depends, in part, on the wood species and the environment where a tree grew.

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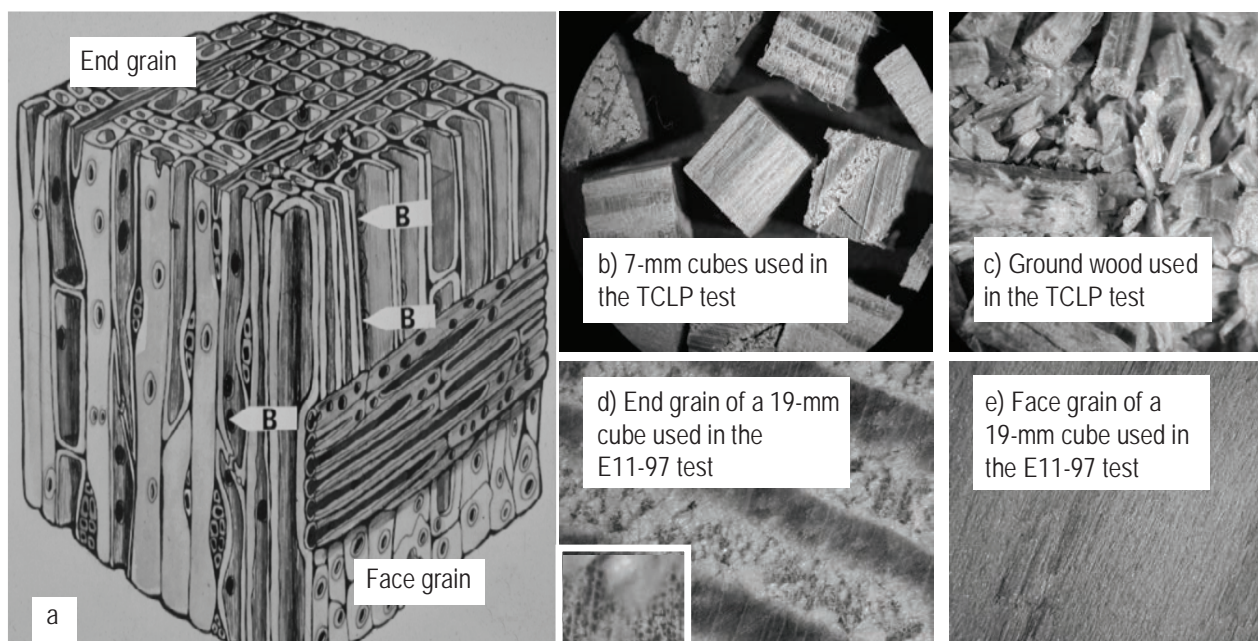


Figure 7.1 (a) The structure of wood, provided by Dr. Jeff Morrell, Oregon State University. Photomicrographs of (b) the 7-mm cubes and (c) ground wood used in the TCLP tests; (d) the end grain of 19-mm CCA-C treated cubes of wood samples used to estimate copper loss rates using AWWA E11-97, and (e) face grain of the 19-mm cubes.

The typical structure of softwood is shown in Figure 7.1a. Cell lumens are relatively open across the end grain and wood is consequently much more permeable along the grain. It is less permeable in the radial and tangential directions where transport is restricted by movement through the wood pitting structure. This structure is important to the transport of water and nutrients between the tree's root system and its foliage, where most of the photosynthesis takes place. The cellular structure is also important for penetration of wood preservatives, which are forced radially, tangentially, and longitudinally into the wood under pressure during the treating process.

The three-dimensional cellular structure of wood and its integrity are important considerations when defining protocols for assessing preservative losses. The cell lumens contain the preservative while fixation occurs and contain preservatives that do not chemically bind to the wood, such as creosote. For unsealed samples, the ratio of the area of end-grain to flat grain will affect preservative loss rates. Wood used in construction normally has high face-grain to end-grain ratios. For instance, a 5-m long 3.8 × 8.9-cm board has a face-grain to end-grain ratio of 188:1. In contrast, cubes such as those used in the American Wood Protection Association (AWPA) E11-97 protocol, have a face-grain to end-grain ratio of 2:1 with relatively large areas of open cell lumens exposed to the environment. This is recognized in some leaching tests (for example

the proposed OECD leaching protocols), which specify that sample end-grain be sealed with paraffin or epoxy resin, leaving only the face grain exposed to the leaching water. Protocols, such as AWWA E11-97, which were developed for efficacy testing rather than for determining environmental losses of preservative, do not require sealing of end-grains, which may unrealistically exacerbate preservative loss rates. Inevitably, sample preparation for the EPA Method 1311-Toxicity Characteristic Leaching Procedure (TCLP) and the EPA Method 1312-Synthetic Precipitation Leaching Procedure (SPLP) tests not only exposes the end grain, but grinding also shatters the cell walls randomly, as seen in Figure 7.1c (EPA 1992; 1994).

The porosity of the wood and degree of closure or aspiration of the pits affect both the treatability of wood and the retention of the preservative. Sapwood of southern pine (*Pinus* spp.) is more easily treated than heartwood of the same species, whereas Douglas-fir (*Pseudotsuga menziesii*), spruce (*Picea*) species, and many hardwoods, are difficult to treat. These difficult-to-treat species can be incised to facilitate penetration of the preservative. Ammoniacal copper zinc arsenate (ACZA) was developed specifically to treat the refractory western softwoods, Douglas-fir and western hemlock (*Tsuga heterophylla*).

Not only does treatability vary by species of tree, it also varies with the region in which the tree grows. For these reasons, the American Wood Protection Association

Standard penetration and retention requirements (AWPA 2009) vary by species, preservative, and, in some cases, by region where the wood was grown. It is not the intention of this chapter to review these issues in depth, but rather to point out that preservative loss rates from pressure-treated wood vary with treatability of tree species and location where the trees are grown. Generally, pressure-treated wood products made from more difficult-to-treat species have been found to have higher preservative loss rates than do products from easily treated species, such as southern pine, because the preservative is concentrated near the surfaces (e.g., Taylor and Cooper 2003).

Some preservatives are simply retained as coatings on the wood's cellular structure. Other preservatives, such as CCA-C, form relatively insoluble complexes within the wood structure, reducing the loss of preservative to the environment. However, the state and solubility of ACZA or CCA metal complexes within the wood is most likely dynamic—not static. The bonds that “fix” the metal complexes in the wood are constantly being broken and re-established. The frequency of these actions is undoubtedly related to the temperature of the wood (kinetic energy of the metal complexes) and other factors such as pH, ionic strength, and the presence of any chelators in intracellular water. The important point is that it is the wood's cell structure that contains the ions while they are seeking new sites to bind to. Sample preparations that fracture cell walls will likely lead to high preservative loss rates that would not occur in actual use.

7.1.3 Specimen size

Published CCA-C leaching studies by Cooper (1990, 1991), Kim and Kim (1993), Stanley (1994a, 1994b), Breslin and Adler-Ivanbrooks (1998), Van Eetvelde et al. (1995), Lebow et al. (1999), Brooks (2003) and Dubey et al. (2005) have examined a variety of sample sizes ranging from finely ground wood evaluated using TCLP (EPA 1992) and SPLP (EPA 1994), a variety of small blocks of varying sizes, such as the 19 mm cubes specified in AWPA E11-97, and commodity-size samples examined in surface waters. These studies have reported initial copper loss rates from CCA-C treated wood varying between 2.17 and 7.62 $\mu\text{g Cu}/\text{cm}^2\text{-day}$. The variability in these results is not surprising because of differences in diluent pH and because the cellular integrity of the wood was more or less compromised depending on the protocol used. Wood is a natural product with inherent variability between species, between trees within a species, and within individual boards. For instance,

Breslin and Adler-Ivanbrook (1998) cut $1.3 \times 1.3 \times 1.9$ cm samples from the outer 1.3 cm of single southern pine boards treated to a nominal retention of 34.2 kg CCA-C/ m^3 [2.13 pounds per cubic foot (pcf)]. Random samples of the small blocks were analyzed for preservative retention, which varied between 4.5 and 64 kg/m^3 (0.3 to 4.0 pcf). There was correspondingly high variability in the migration of metals from nine replicate samples. This variability requires that either large numbers of small samples be analyzed, or that large samples, which average the small-scale variability associated with the wood's structure, be used.

In addition, round piles, poles, and posts are commonly used pressure-treated wood commodities. It is difficult to mimic the loss of preservative from these products using small blocks cut from the round stock because the exposure of wood cells in round stock is primarily on the tangential surface (radial movement of chemicals) compared to exposure of all surfaces with sawn lumber. Due to the inherent variability associated with wood, it is recommended that commodity-size samples be examined in leaching tests, for example whole piling sections or whole sections of lumber. This procedure has the added advantage of including surface deposits of preservative in the analysis that are lost when the wood is reduced to small blocks. Definition of what constitutes a minimum commodity size has not been rigorously established. However, samples of whole piling or boards with sealed end grain and a leaching surface area of several thousand square centimeters should be sufficient to retain surface deposits associated with treating and to average small-scale differences in retention.



Figure 7.2 Commodity size samples used to evaluate preservative loss rates.

Leaching study results for commodity-size samples, such as those shown in Figure 7.2, reported later in this chapter, were 2×6 in. or 4×4 in. sawn lumber or whole piling sections varying between 20 and 30 cm in dia. Two pieces of 2×6 -in. lumber were joined using stainless steel screws with a short, untreated 2×6 in. spacer to create samples for assessment of preservative loss from immersed, sawn lumber. All commodity-size samples were 60 cm in length. The stainless steel screws and spacer were located at the end of the board that was above the diluent. Both ends of these samples were sealed with two coats of fiberglass resin.

7.1.4 Sample production and handling

Pressure-treated wood used in leaching studies should be produced in the same manner as the products being marketed for the intended use. Preservative retention should be assayed by a certified examiner, and wood not meeting the AWPA Standard (2009) by a significant amount (either over-treated or under-treated) should be rejected for testing. The wood should be kept under cover following production to prevent wetting from rain and shipped to the assessing laboratory wrapped in 60-ml plastic sheeting or other impermeable material. Wood intended for

use as untreated controls should be from the same parent stock and it should be bundled and wrapped separately. This is considered especially important when bioassays will be conducted on the diluent, since untreated southern pine, Douglas-fir, and mixed hemlock-fir have been found to be toxic to aquatic organisms. Minimum handling of pressure-treated wood is recommended. The end grain of all samples, including the controls, should be sealed with two coats of fiberglass resin or other suitable sealant. The dimensions of each sample should be accurately measured. Samples can be lightly dusted to remove sawdust and other residue associated with cutting the samples to size. However, the wood should not be scrubbed to remove surface deposits of preservative and no water should come into contact with the samples until they are exposed to the diluent in the leaching system.

7.1.5 Preservative retention

The relationships between preservative loss rates and retention are complex and depend on preservative type and even on components within a single preservative system. In general, preservative loss rates (expressed as $\mu\text{g}/\text{cm}^2$ per unit time) increase with increased retention. As seen in Figure 7.3, higher preservative loss rates should

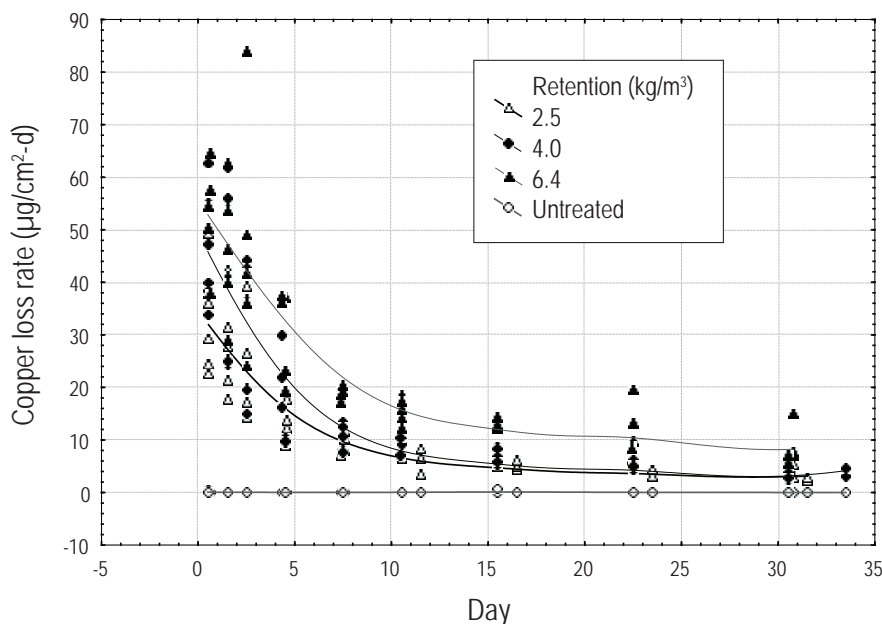


Figure 7.3 Copper loss rates ($\mu\text{g Cu}/\text{cm}^2\text{-day}$) as a function time of immersion and ACQ-C preservative retention (kg/m^3) from southern yellow pine treated to 6.4, 4.0, and 2.5 kg/m^3 with ACQ-C (irrespective of the use of water repellants). Retention 2.5 kg/m^3 ($r = -0.72$, $p < 0.000$) $Y = 22.99 - 0.84 \times \text{day}$; 4.0 kg/m^3 ($r = -0.68$, $p < 0.000$) $Y = 32.0 - 1.17 \times \text{day}$; 6.4 kg/m^3 ($r = -0.76$, $p < 0.000$) $Y = 42.17 - 1.41 \times \text{day}$.

be expected at higher retentions. However, the data suggest that loss rates are not proportional to retention. Initial loss rates from ACQ-C decking treated to a retention of 6.4 kg/m³ were 1.83 times greater than the loss from the same lot of southern pine treated to a retention of 2.5 kg/m³ (39% of the higher retention). In contrast, very low retentions of CCA resulted in abnormally high arsenic leaching rates (Cooper 2003). Appropriate retentions are specified in the latest edition of the AWWA Standards (2009). Specified retentions vary by preservative, wood species, and use category. It is important to carefully follow these standards and, as noted above, wood not meeting the AWWA specified retention should be rejected.

7.1.6 Preservative fixation

In general, the oil-type preservatives, such as creosote, do not fix within the wood, but form coatings on the wood cell walls. However, preservatives such as CCA-C fix in the wood through complex chemical reactions, in which copper, arsenic, and chromium form soluble and insoluble complexes with the lignocellulosic components of the wood's cellular structure. Pizzi (1982) and Hingston et al. (2001) provide reviews of the chemistry and kinetic behavior of arsenic, copper, and chromium during fixation of CCA in treated wood. The CCA-C fixation process is highly dependent on the reduction of hexavalent chromium, Cr(VI), to trivalent chromium, Cr(III), and the formation of chromium-copper and chromium-arsenic complexes. However, Murphy (1998) also describes the direct binding of copper to wood complexes. The degree of fixation in CCA-C preserved wood can be monitored by determining the proportion of chromium Cr(VI) that has not been reduced to chromium Cr(III) using the chromotropic acid test (AWPA A3/11). This blot test has a minimum detection limit of 15 ppm Cr(VI). The term "fixation" as it applies to CCA implies that the reactions are permanent, when in fact it is a dynamic process in which the reacted preservative components are in equilibrium with the chemical environment in which the wood is placed. Liquid mass flow and diffusion processes on both a macro and micro level can impact this equilibrium significantly.

Fixation has not been as well defined for other inorganic waterborne preservatives. Copper and quaternary ammonium compound components of alkaline copper quaternary (ACQ) preservatives and copper in copper azole (CA) preservatives are to a large extent fixed in wood by cation exchange reactions. It is likely that there is additional precipitation of copper in these systems through the

formation of copper carbonate and other low-solubility copper compounds.

Fixation rates of CCA-C-, ACQ-, and CA-preserved wood are known to be dependent on temperature and the availability of moisture within the cell lumens allowing migration of the metal ions to unoccupied reaction sites. The length of the fixation period is temperature sensitive and can last from several hours at 45°C to 2 mo at 5°C. Studies by Jain and Lagus (cited in Baldwin 1989) measuring the efficiency of the fixation mechanism have shown that drying at 21°C will fix 95% of the metals within 4 d and 99% within 5 d. Further studies by Alexander and Cooper (1993) found that the rates of fixation in all wood species are significantly inhibited if the wood is allowed to dry extensively during the fixation process, and that improper fixation can result in significantly increased leaching of all CCA components. Cooper and Ung (1992) reported complete fixation (passing the chromotropic acid test) of southern pine treated with CCA-C following one hour of accelerated fixation at temperatures >85°C. However, Dahlgren (1975) observed nearly twice the copper loss rates from wood dried at 60° to 80°C, compared with wood fixed at ambient temperatures, and Lee et al. (1993) found that copper losses were directly related to fixation temperature (1.7% at 24°C, 2.3% at 60°C, and 3.9% at 82°C). Their study demonstrated the importance of maintaining wood moisture content (>22% recommended) during fixation.

Fixation of metals in ACZA preservative systems occurs as the ammonia carrier diffuses out of the wood during production. The loss of the ammonia results in the precipitation of zinc arsenate, which is very leach resistant, leading to the low arsenic loss rates from wood treated with this preservative. Copper oxides are more water soluble and have been identified as the last component in many waterborne copper-based preservatives to fix in the wood's cellular structure. Fixation of ACZA preservatives does not require drying of the wood. Like CCA, maximum fixation requires adequate moisture content in the wood to allow for optimum ion mobility. Fixation is also improved by maintaining high intra-cellular ammonia concentrations through wrapping or aqua-ammonia steaming. There is currently no test for fixation of ACZA.

Fixation processes are relatively well characterized for CCA-C preservative in southern pine and for ACZA in western species, but are less well understood for other preservatives and species. The chromotropic acid test for CCA preservative is the only currently available test for

assuring fixation. However, the American Wood Protection Association has developed a standard for evaluating copper and other preservative emissions from fresh-treated and conditioned wood, based on leaching from increment borings as a quality control standard for the treating plant (AWPA 2009).

7.1.7 Static versus dynamic tests

Most leaching procedures allow samples to be exposed to a standard volume of water, with periodic replacement of the leaching water. However, the buildup of leached components in the leaching water has been shown to affect leaching rates. The importance of maintaining reasonably low diluent concentrations was emphasized in an analysis of the report of Stanley (1994b), who evaluated copper loss rates from three replicate Douglas-fir sapwood blocks, measuring $3.8 \times 3.8 \times 30$ cm, treated to a retention of 40 kg ACZA/m³ and immersed in seawater with a salinity of 30 practical salinity units (PSU) for 60 d. Copper concentrations rose quickly in the test, reaching 16,100 µg/L at the end of 21 d. Following that, copper concentrations were fairly constant, with losses of copper from the diluent observed on days 45 and 52, suggesting that the wood took up copper from the diluent.

Brooks (2003) leached sections of southern pine piling (18 to 20 cm dia immersed in 48 cm water depth) that had been removed from service at a Virginia marina following 16 mo of immersion in seawater at 18 PSU. The purpose of the test was to determine long-term metal loss rates from CCA-C pressure-treated wood that are important to predicting sediment accumulations of metal. The test was conducted in 37-L high-density polyethylene (HDPE) tanks under static conditions with no water circulation. The concentration of copper in the water following 17 d of immersion was 651 ± 166 µg Cu/L, and it did not increase significantly ($\alpha = 0.05$) between day 17 and day 34, when the concentration was 677 ± 302 µg Cu/L. It was hypothesized that the low diluent-to-sample-volume ratio (2.7:1) and static conditions, which did not include internal recirculation of the diluent, resulted in copper concentrations in water immediately adjacent to the piling that were high enough to inhibit further migration of metal from the wood. These results prompted Brooks (2002b, 2003, 2005a, and 2005b) to conduct future tests under dynamic conditions in which water was circulated through the leaching chambers using peristaltic pumps at rates sufficiently low to keep copper concentrations above the 0.030 µg Cu/L

detection limit, but high enough to maintain copper concentrations at less than 600 µg Cu/L when testing CCA-C preserved wood.

Brooks (2007) conducted static and dynamic testing of 60-cm-long sections of a single Douglas-fir piling treated to 38.2 kg/m³ (2.38 pcf) with ACZA preservative and immersed in 28 PSU seawater. Diluent in the static and dynamic tests was recirculated in the tanks at 120 gallons per hour (gph) throughout each study. The ends of all piling sections were sealed with two coats of fiberglass resin. In the dynamic test, an initial loss rate of about 40 µg/cm²-d declined exponentially to 7 µg/cm²-d at the end of 14 d with a further slow decline to 5 µg/cm²-d at the end of the 28-d test. In contrast, copper loss rates in the static test varied between 40 and 120 µg/cm²-d during the first 14 d and remained high at between 45 and 70 µg/cm²-d through the end of the 28-d test. Copper concentration in the diluent of the static test reached 40,000 µg/L at the end of the third day and varied between 100,000 and 320,000 µg/L at the end of the test. Why were the results of dynamic and static testing so very different?

In another study, Douglas-fir piling were treated by a Canadian facility (Brooks 2005c) who stored the treated pile outside for several days to allow formation of surface deposits of ACZA associated with rainwater wetting. The treated material was then loaded into a retort and covered with a dilute ACZA treating solution for one hour. The company suggested found that this dilute ACZA bath dissolved the surface deposits, leaving a clean product that was not subject to subsequent blooming (surface deposits of preservative). It is hypothesized that in the static test reported by Brooks (2007), concentrations of copper, arsenic, zinc, and ammonia in the diluent quickly reached levels that unfixed the preservative in surficial layers of the piling, resulting in excessive leaching. This hypothesis was supported by the appearance of turquoise deposits on the surface of the static test samples. The point is that in one case, a comparison of static and dynamic testing led to negative copper loss rates in the static test, whereas in the second comparison, the static test resulted in exceptionally high concentrations of metals in the diluent and prolonged high loss rates. Importantly, the results of the two dynamic tests were similar, whereas the results of the two static tests gave highly variable results that could not be used to characterize preservative losses to aquatic environments.

7.1.8 Effects of checking and interaction with internal recirculation of the diluent

For purposes of modeling poles or piling, the leaching surface area is determined by measuring the sample circumference and its immersed depth. Douglas-fir piling treated with ACZA tends to develop more numerous and deeper checks than does copper naphthenate (Figure 7.4). Nearly all of the checks in the pole treated with copper naphthenate (an oil-borne preservative) were hairline fractures restricted to the interior of the piling. The length of each check reaching the surface of the wood in the ACZA-treated Douglas-fir piling was measured and multiplied by two (two sides to each check). The total potential leaching surface area in a one-centimeter-high section of pole was then determined by measuring the circumference of the piling and adding to that the sum of the leaching surface area associated with the checking (twice the depth of the check times its length). Total check-wall depths of 112.4 and 91 cm were measured in the two ACZA piling sections seen in Figure 7.4. The sum of the poles circumferences and their checking lengths was divided by their circumferences to show that the total leaching surface area was 2.8 and 2.4 times the circumference. The exposure

of diluent to these surfaces was somewhat problematic because the “openness” of the checks was likely affected by swelling of the wood following immersion. However, anecdotal observation of the checks suggested that their geometry changed little and that they remained open to the diluent.

Another example of the importance of internal circulation and dynamic testing is provided by Kang et al. (2005) who examined PAH loss from commodity-size samples of creosote-treated Douglas-fir lumber, treated to a retention of 192 kg/m³ (12 pcf) and immersed in 12.5°C freshwater flowing at speeds of 0.47, 1.2, and 3.3 cm/s. Using high-resolution gas chromatography, the limits of detection varied between 0.28 µg fluoranthene/L and 0.87 µg benzo[b]fluoranthene/L. They observed six low-molecular weight and one intermediate-weight compound (fluoranthene) downstream from the samples. The authors concluded that the absence of high molecular weight PAH was due to their low water solubility. The results, showing increased loss rates at higher current speeds, are summarized in Figure 7.5. As will be seen in following chapters, little dissolved PAH has been observed in water immediately adjacent to creosote-treated piling, and significant accumulation in sediments takes weeks to months.

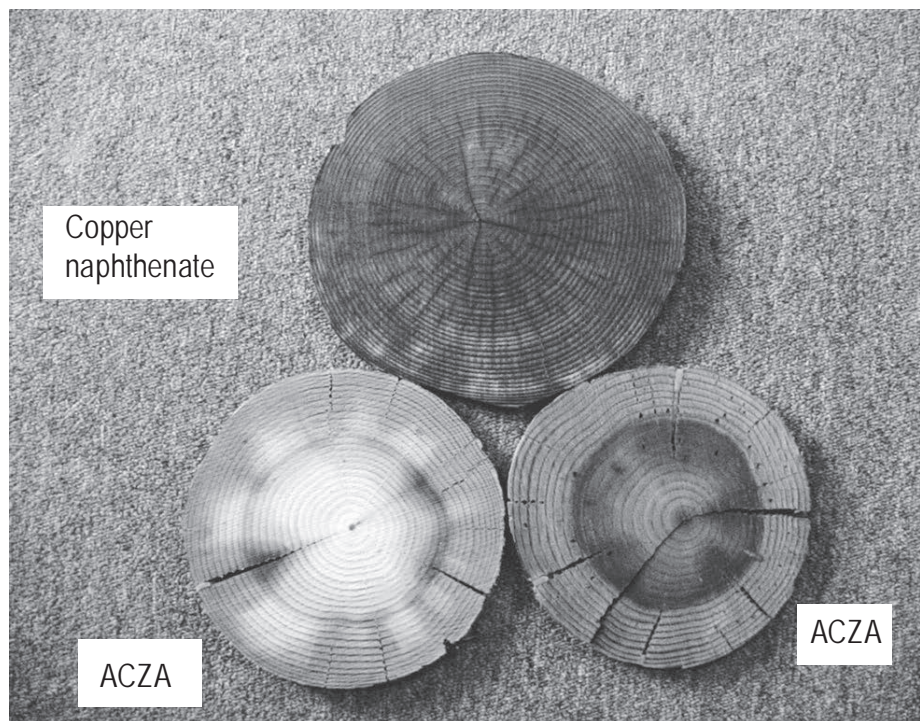


Figure 7.4 Cross sections of Douglas-fir poles treated with copper naphthenate and ACZA.

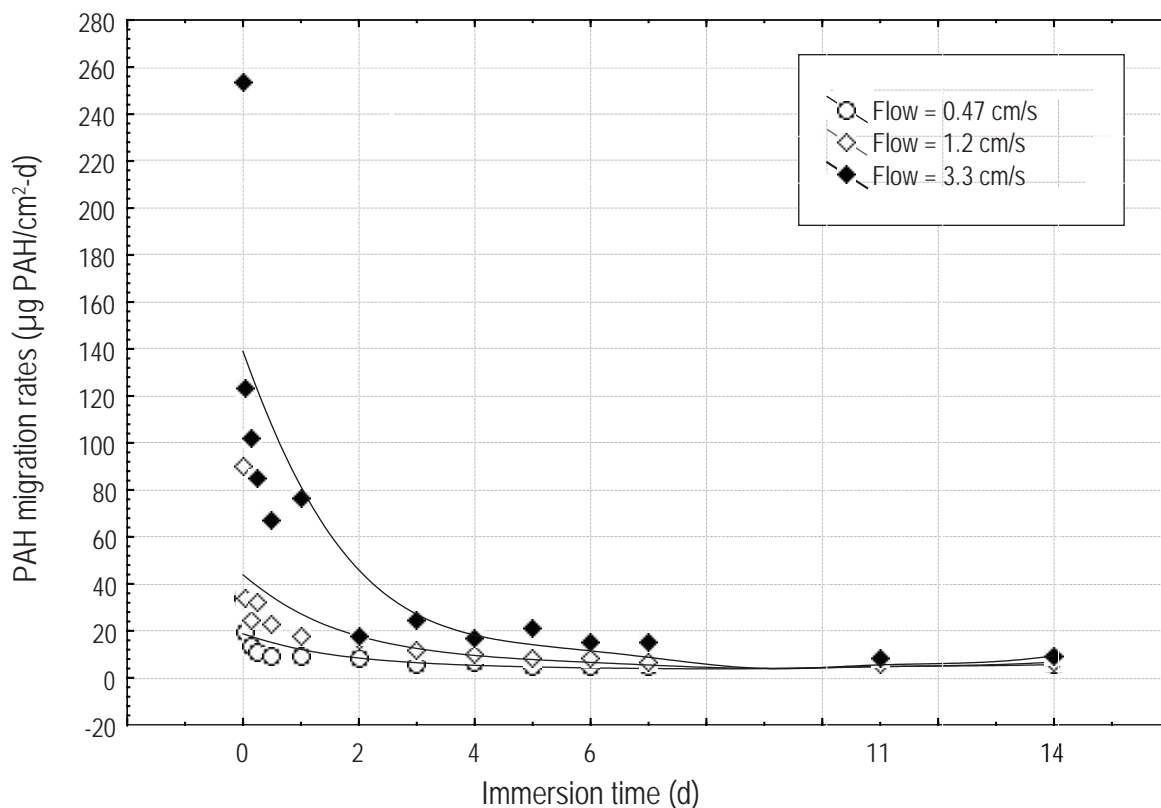


Figure 7.5 Creosote-derived PAH migration rates from pressure treated wood (192 kg/m^3) into fresh water flowing at 0.47, 1.2, or 3.3 cm/s.

Therefore, it is the integral under the curves representing total loss of PAH in Figure 7.5 that contributes to potential environmental risk associated with creosote-treated wood and not the initial values. The three curves, representing three current speeds, converged to essentially the same values following one week of immersion and the initial differences had little effect on the long-term accumulation of PAH in sediments. However, current speed was shown to be important for predicting acute toxicity associated with the initial flush of low-molecular weight PAH from creosote-treated lumber.

In the case of checking, it seems likely that vigorous water circulation would cause the residence time of water within the checks of ACZA-preserved wood to decrease (more water exchanged inside the checks with increased circulation). This would increase the metal concentration gradients across the wood-water interface within the checks, leading to increased diffusion of metal out of the wood. Water within the leaching tanks was gently stirred with a stream of air bubbles during a series of studies on Douglas-fir piling treated to 1.5 pcf with ACZA in 2002. In a 2005 study, also using Douglas-fir piling treated to 1.5 pcf, a plastic pump with a magnetic drive head was used

to vigorously circulate the diluent water at 120 L/h within the tanks. The results of these two studies are provided in Figure 7.6. Initial losses of copper, chromium, and arsenic were about 60% higher in the highly circulated (F) test when compared with the slowly circulated test (S). The measured loss of copper after 2 wk in test was nearly three times higher in the (F) test than in the (S) test.

It is reasonable to ask what current speed might be equivalent to a flow of 120 gph (452 L/h) past a piling immersed 50 cm deep in a lake, pond, stream, or bay. The cross-sectional area of the piling is about 20 cm dia \times 50 cm depth in the water or 1,000 cm^2 . A flow of 452 L/h past such a piling would be equivalent to a current speed of only 0.13 cm/s, suggesting that flows in open aquatic environments, where current speeds are more typically at least several cm/s, would more vigorously interact with the wood and allow water to circulate in open spaces. Figure 7.7 provides a conceptual model describing a hypothetical explanation for the increased metal loss rates with greater internal circulation. Recall that dynamic (flow-through) testing was undertaken in response to evidence from Brooks (2003) and Stanley (1994b) suggesting that static testing could result in developing metal concentra-

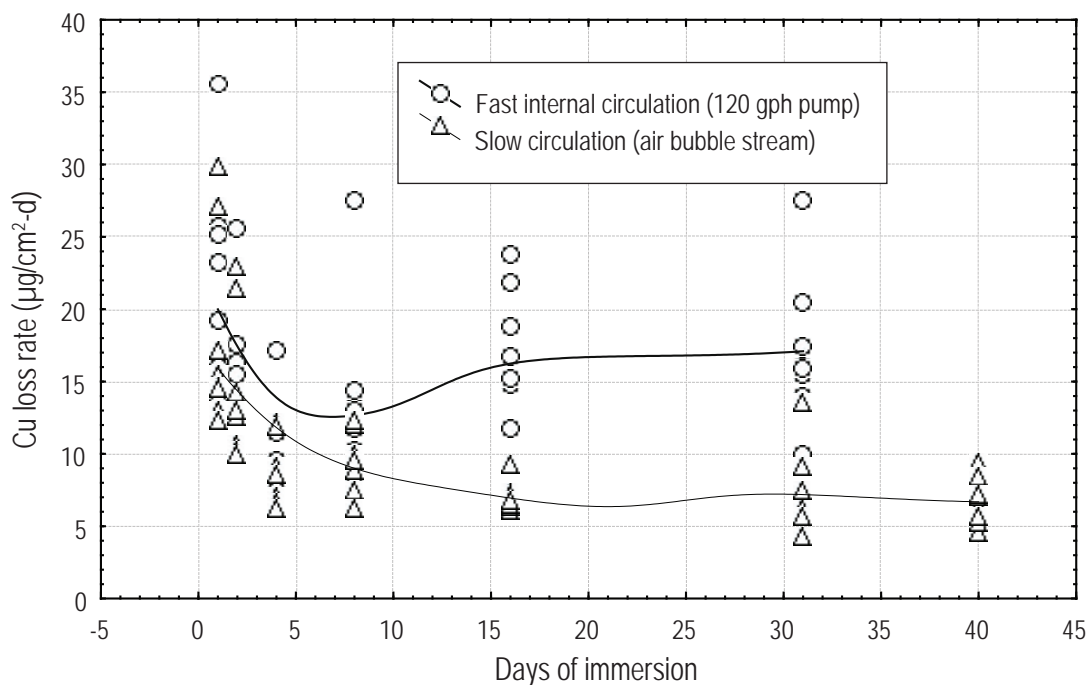


Figure 7.6 Comparison of copper loss rates from a 2002 ACZA study conducted with slow water circulation with the 2005 study in which water was circulated within the tanks at a rate of 120 gallons/hour.

tions in the diluent that approached the concentration of free metal ions in the wood, resulting in a shallow diffusion gradient that would inhibit further metal loss from the wood. In other words, when the metal concentration in

the diluent approaches the concentration of free (unbound) metal ions in the wood, then as much metal migrates from water back into the wood as from the wood into the water. The negative metal loss rates from wood reported in Stanley (1994b) substantiate this hypothesis. However, in the real world, dilution factors are so high that the diffusion gradients are maintained and metal continues to leach from the wood into the water. It appears reasonable to suggest that the same mechanism occurs here. Figure 7.7 suggests that the dynamic nature of these tests may be sufficient to maintain a shallow diffusion gradient on the perimeter of the piling. However, water circulation in the narrow checks does not occur, or occurs at rates so low that metals accumulate in the checks, but remain there and do not contribute significantly to the concentrations observed in the main body of the diluent flowing through the tanks. In contrast, the higher recirculation speeds created by the more rigorous recirculation of diluent in the tanks results in water continually being driven into the checks, flushing the metal to maintain the diffusion gradients and increase overall metal concentrations in the diluent.

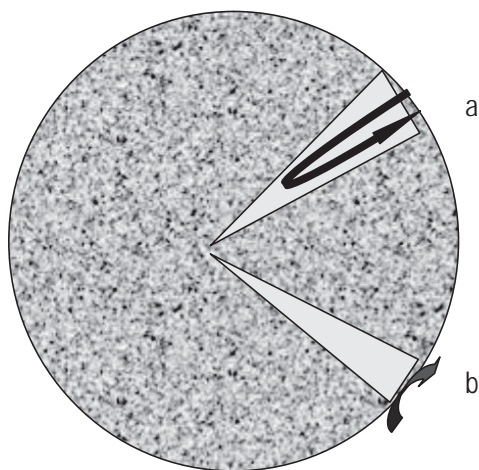


Figure 7.7 Conceptual model describing the relative flushing of metals from checks during slow circulation (stream of air bubbles) and fast circulation (internal pumping at 120 gph). The length of the arrows is proportional to the rate of internal circulation in the tanks. (a) With fast circulation, water is forced deep into the checks and continually flushes the accumulating metals out, maintaining a steep diffusion gradient between the wood-water interface, leading to higher metal losses. (b) Slowly circulating water does not penetrate the checks deeply, allowing metal concentrations to increase to the point where further loss from the wood exposed within the check is inhibited—resulting in lower apparent loss rates.

7.1.9 Use of natural versus deionized or distilled water

With a few exceptions, most leaching studies have been conducted in distilled or deionized water. While this di-

minishes the unknown influence of other constituents found in natural water, it also adds an element of artificiality to the tests when the questions being asked are, "What are predicted loss rates of wood preservatives to surface waters?" and/or "What are the likely biological effects?" In addition, the low hardness and alkalinity of deionized water unnaturally compromise bioassays conducted on the effluent from treated wood studies.

Are leaching rates different in deionized versus natural surface water? Dubey et al. (2005) leached $3.8 \times 8.9 \times 5.8$ cm (average surface area = 146 cm^2) southern pine blocks treated to a nominal retention of 4.0 kg CCA-C/m^3 (0.25 pcf) for 24 h into deionized water and two natural waters from a Florida pond and from the Florida Everglades. At the end of 24 h, the copper concentration in the deionized water was 1.5 mg Cu/L . The copper concentration was 6 times lower in the Everglades water (0.25 mg/L) and 3.3 times lower in the pond water (0.46 mg/L). The natural waters were not characterized by hardness, alkalinity, sulfate, dissolved organic carbon, humic acid, etc.; the effects that these characteristics and/or other dissolved substances found in natural waters might have on metal loss rates from pressure-treated wood are unknown. However, this study suggests that leaching studies conducted in deionized water overestimate copper loss rates compared with studies conducted with natural surface waters. In addition, dynamic tests at flow rates of 0.5 to 4 ml/s require up to $1,382 \text{ L}$ of water/day for three replicates plus a control, and supplying that quantity of deionized water for 30-d tests is problematic for most testing facilities.

7.1.10 Diluent pH

Surface waters of North America generally have pH values ranging between 6.5 and 8.0. The U.S. Environmental Protection Agency (EPA) Water Quality Criteria (WQC) for pH is 6.0 to 9.0 and the Florida pH WQC (FAC 17-320.530) for Class III water is 6.0 to 8.5. Natural surface- or ground-water contains organic and inorganic compounds that buffer pH—particularly at typical hardness values of 50 to 200 mg/L as CaCO_3 . However, water passing through extensive wetlands may accumulate humic acids and have reduced pH—such as found in Pine Barrens streams in the Atlantic coastal plain. These "black waters" have highly altered biotic communities with few crustaceans and fish (EPA 2008). Thus, there are exceptions to a lower limit of pH 6.0—but they are not typical of most surface waters.

Dahlgren (1975) examined the relative leaching of copper from CCA-C treated southern pine as a function of pH and found that leaching rates exceeding 9% at pH 4.0 were reduced to $<0.5\%$ at pH 6.8. Cooper (1990, 1991) also examined pH effects on the leaching of CCA-treated wood. He cautioned that when treated wood is exposed to acidified water maintained at low pH, the CCA losses are increased compared to more neutral water. He went on to demonstrate that the citric acid buffer system used by Warner and Solomon (1990) caused excessive metal losses not solely associated with low pH. Cooper (1990) acknowledged that it is possible for some naturally occurring complex organic acids to accelerate leaching of CCA components by an undetermined amount at pH values < 4.5 . However, pH values this low will likely cause the wood to deteriorate, making the use of any wood in these environments problematic. Brooks (2005a) conducted dynamic leaching studies on commodity-size southern pine decking treated with CA-B preservative that was immersed in well water flowing through the 37 L tanks at a rate of 0.5 ml/s . The diluent's pH was continuously modified in the system to maintain values of 5.5 ± 0.15 , 7.0 ± 0.15 , or 8.5 ± 0.015 units, using sodium hydroxide to increase pH or a 60:40 mixture of sulfuric:nitric acid to reduce the pH below the well water's natural pH of 7.7. The inorganic acids used in this system mimic those required by SPLP (EPA 1994). Figure 7.8 describes changes in diluent water pH as it flowed through the 37 L chambers containing the treated wood. The effluent pH was buffered upward toward

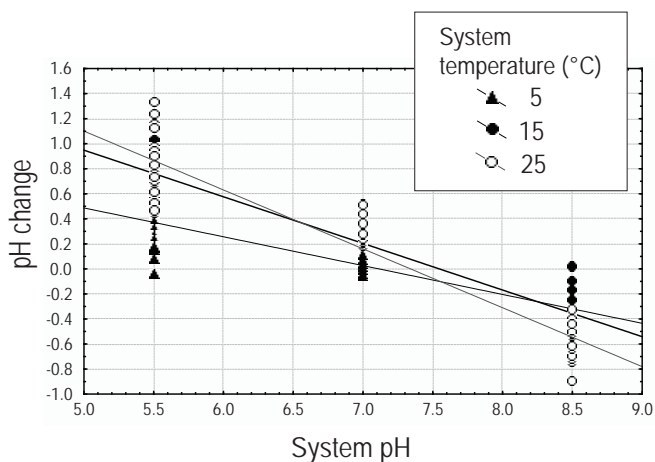


Figure 7.8 Influence of temperature on the buffering capacity of southern yellow pine under the test conditions imposed during the evaluation of CA-B pressure treated wood in dynamic (flow-through) immersion tests.

neutral (positive values on the y-axis) when the system pH was 5.5 and effluent pH was buffered downward toward neutral (negative y-axis values) when the system pH was high (8.5). Note that the buffering capacity of the treated wood was higher at 15°C and 25°C, but that it was reduced at a low diluent temperature of 5°C. The observed buffering appears to be an inherent property of southern pine, as the same pattern was observed for the untreated controls in this study. This buffering may or may not be an inherent property of other wood species.

Consistent with the results previously reported for CCA-C, Figure 7.9 describes the loss of copper from CA-B treated decking exposed to three pH values in this system. Note that copper loss rates at pH 8.5 were approximately half those observed at pH 7.0 or 5.5. Also note that the differences in loss rates at the three pH values decreased with time. The history of leaching studies undertaken to assess metal loss rates from pressure-treated wood indicates that at least for some preservatives, the use of organic acids may significantly increase loss rates compared with the use of inorganic acids. Leaching studies should reasonably mimic the environments being modeled. For the broadest applications, it is recommended that a pH range of 5.5 to 8.5 be tested and that inorganic acids be used to decrease pH because wood will tend to neutralize the acids, which must be replenished to maintain the target pH. If the intent of the studies is to assess the environmental response to pressure-treated wood immersed in natural waters with low pH associated with humic and/or other organic acids, then those acids should be used to amend pH.

7.1.11 Diluent temperatures

The fixation and/or mobilization of wood preservatives in wood cells is a dynamic process. At temperatures near the freezing point, oil-borne or oil-type preservatives are highly viscous, reducing the potential for their transport to the wood surface. For those preservatives that fix within the cellular structure of the wood, such as CCA-C and ACZA, the metal complexes involve a number of binding mechanisms, each with a different strength (covalent bonds > ionic bonds > van der Waals bonds, etc.). At higher temperatures, these reaction products are less stable and more soluble, resulting in higher preservative loss rates. The temperature of surface water ranges from <0°C (seawater) to near boiling (100°C) in hot-springs. However for most treated-wood applications, surface waters will vary be-

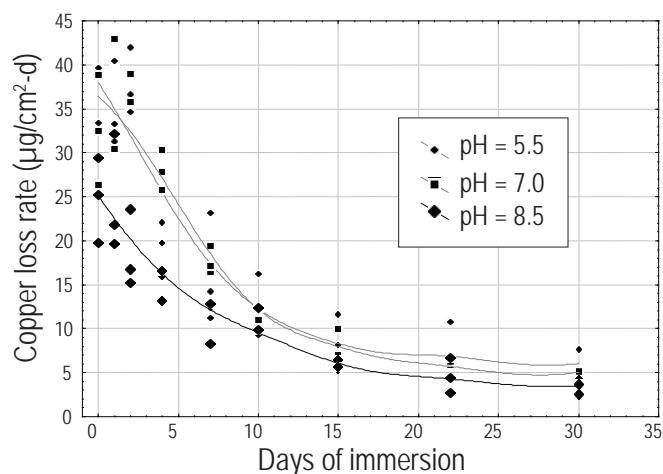


Figure 7.9 Copper loss rates ($\mu\text{g Cu/cm}^2\text{-day}$) from southern pine decking treated to a retention of 0.246 pcf with copper azole Type B (CA-B) preservative as a function of days of immersion and diluent pH.

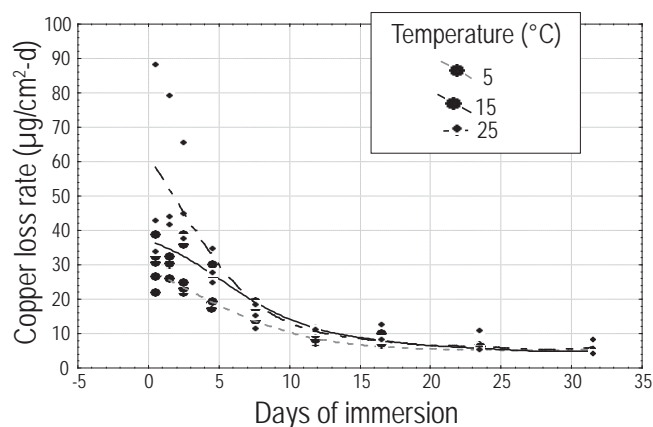


Figure 7.10 Effects of leaching temperatures of 5°C, 15°C, and 25°C on copper losses to fresh water at pH = 7 associated with southern pine lumber treated to a retention of 0.246 pcf with copper azole preservative.

tween 5°C and 35°C. Consideration of special environments may warrant additional study at higher temperatures. Figure 7.10 describes copper loss rates from southern pine lumber treated to a retention of 0.246 pcf with copper azole preservative and immersed in a dynamic leaching system at pH 7.0 (Brooks 2005a). The three high values observed at 0.5, 1.5, and 2.5 d of immersion were all associated with the same replicate and appear to be real. These values were likely associated with surface deposits of preservative on the sample or with poorly bound copper migrating out of the wood. A trend to higher copper loss rates with increasing temperature was observed during the first week of immersion. However, long-term loss rates were less affected by temperature. Copper azole

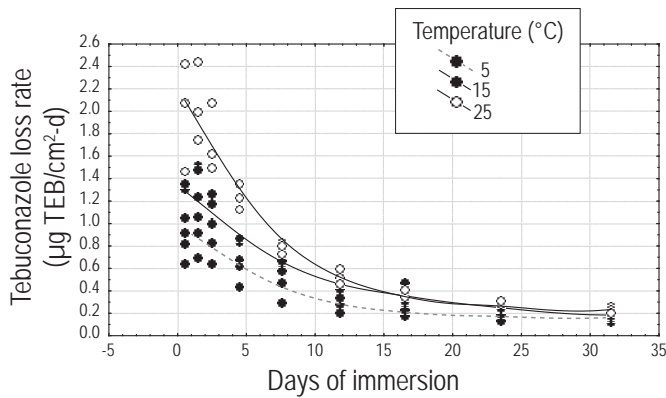


Figure 7.11 Loss rates (μg Tebuconazole/ $\text{cm}^2\text{-day}$) from southern pine treated to a retention of 0.246 pcf with Copper Azole preservative as a function of diluent temperature and days of immersion.

(CA-B) also contains tebuconazole, which is an organic biocide. Figure 7.11 describes the loss rates of tebuconazole recorded as a function of days of immersion and temperature observed during the same study represented in Figure 7.10. Differences in loss rate as a function of temperature were more pronounced for the organic biocide during the first 2 wk of immersion. Fixation of copper azole preservative was not well characterized. However, it is hypothesized that the differences observed early in the immersion history were associated primarily with poorly bound preservative or preservative on the outside of surficial cell lumens, and that as the poorly bound copper and tebuconazole were lost from the wood, biocides that were either chemically bound or well confined within cell lumens were not as available for leaching. It is this well-bound and or contained portion of the preservative that contributes to long-term wood protection.

7.1.12 Salinity

The only currently used preservatives with AWPAs Standards (2009) for use in saltwater are ACA, CCA-C, and ACZA (1.5 pcf in northern latitudes and 2.5 pcf in high-hazard southern environments) and creosote (20 pcf). Irvine et al. (1972) examined the retention of CCA in small wood blocks exposed to seawater from cooling towers. They found that metals leached more readily in cooling tower water than in conventional laboratory leach tests. Irvine and Dahlgren (1976) investigated the effects of salts on the leaching of CCA components and developed a theoretical mechanism to explain the increased leaching rates of CCA components exposed to marine environments. They concluded that sodium chloride had a coagulating effect on the copper at low salinity, reducing its rate of leaching. At higher salinity, complexation of copper and chromium with chlorine

and sodium ions results in increased leaching of these metals. At high CCA retentions, arsenic loss lags behind that of chromium and copper due to complexation of the liberated copper and chromium ions. At lower retentions [$<28.9 \text{ kg/m}^3$ ($< 1.8 \text{ pcf}$)] this trend is reversed and arsenic is more easily leached than is copper. Current AWPAs standards generally call for retentions of 9.6 kg/m^2 (0.6 pcf) in dimension lumber, 16 kg/m^3 (1.0 pcf) for piling used in freshwater applications, and 24 or 40 kg/m^3 (1.5 or 2.5 pcf) in marine environments (AWPA 2009).

Figure 7.12 is provided as an example of the copper loss rates from Douglas-fir piling that had been treated to 16 kg/m^3 (1.0 pcf) and immersed in freshwater compared with the same species treated to 38.2 kg/m^3 (2.38 pcf) and immersed in 28 PSU seawater. Both studies (Brooks 2005c), were conducted at 10°C to 15°C in dynamic (flow-through) tests. It was not possible to partition the differences between retention and diluent salinity. Decreased loss rates during the first 3 d of immersion has frequently been observed in dry wood and is thought to be associated with rehydration. Losses in seawater during the first 3 d were four to seven times higher than in freshwater. However, following this first flush, the variability between samples was greatly reduced and the loss rates were similar.

The most complete analysis of salinity effects associated with CCA-C was found in Irvine and Dahlgren (1975). In the short term (20 wk in test), they reported relatively low levels of copper loss at salinities less than 10 PSU. A

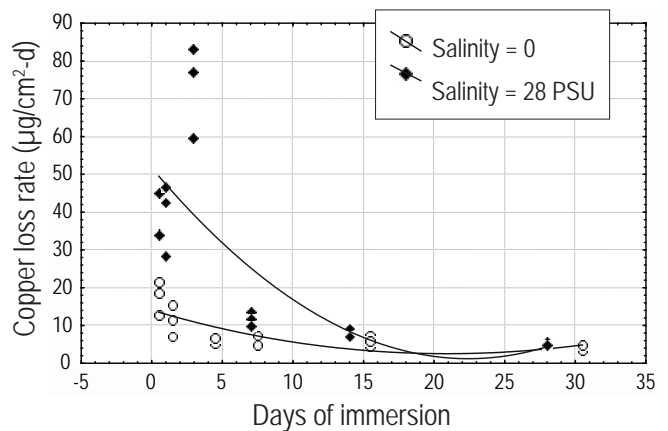


Figure 7.12 Copper loss rates ($\mu\text{g}/\text{cm}^2\text{-d}$) from Douglas-fir piling treated to 1.03 pcf with ACZA and immersed in freshwater in comparison with the same species treated to 2.38 pcf and immersed in 28 PSU seawater. Both tests were conducted in a dynamic (flow-through) system with rigorous (120 gph) internal circulation of the diluent.

significant increase to approximately twice this loss was observed at about 22 PSU. Above 22 PSU, losses increased slightly as salinity increased to 35 PSU. Most of the leaching data for CCA has been developed in saltwater (ca. 30 PSU). Based on these results, Brooks (1997b) developed the following relationship describing copper loss from CCA-C treated wood as a function of diluent salinity (Equation [7.1]):

$$\text{Relative copper losses}_{(\text{salinity})} = 0.51 e^{0.02 (\text{salinity})} \quad [7.1]$$

where, salinity is measured in PSU.

This relationship is marginally significant ($P < 0.06$) and explained 61% of the variability in the database. It predicts freshwater copper loss rates at 51% of those observed at 30 PSU salinity. It should be emphasized that this factor is appropriate to describe early metal losses for the first 20 wk of immersion. Irvine and Dahlgren (1975) did not find significant differences in loss rates at salinities between 0.0 and 25 ppt after 40 wk of leaching. However, they observed an increase of approximately 50% in copper losses at salinities greater than 25 ppt in the long term (40 wk). The relationship given in Equation [7.1] will tend to slightly overestimate losses in areas where the salinity is between 5 and 15 ppt.

Where resources allow, leaching studies could be conducted at 0, 10, 20, and 30 PSU to fully characterize performance in estuarine environments. For purposes of characterizing the loss of preservative as a function of salinity, it is recommended that freshwater studies be conducted at 0.0 PSU and marine studies at 30 PSU. Oceanic seawater is typically 35 PSU, but the lower value recommended is characteristic of near-shore environments where treated wood projects are more likely to be constructed.

7.1.13 Length of tests

Preservative loss rates described in Figures 7.9–7.11 (CA-B) and 7.12 (ACZA) all show the same exponential decline in loss rate as a function of time. Also note that the variability

between the three replicates in each study decreased quickly with time. The early first-flush losses are likely associated with residual surface deposits of preservative and migration of poorly bound preservative in surficial layers of the wood. As will be seen in Chapter 9, water column concentrations of the active ingredients will be highest in association with this first flush, and it is these initially high concentrations that will be modeled to assess the potential for acute toxicity to aquatic organisms. Models will assume that all of the preservative lost from treated wood is transported to sediments where they remain for the life of the project. Therefore, it is the area under the loss rate curves over the life of the project that is important for estimating sediment accumulations of active ingredients to assess sediment toxicity. Most treated-wood projects are expected to last for 35 to 75 y and it is not feasible to conduct leaching studies over that length of time. The question then is how long is long enough?

Loss rates in dynamic tests were generally evaluated over a period of 30.5 d. The samples were then immersed in an experimental freshwater pond for one to two years and reassessed in the same dynamic test apparatus used for the original study. Full data sets for ACQ-C and copper naphthenate are described in Figures 7.13 and 7.14. Further small reductions in copper loss rates after 30.5 d were observed in both cases. Table 7.1 indicates that the long-term (410 d) loss rates of copper and tebuconazole from southern pine treated with copper azole were significantly less than observed at the end of 30.5 d ($p < 0.00$ in both cases); however, the differences were relatively small. Based on the shape of the loss rate curves, it is recommended that tests be carried out for 30.5 d. Long-term preservative loss rates are important for understanding the potential accumulation of active ingredients in sediments. In all cases examined to date, loss rates at the end of 30.5 d of testing have been slightly higher than losses at the end of one or two years of immersion. Use of the 30.5-d data will result in somewhat higher predictions of the accumulation of active components in sediments than is actually expected, making the models conservative in this respect.

Table 7.1 Comparison of copper and tebuconazole loss rates from copper azole preserved southern pine lumber determined after 31.5 and 410 days of immersion.

Variable	Mean 30	Mean 410	t-value	df	p	t separ. var.est.	df	P 2-sided	Valid N 30	Valid N 410
Cu loss rate	5.32	3.59	4.26	52.00	0.00	4.26	51.92	0.00	27	27
TEB loss rate	0.17	0.07	8.33	52.00	0.00	8.33	51.98	0.00	27	27

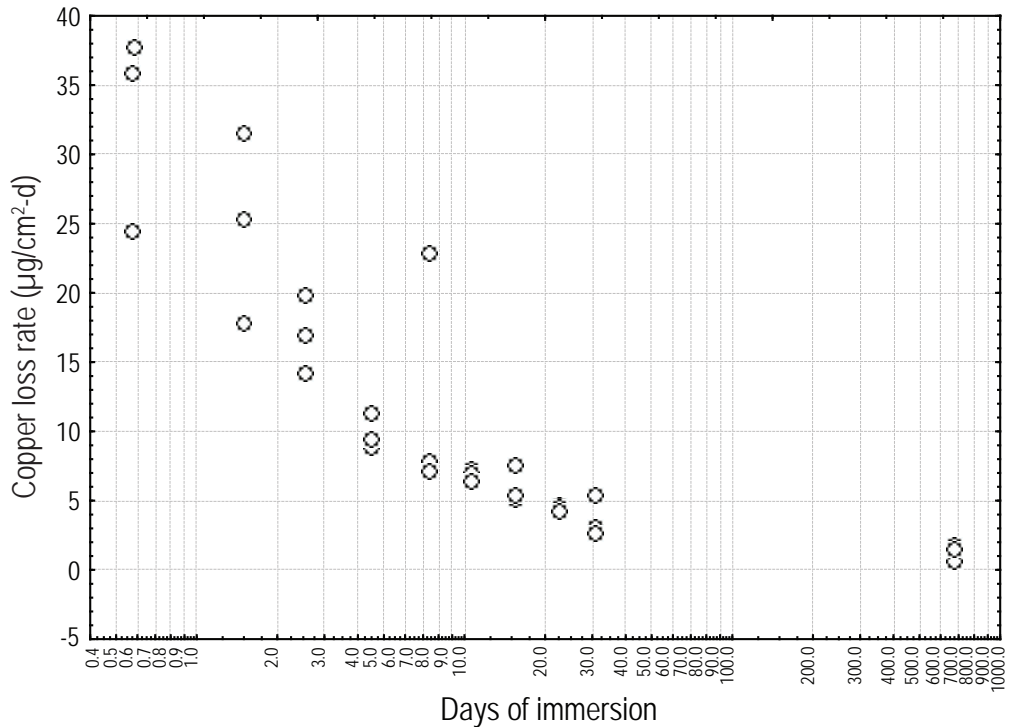


Figure 7.13 Copper loss rates from southern pine decking treated to 2.680 pcf with ACQ-C preservative amended with 4.280 pcf of a proprietary water repellent and immersed in freshwater at pH = 7.0 and 15°C.

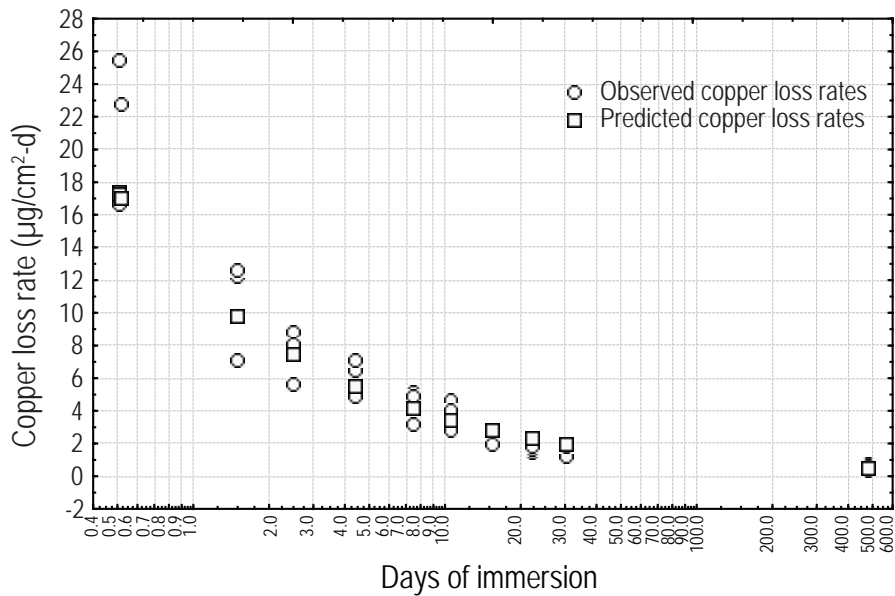


Figure 7.14 Predicted and observed values of copper loss rates in µg Cu/cm²-d from Douglas-fir pressure treated with 0.14 pcf copper naphthenate preservative and immersed in freshwater at pH = 7.0 and T = 15°C for 30.5 d followed by immersion in a Pacific Northwest freshwater pond for 482 d and reintroduction into the dynamic testing facility for 2 d at pH = 7.0 and T = 15°C.

Table 7.2 Summary of recommendations.

Attribute	Recommendation
What to measure	Concentrations of active ingredients in the diluent
Sample size	Commodity size containing several thousand square centimeters of leaching surface area.
End treatment	Seal open grain on cut ends with fiberglass resin or another appropriate sealant.
Preservative retention	As specified by AWWA standards for the preservative, wood species and end use
Preservative fixation	Use available tests to assure fixation and that the wood is ready for immersion
Type of test	Insure that the test is appropriate for the question (static or dynamic)
Diluent recirculation	Insure that test protocol does not allow for high diffusion gradients to build next to wood
Diluent characteristics	Appropriate for the end-use. Natural surface or well water capable of supporting test species is needed if the effluent will be used for bioassay testing.
Temperature range (°C)	5, 15, 35
pH range	5.5, 7.0, 8.5. Unusual environments may require additional tests.
Amending pH	Inorganic acids are recommended for general testing. Organic acids for special tests.
Salinity (PSU)	0, 30
Length of tests	30 days

7.1.14 Range of temperatures, pH and salinity for preservative loss rate characterization

Recommendations following from this discussion are summarized in Table 7.2. It is emphasized that these recommendations are provided to generally characterize the environmental performance of treated wood in typical surface waters. Unusual circumstances may require modification by the researcher depending on the question being asked. For preservatives used only in freshwater, this matrix requires nine studies. For preservatives used in freshwater and marine environments, the matrix requires 18 studies. The initial characterization may require further examination of intermediate salinity values.

7.2 COMPARISON OF AVAILABLE PROTOCOLS FOR ASSESSING PRESERVATIVE LOSS RATES

Numerous protocols have been used to assess preservative loss rates from pressure-treated wood: AWWA E11-97, TCLP, SPLP, static testing of blocks of various dimensions, and dynamic testing of commodity-size samples. It should be noted that the TCLP test was developed to estimate contaminant losses in low pH landfill environments (EPA 1992); SPLP was designed to estimate contaminant losses to acid rain (EPA 1994); and E11-97 was developed by AWWA to determine preservative depletion as part of its wood preservative efficacy testing program. None of these protocols were designed to estimate contaminant loss rates to aquatic environments.

Brooks (2005) examined the results of using these various procedures for estimating losses of preservative active ingredients to aquatic environments. This study has not previously been published and it is described in detail here to provide readers with information regarding the study as well as the dynamic testing system used to generate loss data described in this chapter.

7.2.1 Materials and methods

This study compared copper loss rates to freshwater from CCAC-preserved southern pine treated to a nominal retention of 6.4 kg/m³ for use in freshwater in accordance with AWWA Standard C2 (AWWA 2009), using the TCLP, AWWA E11-97, static leaching of commodity-size lumber with internal circulation, and dynamic leaching of commodity-size lumber with internal circulation. All of the samples were cut and randomly selected from a single stock of lumber.

7.2.1.1 Study design

All tests in this study were run in triplicate and compared with untreated control samples as a quality assurance measure. Two versions or variations of the TCLP procedure were conducted to evaluate the impact of sample size. The "coarse test" was conducted on 7 mm cubes with a well-defined and quantifiable surface area; the "fine test" used ground wood. Figure 7.1 describes the samples, both of which met the size reduction requirements of TCLP (EPA 1992). The results of all tests were analyzed using non-linear regression analysis to develop copper loss-rate algorithms in $\mu\text{g Cu/cm}^2\text{-d}$. Predicted copper loss rates for

short-term TCLP tests were determined and the results compared using analysis of variance and *t*-tests. Ninety-five percent confidence limits were provided where appropriate and null hypotheses were rejected at $\alpha = 0.05$.

7.2.1.2 Treatment and control samples

Sixty centimeters was cut and labeled from each end of the eight, southern pine 3.8×13.9 cm (2 in. \times 6 in.) boards. The remainder of each board was treated to a nominal target retention of 6.4 kg/m^3 (0.4 pcf) with CCA-C using modified cycles involving a 22-in. Hg initial vacuum for 5 min, followed by a 150 pound per square inch (psi) press for 15 min, and ending with a 24-in. Hg final vacuum for 10 min. The measured retention was 6.6 kg/m^3 . After treatment, the samples were placed under cover at ambient temperature for 3 d to allow for fixation, which was assured by using the chromotropic acid test (AWPA A3-04 #11). End-grain effects were reduced by removing 10.2 cm from each end of the boards. Two 60-cm-long treated wood samples were then cut and labeled from each end of the boards. The remaining 10.2 cm from the center was used for fixation and retention determinations. This provided 16 samples treated to the retentions shown in Table 7.3 and 8 untreated controls from the same parent stock.

The samples were individually wrapped and shipped to Aquatic Environmental Sciences, (Port Townsend, WA). Upon arrival, 19 ± 0.2 mm was cut from each end of 12 randomly selected boards for use in the TCLP and AWPA E11-97 tests. The remaining four boards were retained in reserve. Two 19-mm-thick cubes were then cut from these pieces, producing 48 cubes for use in the AWPA E11-97 procedure. The remainder of the sample was converted into 7-mm cubes. The 7-mm cube stock was randomly

subsampled for use in the coarse TCLP test, and then all remaining material was ground in an acid-washed Waring® blender for fine TCLP testing. The twelve $3.8 \times 13.9 \times 57.2$ cm treated samples were combined in six replicate test stacks of two boards each that were held apart on the above-water end with 7.5-cm-long pieces of untreated wood from the control stock and stainless steel screws. Two similar test assemblies, constructed of untreated material, were also fabricated. The end-grain of all samples used in the commodity-size static and dynamic tests (see Paragraph 7.2.1.3 for a detailed description of these procedures) was sealed with two coats of epoxy resin. Three treated replicates and one untreated control sample were assessed in the 14-d static test, and the remaining three samples plus a control were used in the dynamic (flow-through) test. The width and thickness of each board was measured at the time of construction. The depth of immersion was measured from the bottom of the test samples to the marked waterline when samples were removed from the tanks at the end of the test.

7.2.1.3 Static and dynamic test procedures

The following procedures have been used by Brooks (2002b, 2003, 2005a and 2005b) to evaluate preservative loss rates from commodity-size samples of wood pressure treated with a variety of wood preservatives. Figure 7.15 is a schematic describing the dynamic test system leaching tanks, water conditioning, circulation, and delivery to the test chambers. Well water for the static and dynamic tests was supplied via PVC pipes with no copper fittings in the system. The water had a hardness of $75 \text{ mg CaCO}_3/\text{L}$ and a pH of 6.8. It was conditioned as follows:

50- μM filter \rightarrow UV filter \rightarrow titanium heat pump \rightarrow
4-20 mA pH control

Table 7.3 Measured CCA-C retention in each of 8 southern pine boards treated to a nominal retention of 6.4 kg/m^3 .

Sample	Analyzed retention (kg/m^3)
9099-10	6.78
9129-1	7.10
9129-5	6.54
9129-6	6.39
9132-2	6.57
9132-3	6.63
9132-4	6.39
9132-6	6.43
Average	6.60

7.2.1.4 pH control

Dilute sodium hydroxide or a 60:40 mixture of sulfuric:nitric acid diluted 10:1 with distilled water was pumped with a 4-20 mA circuit controlled solenoid pump and mixed in a 120 L head tank. Water in the head tanks was continuously recirculated through the treatments described above. Continuous pH control was achieved in this system with an accuracy of ± 0.15 pH units. In these studies, the pH control probe was placed in the system head tank for continuous recording on a chart recorder. The pH of effluent from each tank was measured daily using a Thermo Orion Model 290A pH/ISE meter equipped with a Model

9107 Orion Low Maintenance Triode™ pH probe. The meter and probe were calibrated at pH 4.0, 7.0, and 10.0 prior to each use.

7.2.1.5 Temperature control

A titanium heat pump was used to maintain a temperature of 5°C in the recirculating system. Temperatures of 15°C and 25°C were maintained in two additional 150 L head tanks using 110 and 220V stainless steel immersion heaters with separate controllers and chart recorders. For those portions of the study conducted at 25°C, it was necessary to use glass aquarium heaters in each sample chamber to compensate for heat losses in the distribution system. Tanks for the low temperature portion of the study were housed in a double door Revco refrigerator with a modified thermostat. This extra cooling resulted in temperatures of $7.9 \pm 0.3^\circ\text{C}$, which was 2.9 degrees above the study’s design low temperature. The system’s temperature and the temperature of a representative leaching chamber for each thermal regime were recorded on chart recorders throughout the study.

7.2.1.6 Maintenance of flow rates through the chambers during the dynamic test.

Diluent water was fed to each chamber at a rate of 0.5 ml/s by Masterflex® Console Drives (Model 7521-50), each equipped with four Easyload II® peristaltic pump heads (Model 77200-52). Water was delivered through acid-washed platinized silicone tubing.

Water was continuously circulated within each 40 L Hero-Ryan HDPE leaching tank (Figure 7.15) at a rate of 450 L/h using epoxy-sealed magnetic drive pumps (MD-2). Recirculating water was taken from the bottom of each tank and reintroduced at the top of the tank through a PVC “T”. Recirculating flows were regulated with a PVC ball valve and monitored using 90 to 1,100 L/h Cole-Parmer acrylic flow meters.

7.2.1.7 Sampling

For consistency, samples were collected at 0.25, 1, 2, 4, 6, 8, 10, 12, and 14 d in the static, dynamic, and AWPA E11-97 tests. Samples were collected at 18 h (0.75 d) in the two TCLP tests. The water intake for the overflow was located

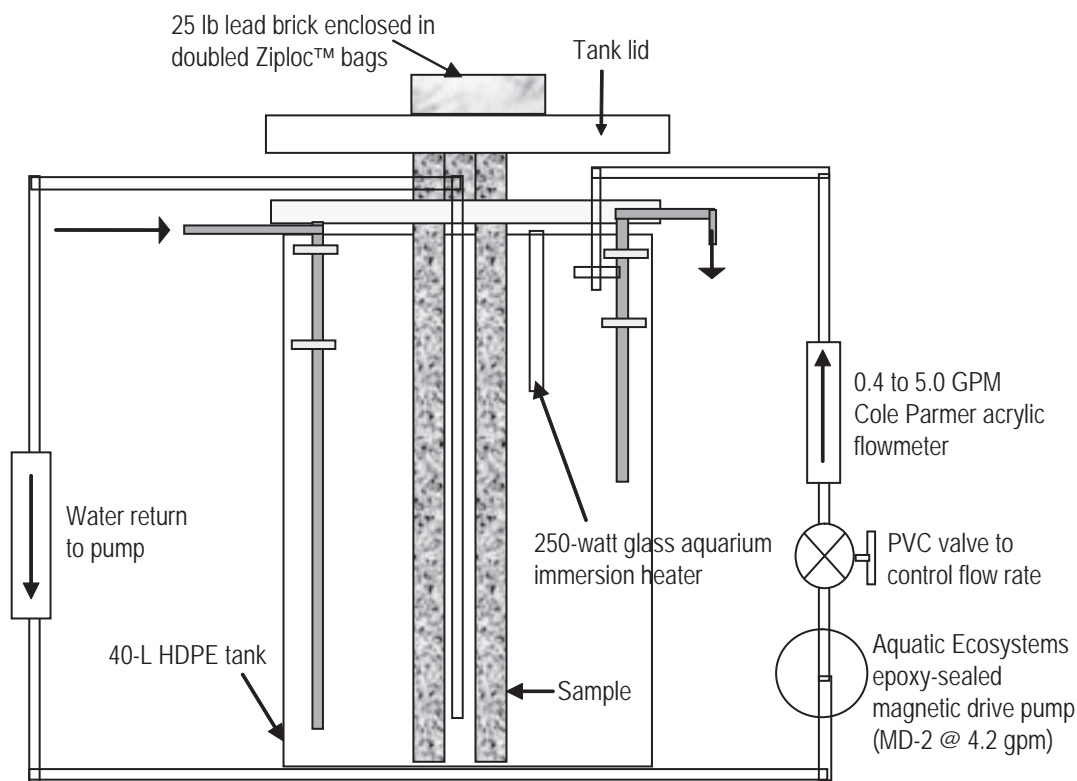


Figure 7.15 Dynamic leaching tank configuration. The treated wood and lid will extend above the tank an amount sufficient to allow inspection of the interior of the tank during operation (~5 cm). The exposed area was covered with Saran Wrap®. All plumbing is either glass or PVC that is acid washed at the beginning of each study segment.

at mid depth (25 cm below the surface). Twenty ml pre-cleaned scintillation vials were placed under the overflow and approximately 90 ml of water allowed to flow through them. They were then capped and stored at 4°C until analyzed. The static system was sampled by forcing a new, acid-washed, 100 ml HDPE bottle into the tank, forcing water to flow from the outlet port. A measured amount of diluent water was then added to each tank until the first drop appeared at the overflow port to compensate for evaporation and sampling. These additions were included in the analysis.

A sample of the diluent water was collected and analyzed for copper during the initial filling and at the end of the study. The flow through each test chamber was measured daily and just prior to collecting each sample by triplicate measurements of the time required to collect a 20-ml sample from the outlet port in a graduated cylinder. No corrections to flow rates or temperature were made within 24 h of collecting the samples.

7.2.1.8 Copper analysis

Copper analyses were conducted by the Battelle Marine Sciences Laboratory (MSL). Upon receipt at MSL, the 20 ml water samples were filtered on 0.45 µm Corning Costar Nucleopore® polycarbonate filters and acidified to pH <2.0 using reagent grade nitric acid. Copper concentrations were determined using ICP-MS with a detection limit of 0.030 µg Cu/L. Quality assurance included blanks, one duplicate for each batch or one per 20 samples, whichever was greater, and samples spiked with copper.

7.2.1.9 TCLP Testing (EPA Method 1311).

Four hundred grams of the 7.0 mm cubes were set aside for TCLP testing on a sample with known geometry and leaching surface area (Figure 7.1d,e). The width of each face of a subsample of twenty-five 7.0 mm blocks was measured using Starrett® Model 721 electronic digital calipers with a resolution of 0.01 mm. A second random sample containing 165 g of 7 mm cubes was placed in a blender and further reduced (Figure 7.1c). Triplicate TCLP extractions were completed for each size class by Analytical Resources Incorporated using EPA Method 1311, followed by copper analysis using inductively coupled plasma spectroscopy (ICP).

7.2.1.10 AWWA E11-97.

The procedure deviated from the published protocol in that AWWA E11-97 calls for treating the 19 mm cube test

samples rather than cutting the samples from larger pieces of previously treated wood. The treatment of small cubes would increase metal loss rates because more preservative is absorbed through the exposed cell lumens across the end-grain. The purpose of this study was to evaluate the effects of sample size, end-grain-to-surface-grain ratios, and diluent characteristics. To minimize differences associated with wood structure, subsamples were reduced from the same test material and randomly selected for use in each protocol. Treating the AWWA E11-97 samples after reduction to 19 mm cubes would have made this random selection process impossible. It should be emphasized that post-reduction treatment of the 19-mm cubes would have resulted in higher copper loss rates in this test. For the AWWA E11-97 test, forty-eight 19 mm test blocks were labeled and weighed (0.0001 g). The 18 blocks lying closest to the mean weight of the entire sample were used for this test. Each face of the blocks was measured using digital calipers (nearest 0.01 mm). Six blocks were used in each of three replicate tests. The blocks in each test were weighed down in a 500-ml flask containing 300 ml of deionized water and placed under a vacuum of 3.94 in. of mercury for 20 min to impregnate the dry blocks with water. At the end of this time, the vacuum was relieved and the wood removed and placed in a 500-ml beaker equipped with a magnetic stir bar covered with a 0.6 cm² square plastic grating setting on plastics supports to isolate the samples from the stir bar. Sufficient deionized water was added to the remainder of the 300 ml of impregnating water to make a total volume of 300 ml of diluent. The blocks were completely submerged by placing another 0.6 cm square plastic grating over their top, which was weighted down with a partially full 50 ml glass beaker. The samples were then sealed with Saran Wrap® and placed on a stirrer producing a tip speed of 250 to 500 mm/s. The apparatus was placed in an incubator at 23 ± 0.5°C. The leachate water was sampled and changed after 0.25, 1, 2, 4, 6, 8, 10, 12, and 14 d. The beakers were rinsed twice with 50 ml of deionized water, which was added to the leachate—giving a total of 400 ml of sample. A 250 ml subsample of this leachate was placed in pre-labeled and pre-cleaned HDPE for metals analyses. On each sampling day, 300 ml of new deionized water was added and the beakers covered and returned to the incubator at 23°C.

7.2.1.11 Data analysis

Data were entered into Microsoft Excel® spreadsheets for determination of copper loss rates. Inferential statistics,

including development of statistical models describing the loss rates, were accomplished in Statistica Version 6® software.

7.2.2 Results

Published CCA-C leaching studies by Cooper (1990, 1991), Kim and Kim (1993), Stanley (1994a), Breslin and Adler-Ivanbrooks (1998), Van Eetvelde et al. (1995), Lebow et al. (1999), Brooks (2003) and Dubey et al. (2005) have examined a variety of samples ranging from finely ground wood evaluated using the TCLP and SPLP tests; a variety of small blocks of varying sizes; and commodity size samples examined in surface waters. These studies have reported initial copper loss rates varying between 2.17 and 7.62 $\mu\text{g Cu/cm}^2\text{-d}$. The variability in these results is not surprising given differences in diluent pH and because the cellular integrity of the wood was more or less compromised depending on the protocol.

7.2.2.1 Surface area to sample volume and surface to end-grain area ratios

This study assessed samples with four surface-area-to-sample-volume ratios and three quantifiable surface-to-end-grain ratios (Table 7.4). The surface-to-end-grain-area ratio for a typical treated brace used in construction of treated wood structures (8.9 × 29.2 × 304.8 cm) is 40:1, while it is 162.9 for a 3.81 × 14.0 × 487.7 cm plank.

7.2.2.2 TCLP

Results from the TCLP tests using 7 mm cubes (coarse or "C") and ground wood (fine or "F") are summarized in Table

7.5 and Figure 7.16. The concentration of copper in the 7 mm cube diluent following 18 h of extraction was $12.3 \pm 1.8 \text{ mg Cu/L}$. The concentration in the ground sample diluent was 53% higher at $18.2 \pm 0.1 \text{ mg Cu/L}$. The differences were statistically significant (ANOVA; $F = 191.03$, $p < 0.000$). The surface area of the ground sample could not be determined and it is not feasible to estimate copper loss rates as a function of surface area. The average copper loss rate during the first 18 h of leaching from the 7 mm cubes was $21.6 \mu\text{g Cu/cm}^2\text{-d}$.

7.2.2.3 AWWA E11-97

Triplicate analyses were conducted in deionized water having an initial pH of 6.92. The mean of all final pH values taken when the water was changed was 6.99. The mean temperature for all samples ($\pm 95\%$ confidence) was $23.08 \pm 0.57^\circ\text{C}$ with a minimum of 22.5°C and a maximum of 23.6°C . Copper loss rates are summarized in Table 7.6 and Figure 7.17. The ratio of the sample variances to sample means was greater than one for samples collected during the first 2 d. After that, they were less than one, indicating a regularly distributed pattern. Non-linear regression analysis was used to model copper loss rates, resulting in a predictive algorithm that explained 92% of the variation in the data (Equation [7.1] and Figure 7.17).

Consecutive case numbers in Figure 7.17 represent the same replicate. All of the highest values were associated with the same sample, demonstrating that loss rates from each of the three samples were internally consistent and that the unexplained variation was associated with small differences in behavior of the three samples. Based on the

Table 7.4 Surface area to sample volume and surface to end-grain ratios for materials evaluated in various leaching procedures.

Test	Dimensions	Surface area:sample volume	Surface:end-grain areas
TCLP Ground	$\leq 9.0 \text{ mm}$	Very large	Unknown but small
TCLP 7 mm cube	$7.06 \times 6.89 \times 7.10 \text{ mm}$	8.58:1	2:1
AWPA E11-97	$18.8 \times 19.0 \times 18.9 \text{ mm}$	3.16:1	2:1
Static and Dynamic Test	$39.0 \times 139.7 \times 502.0 \text{ mm}$	0.65:1	Infinite (end-grain sealed)

Table 7.5 Summary statistics describing copper losses from 7 mm cubes and ground CCA-C treated southern pine leached in accordance with the Toxicity Characteristic Leaching Procedure (EPA Method 1311). Smallest N for any variable: 3.

Test	Temp means (°C)	Confidence +95.000%	Final pH means	Confidence +95.000%	Cu in diluent ($\mu\text{g/L}$) means	Confidence +95.000%	Loss rate ($\mu\text{g/cm}^2\text{-d}$) means	Confidence +95.000%
TCLP C	26.5		4.93	4.95	12266.7	14097.8	20.73	21.55
TCLP F	26.5		4.94		18166.7	18310.1		
All groups	26.5		4.937	4.942	15216.667	18643.306	20.730	21.554

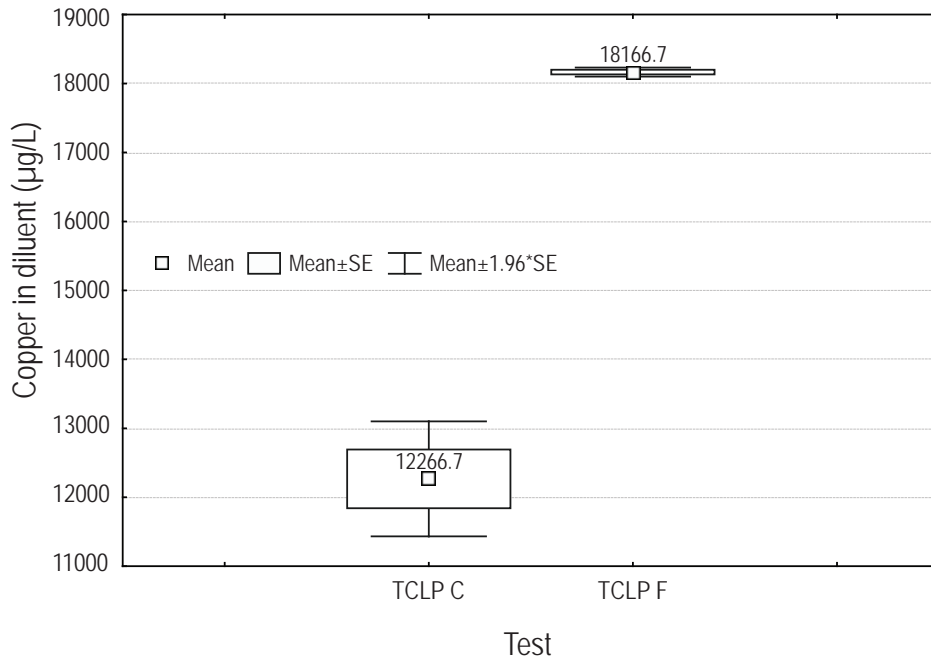


Figure 7.16 Box and whisker plot describing Cu losses from southern pine treated to a retention of 6.6 kg CCA-C/m³ and either ground (TCLP F) or cut into 7-mm cubes (TCLP C). Note that mmg Cu/L = µg Cu/L.

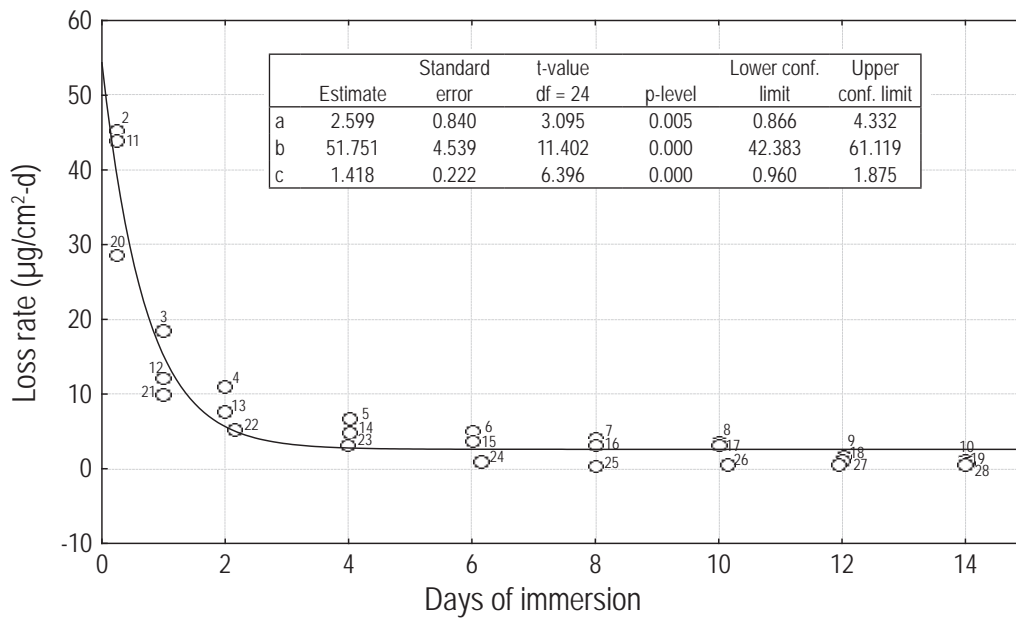


Figure 7.17 Results of modeling copper loss rates determined using AWWA E11-97 from southern pine treated to a retention of 6.6 kg CCA-C/m³. Loss rate = 2.599 + 51.75 * exp^{(-1.48 * time (days))}; R²_a = 0.92

Table 7.6 Summary statistics describing the results of copper loss rate testing on 19 mm CCA-C treated southern pine cubes using the AWPA E11-97 protocol. N = 27.

Day code	Mean copper loss rate (mmg/cm ² -d)	Confidence		Copper loss rate (mmg/cm ² -d)		
		-95.000%	+95.000%	Variance	Minimum	Maximum
0.25	39.217	16.287	62.147	85.204	28.583	45.156
1	13.508	2.430	24.586	19.886	9.892	18.491
2	7.940	0.562	15.318	8.821	5.122	11.042
4	4.843	0.583	9.103	2.941	3.151	6.580
6	3.139	-2.029	8.308	4.329	0.867	4.951
8	2.481	-2.211	7.172	3.567	0.377	4.031
10	2.325	-1.711	6.361	2.640	0.459	3.425
12	1.012	-0.352	2.376	0.302	0.472	1.570
14	0.730	-0.200	1.659	0.140	0.392	1.132

results of AWPA E11-97, the model predicts an initial copper loss rate (day 0.5) of 28.07 $\mu\text{g Cu/cm}^2\text{-d}$ and a long-term copper loss rate of 2.60 $\mu\text{g Cu/cm}^2\text{-d}$ (Equation [7.2]).

$$\text{Copper loss rate } (\mu\text{g Cu/cm}^2\text{-day}) = 2.60 + 51.8 \times \exp^{-1.42 \times \text{day}}; R_a^2 = 0.92 \quad [7.2]$$

7.2.2.4 Static tests

Table 7.7 compares the ratio of sample leaching area to diluent volume (A/V) with the maximum copper concentration observed in the diluent for each test. The TCLP test had the highest A/V ratio and the highest diluent copper concentration. The A/V ratios were similar between AWPA E11-97 (A/V = 0.07) and the static test of commodity size lumber (A/V = 0.11). The higher maximum copper concentration in the AWPA E11-97 test can likely be attributed to the higher-surface-to-end-grain ratio (2:1) in those samples relative to the samples in the static test, in which the end-grain was sealed. The concentration of free (unbound) copper in the treated wood cell lumens has not been determined. However, the results of Brooks (2002b) suggest that copper concentrations in the diluent from

the TCLP and AWPA E11-97 tests were sufficiently high to inhibit further copper losses.

Diluent characteristics for the static test.

A mean static leaching tank temperature of $23 \pm 0.47^\circ\text{C}$ was maintained during the test. The diluent's initial pH of 6.85 declined to 6.78 during the test, but the differences were not significant at $\alpha = 0.05$. Individual copper concentrations in the diluent are summarized in Figure 7.18, together with the results of a non-linear regression model. With a single exception, the copper concentration in the diluent remained below 600 $\mu\text{g/L}$ at all times.

Cases were organized by replicate and consecutive case numbers represent sequential sample days for the same sample. The case numbers are included on the graph to demonstrate that variability on any sample day was primarily associated with differences between the samples and not as random scatter about the fitted regression, which accounted for 94% of the variation in the database.

Copper loss rates modeled using a static test of commodity size lumber

Copper loss rates ($\mu\text{g Cu/cm}^2\text{-d}$) are summarized by day in Table 7.8 and described graphically in the box and 95%

Table 7.7 Treated-wood leaching surface area to diluent volume (area:volume) ratios and maximum copper concentrations in diluent associated with four tests of CCA-C pressure-treated wood.

Test	Surface area (cm ²)	Diluent volume (ml)	Area:volume (cm ² /ml)	Maximum Cu concentration ($\mu\text{g Cu/L}$)
TCLP 7 mm cube	610.6	800	0.76	12,250
AWPA E11-97 ^a	21.6	300	0.07	1,796
Static test ^a	3,857.7	36,368.6	0.11	657
Dynamic test	3,591.6	Continuous flow		143

a. Other than the size of the samples, the primary difference between these two tests was that the end-grain was sealed in the static test, whereas in the E11-97 test, the end-grain was not sealed and the ratio of face-grain to end-grain was only 2:1.

Table 7.8 Summary statistics describing copper loss rates from southern pine boards (3.9 × 15 × 50 cm long) treated to a retention of 6.6 kg CCA-C/m³ and immersed in 37 L of freshwater under static conditions. N = 3 for each day, N = 27 for all groups.

Day code	Loss rate (mmg/cm ² -d) means	Confidence -95.000%	Confidence +95.000%
0.25	2.512	0.011	5.012
1	0.500	0.167	0.834
2	0.690	0.081	1.300
4	0.420	0.178	0.662
6	0.329	0.267	0.391
8	0.253	0.011	0.495
10	0.297	0.205	0.389
12	0.207	-0.007	0.421
14	0.176	-0.073	0.425
All groups	0.598	0.295	0.901

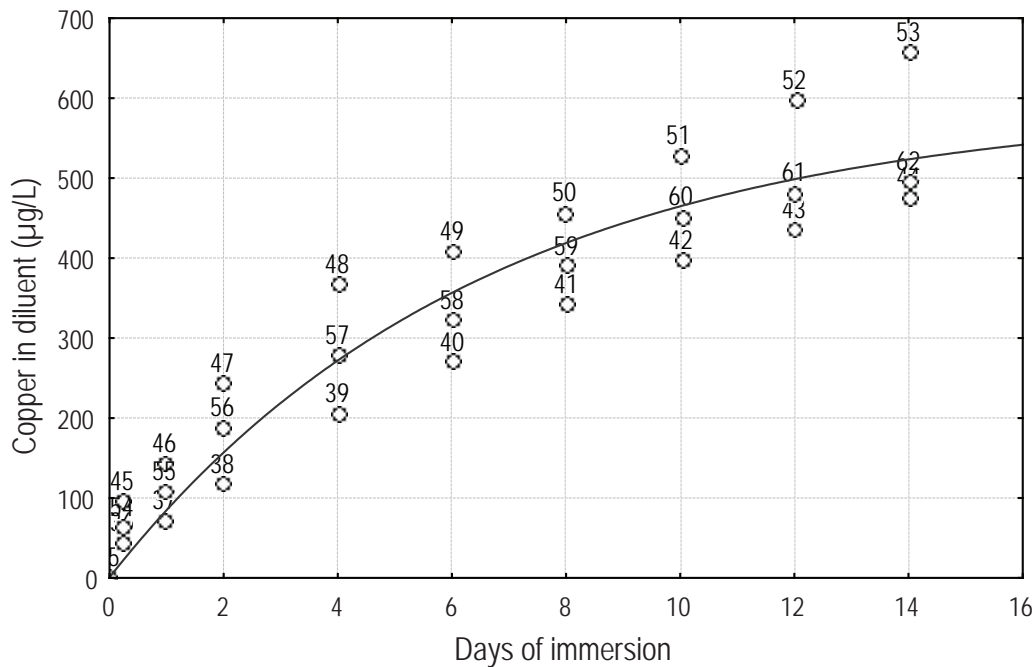


Figure 7.18 Copper concentrations observed in diluent test resulting from the leaching of commodity size southern pine boards treated to a retention of 6.6 kg CCA-C/m³ and exposed under static test conditions with internal recirculation.

confidence whisker plot provided in Figure 7.19. A predictive model was developed using non-linear regression analysis (Equation [7.3]).

$$\text{Cu loss rate } (\mu\text{g Cu/cm}^2\text{-day}) = 0.333 + 4.875 \times \exp(-3.226 \text{ days of immersion}); R^2_a = 0.82 \quad [7.3]$$

The model explained 82% of the variation in the database. All of the coefficients were significant at $\alpha = 0.05$. As seen in Figure 7.19, there was some heteroschedasticity with higher variance at higher loss rates associated with the first day of sampling. The model is only applicable at neutral pH and 23°C under static conditions. The early variability

has been observed in all similar tests (Brooks, unpublished) and is thought to be associated with free copper that has dried, but is not chemically bound, on the surface of the boards during production, and it appears to vary from board to board. The copper loss rate on day 0.25 is predicted (and observed) to be 2.51 $\mu\text{g Cu/cm}^2\text{-d}$ and the long-term loss rate predicted by Equation [7.2] is 0.333 $\mu\text{g Cu/cm}^2\text{-d}$. The higher losses on the first day in this static test were followed by uniformly low losses throughout the remainder of the test. At least two different hypotheses can be proposed to explain this behavior. These two hypotheses will be tested using data developed in the dynamic test, where diluent copper concentrations remained below 147 $\mu\text{g Cu/L}$ at all times.

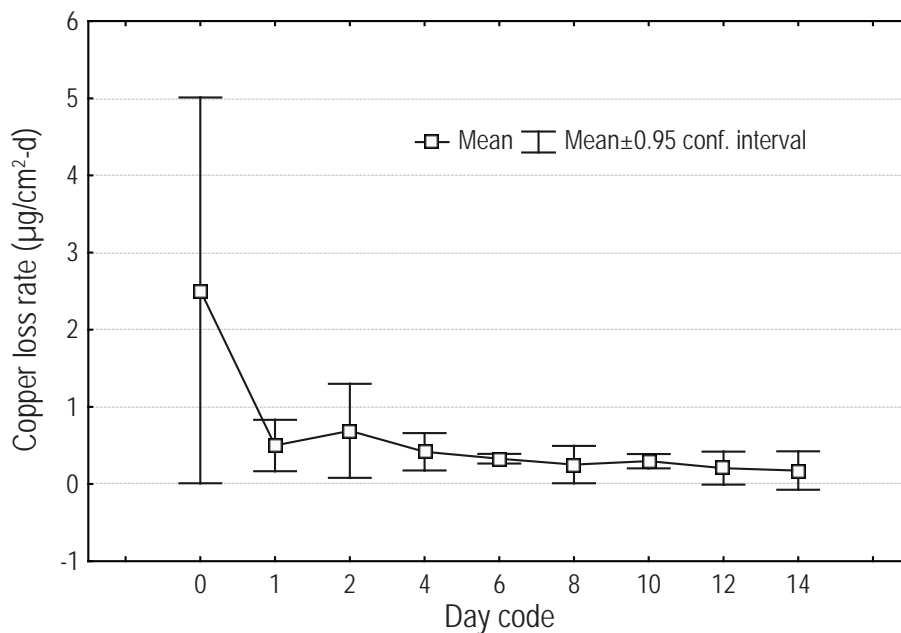


Figure 7.19 Box and 95% confidence interval whisker plot describing copper loss rates from commodity size southern pine lumber treated to a retention of 6.6 kg/m³ with CCA-C and exposed in a freshwater static leaching test.

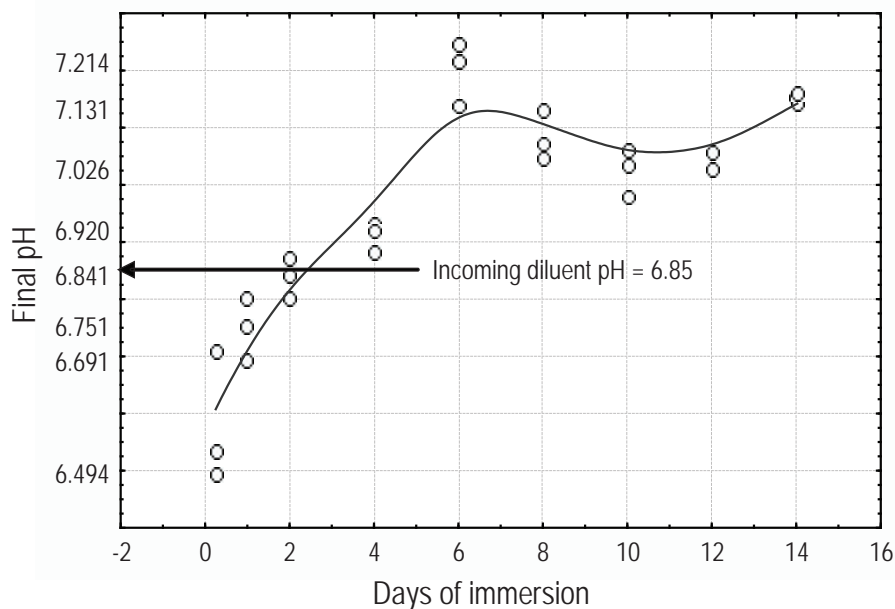


Figure 7.20 Effluent water pH as a function of time during the dynamic leaching study of commodity-size southern pine lumber treated to a retention of 6.6 kg/m³ with CCA-C.

7.2.2.5 Dynamic tests

Due to thermal losses from the distribution manifolds and delivery tubing used with the peristaltic pumps, 100-watt glass immersion heaters were used in each leaching chamber to maintain temperatures at 22.7 ± 0.3°C. Internal flow rates within the tanks averaged 452 L/h. Flow through the tanks was designed at 0.5 ml/s and a flow rate of 0.49 ± 0.02 ml/s was measured.

The response of pH as a function of time is described graphically in Figure 7.20. During the first 6 h of the test, pH declined from 6.85 to 6.58. It steadily increased to >7.0 over the next 6 d and remained there for the remainder of the study. Overall, pH was significantly higher (*t*-test; *t* = 2.68; *p* = 0.01) in the leaching chambers (6.95) when compared with the incoming diluent water (6.85). The pH response was negatively and significantly correlated with

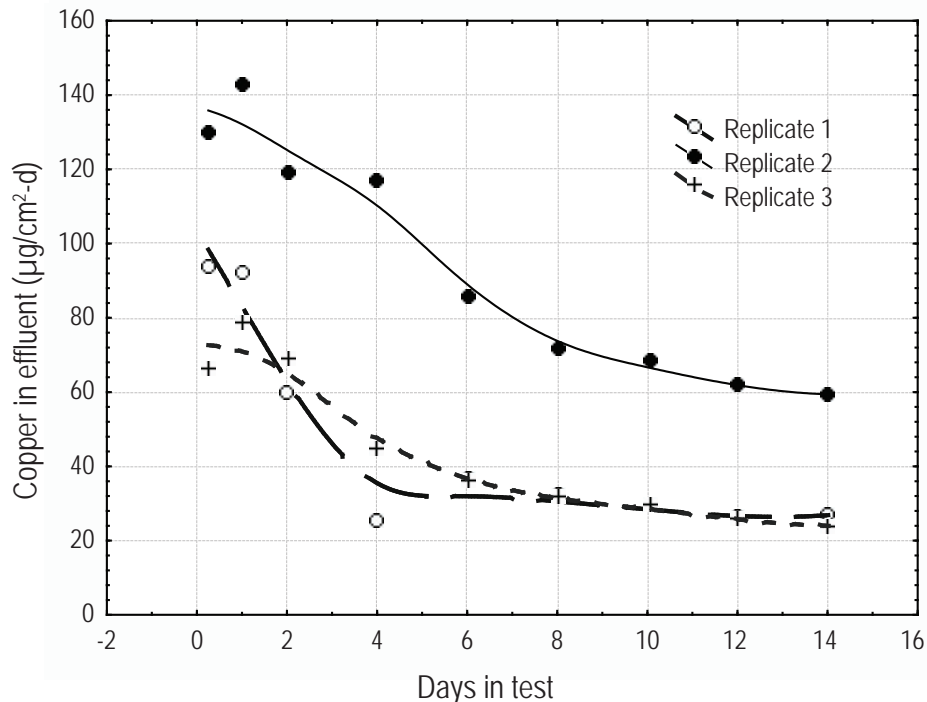


Figure 7.21 Copper concentrations in effluent from dynamic test cylinders containing commodity-size southern pine boards initially treated to a retention of 6.6 kg/m^3 with CCA-C.

copper concentrations (Pearson correlation coefficient = -0.60). It is hypothesized that the initial decrease in pH was associated with the first flush of preservative from the wood and formation of copper oxides. After the first 6 h, the upward pressure on pH associated with wood extractives exceeded the copper influence and the diluent moved toward neutral pH. This hypothesis was not tested.

Copper concentrations in the dynamic test effluent

Copper concentrations measured in the effluent from the tanks are described in Figure 7.21. Unlike the other tests, copper concentrations were less than 147 µg/L in all samples and, with the exception of the first four sampling days in replicate 2, they were less than 100 µg/L . All concentrations were above the method detection limit of 0.50 µg Cu/L achieved for these analyses. Results are described by replicate in Figure 7.21 to emphasize the differences between samples. Distance weighted least squares fits are provided for each replicate in Figure 7.8 to emphasize the temporal consistency of differences between samples.

Predicted copper loss rates using dynamic test methods

Copper loss rates determined from the leaching surface area, water flow rates through the chambers, and copper concentrations in the effluent are summarized in Table 7.9

and Figure 7.22. Note in Table 7.9 that all of the variance:mean ratios were less than one, indicating a regular distribution of loss rates from the three sets of samples, each containing two treated boards measuring $3.9 \times 14.0 \times 50.2 \text{ cm}$. Differences in copper concentrations observed in Figure 7.21 are also apparent in Figure 7.22, with higher variability immediately following immersion and reduced variability between samples as the test progressed. Like the static test, this early variability is hypothesized to be associated with dried, but unbound preservative components on the surface of the boards and perhaps in surficial cell lumens.

A predictive model (Equation [7.3]) was developed using non-linear regression analysis. The constant term describing long-term loss rates was not significant, suggesting that copper losses approached zero asymptotically as a function of time. However, as previously noted in this chapter, the long-term studies (one to two years of immersion) have indicated that loss rates remained measurable and that they were similar to the loss rates observed at the end of 30.5 d. Therefore, the average copper loss rate observed on day 14 of this study ($0.0287 \text{ µg Cu/cm}^2\text{-d}$) was entered into the model as a known constant and the analysis re-run to obtain Equation [7.4] and Figure 7.22.

Table 7.9 Copper loss rates from commodity size southern pine boards treated to a retention of 6.6 kg/m³ with CCA-C preservative and exposed to fresh water in a dynamic (flow-through) test chamber. N = 27.

Day code	Loss rate(mmg/cm ² -d) means	Confidence -95.000%	Confidence +95.000%	Loss rate (mmg/cm ² -d) variance
0.25	4.531	0.815	8.247	2.237
1	1.263	0.225	2.301	0.175
2	0.518	0.135	0.901	0.024
4	0.174	-0.131	0.479	0.015
6	0.096	-0.032	0.223	0.003
8	0.061	-0.018	0.139	0.001
10	0.047	-0.017	0.111	0.001
12	0.035	-0.015	0.085	0.000
14	0.029	-0.010	0.068	0.000

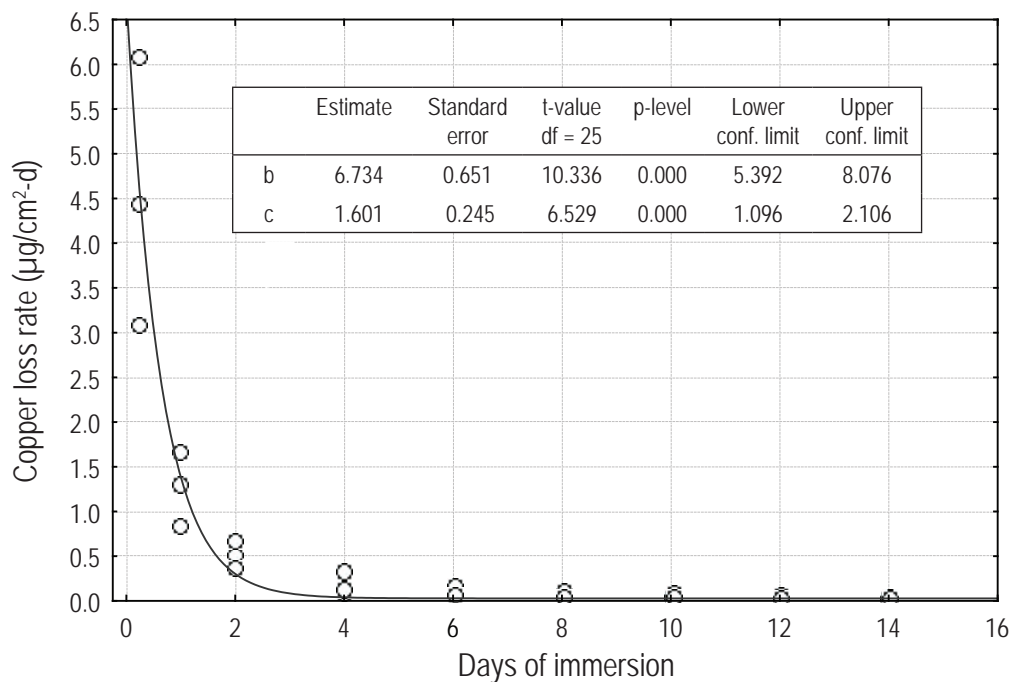


Figure 7.22 Copper loss rates developed from dynamic freshwater leaching data on commodity-size southern pine lumber treated to a retention of 6.6 kg/m³ with CCA-C preservative.

$$\text{Cu loss rate } (\mu\text{g Cu/cm}^2\text{-day}) = 0.029 + 6.734 \times \exp^{(-1.601 \text{ days of immersion})}; R^2_a = 0.91 \quad [7.4]$$

7.2.3 Discussion

The purpose of these tests was to compare results from four protocols historically used to assess aquatic environmental responses to the use of pressure-treated wood containing copper. Random samples taken from a single source of wood treated with CCA-C preservative were used

for these analyses to minimize effects associated with wood species, differences in treating procedures between charges, and subtle differences in post treatment factors affecting preservative fixation and retention. All of the tests were conducted at a nominal temperature of 23°C. The primary differences among the tests reported herein is the proportion of the cell wall lumens exposed to the diluent (end-grain effects and longitudinal compromise of the cell structure associated with grinding); pH of the diluent or extraction fluid; and the maximum concentra-

tions of copper in the diluent. The results for all tests are summarized in Table 7.10 and Figure 7.23.

7.2.3.1 TCLP Tests

The TCLP was originally designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes (EPA 1992). Solid wastes are reduced to pass a 9.5 mm sieve and extracted in one of two fluids. Pressure-treated wood has typically been extracted during TCLP analysis in a buffered solution containing glacial acetic acid and sodium hydroxide with a pH of 4.93 ± 0.05 . In this study, the concentration of copper in the diluent from the ground sample (18,167 $\mu\text{g Cu/L}$) was significantly higher than in the 7-mm-cube diluent (12,266.7 $\mu\text{g Cu/L}$), indicating that size and/or sample size reduction procedures, which are not specified in the TCLP protocol, had a more significant effect on the results than

simply the weight of material, which is specified in the protocol. Figure 7.1 suggests that the grinding process resulted in longitudinal fracturing of cell walls, exposing more of the fixed preservative to the diluent, which would increase the leaching surface area. It is well documented that copper losses from CCA-C treated wood increase at $\text{pH} < 4.5$. Natural surface waters seldom have pH values less than 5.5 or higher than 8.5. The fracturing of cell walls, high wood-surface-area-to-diluent-volume ratios, and high exposure of open-cell lumens across exposed end-grain, combined with low pH, resulted in test conditions that do not characterize the use of pressure-treated wood in constructing bridges, bulkheads, boardwalks, or other structures in natural surface waters. Grinding creates irregular geometries, making a determination of the leaching surface area difficult or impossible. Therefore this procedure is of little value in understanding the environ-

Table 7.10 Predicted early (d 0.67) and long-term (\geq d 14) copper loss rates from CCA-C treated southern pine lumber exposed to four leaching procedures.

Test	Dimensions (cm)	Surface/end-grain	pH	Surface:volume	Day 0.67 loss ($\mu\text{g/cm}^2\text{-d}$)	\geq Day 14 loss($\mu\text{g/cm}^2\text{-d}$)
TCLP ground	<0.7	Unknown	4.9	Large	Not determinable	
TCLP (cubes)	0.7 cm cube	2:1	4.9	8.58:1	21.55	Not determinable
AWPA E11-97	1.9 cm cube	2:1	6.9	3.16:1	22.61	2.60
Commodity static	3.8 × 14.0 × 50.5	End-grain sealed	6.9	0.65:1	0.89	0.33
Commodity dynamic	3.8 × 14.0 × 50.5		7.0	0.65:1	2.33	0.029

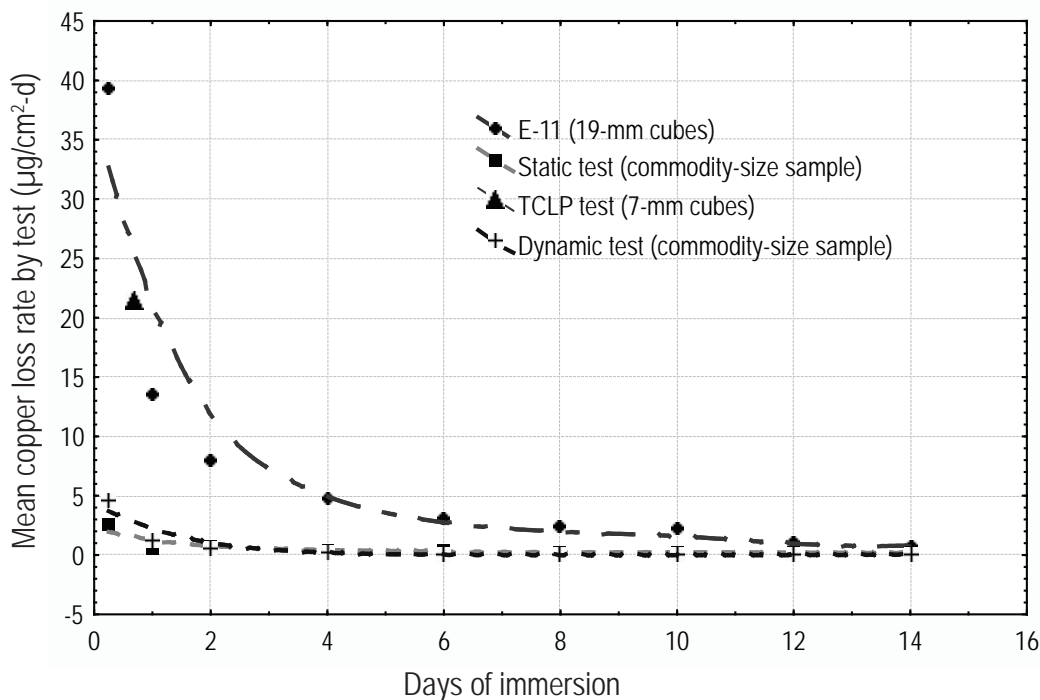


Figure 7.23 Summary results describing predicted copper loss rates from southern pine treated to a retention of 6.6 kg/m³ with CCA-C preservative and exposed using four leaching procedures.

mental risks or managing the use of pressure-treated wood in aquatic environments. It should be noted in Figure 7.20 that the copper loss rate from the 7-mm-cube TCLP test was calculated for the first 18 h of immersion, whereas the other tests were assessed at 6 h. Interestingly, the TCLP value falls on the regression line between the E11 data for 6 h and 24 h suggesting that the two tests gave similar results.

7.2.3.2 AWPA E11-97

This test was developed by the AWPA to measure relative losses of preservative components from small blocks of treated wood and is useful for assessing the preservative efficacy. The basic premise is that for a preservative to demonstrate long-term efficacy, the active ingredients must remain in the wood for as long as possible. The procedure was not designed to assess preservative loss rates to aquatic environments. In this case, the protocols were modified to examine the appropriateness of this protocol for determining metal loss rates to aquatic environments. The initial loss rates for the 7mm TCLP blocks ($21.6 \mu\text{g Cu/cm}^2\text{-d}$) and AWPA E11-97 using 19 mm blocks ($22.6 \mu\text{g Cu/cm}^2\text{-d}$) were both an order of magnitude higher than loss rates observed in the commodity-size lumber tests in which the endgrain was sealed. This suggests that the higher surface-area-to-volume ratios in the cube tests and the higher proportion of open end-grain

surfaces contributed to the higher loss rates that were observed. However, cause and effect relationships in that regard were not pursued in this study.

7.2.3.3 Static and dynamic testing of commodity size lumber

As previously noted, pressure-treated wood used in actual structures typically has low end-grain-to-surface-grain ratios. This situation was mimicked in these tests by sealing the end grain with two coats of reasonably impervious fiberglass resin. The leaching surface area to diluent volume ratio (Table 7.7) of 0.11 was similar to the 0.07 ratio determined for the TCLP test. However, the initial loss rate was 25 times lower in this test with the end-grain sealed than it was in the E11 test having a relatively large area of unsealed endgrain. The predicted long-term loss rate in the commodity static test was eight times lower than in the E11 test, suggesting that higher copper losses across the exposed end-grain continued for at least 14 d. The static and dynamic test results are compared in Figure 7.24.

The dynamic test was conducted at flow rates sufficient to maintain copper concentrations in the diluent below $150 \mu\text{g/L}$ (generally below $100 \mu\text{g/L}$), but higher than the anticipated detection limit of $0.050 \mu\text{g Cu/L}$. The copper loss rate on day 0.25 was significantly higher in the static test than it was in the dynamic test (ANOVA followed by post-hoc testing using Tukey's Honest Significant Difference

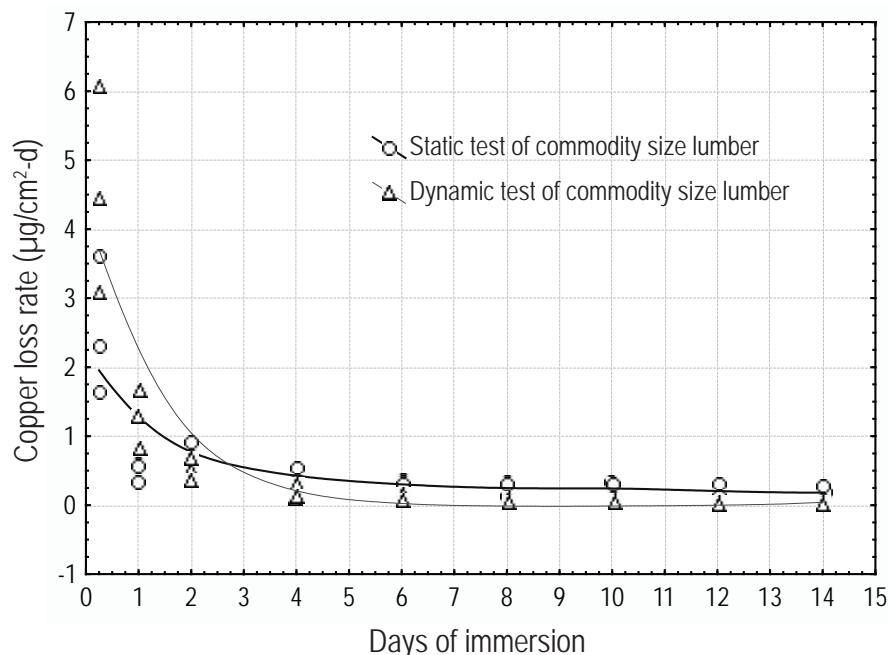


Figure 7.24 Copper loss rates from commodity size samples of southern pine lumber treated to a retention of 6.6 kg/m^3 with CCA-C preserved determined in static and dynamic tests.

test; $p < 0.000$). By the end of d 1 and on following days, however, the differences were not significant ($p > 0.12$).

As noted earlier, Brooks (2002b) initiated dynamic testing in an attempt to address concerns that copper loss rates in static tests using CCA-C treated wood were significantly reduced when the copper concentration in the diluent exceeded 600 to 700 $\mu\text{g Cu/L}$. Copper concentrations in the static diluent reported above exceeded 600 $\mu\text{g/L}$ in one sample collected on the last day of the study. The concentration of unbound copper within the cellular structure of pressure-treated wood is a function of species and preservative. Additionally, the concentration of an active ingredient in the diluent is a function of the surface area of the treated wood sample and the volume of water in the static test. The diluent concentrations at which the diffusion gradient is reduced to a point where further copper loss from the wood is inhibited will be different for different preservatives, different species of wood, and different surface area:volume ratios. These effects are discussed below for ACZA-treated Douglas-fir piling, which is known to lose more copper than CCA-C-treated southern pine piling.

7.2.3.4 Dynamic and static testing of ACZA-treated Douglas-fir piling

Brooks (2007) reported the results of a 2005 study examining Douglas-fir piling treated to 24.5 kg ACZA/ m^3 (1.53 pcf) and immersed in freshwater for 429 d. Initially, these piling

lost 15 to 18 $\mu\text{g Cu/cm}^2\text{-d}$ and at the end of 429 d, the loss rate was 6.9 $\mu\text{g/cm}^2\text{-d}$. Brooks (2007) examined three replicates of Douglas-fir piling treated to a retention of 38.1 kg ACZA/ m^3 (2.38 pcf) in static and dynamic tests using seawater having a salinity of 29 PSU. These tests lasted 28 d. The results of the dynamic test are described in Figure 7.25. Initial loss rates of 40 $\mu\text{g Cu/cm}^2\text{-d}$ declined to <10 $\mu\text{g/cm}^2\text{-d}$ following 10 d of immersion and they were 5.0 $\mu\text{g Cu/cm}^2\text{-d}$ at the end of 28 d. In both of these tests, copper loss rates declined exponentially following immersion and long-term loss rates were 5.0 to 6.9 $\mu\text{g Cu/cm}^2\text{-d}$.

Stanley (1994)b evaluated copper loss rates from three replicate Douglas-fir sapwood blocks measuring $3.8 \times 3.8 \times 30$ cm that were treated to a retention of 40 kg ACZA/ m^3 (2.5 pcf) and immersed in seawater having a salinity of 30 PSU. The test lasted 60 d. Copper concentrations in the static test reached 2,000 $\mu\text{g Cu/L}$ on the second day of immersion and exceeded 16,000 $\mu\text{g Cu/L}$ at the end of 21 d, where they remained for the duration of the study. Consistent with other leaching studies, copper loss rates declined quickly during the first day, followed by further slow declines during the first 45 d of immersion. However, after 45 d, Stanley (1994b) recorded negative loss rates in which the wood took up copper from the diluent. These results suggest that copper concentrations in the wood reached chemical equilibrium with the diluent, which is hypothesized to have inhibited further copper losses from

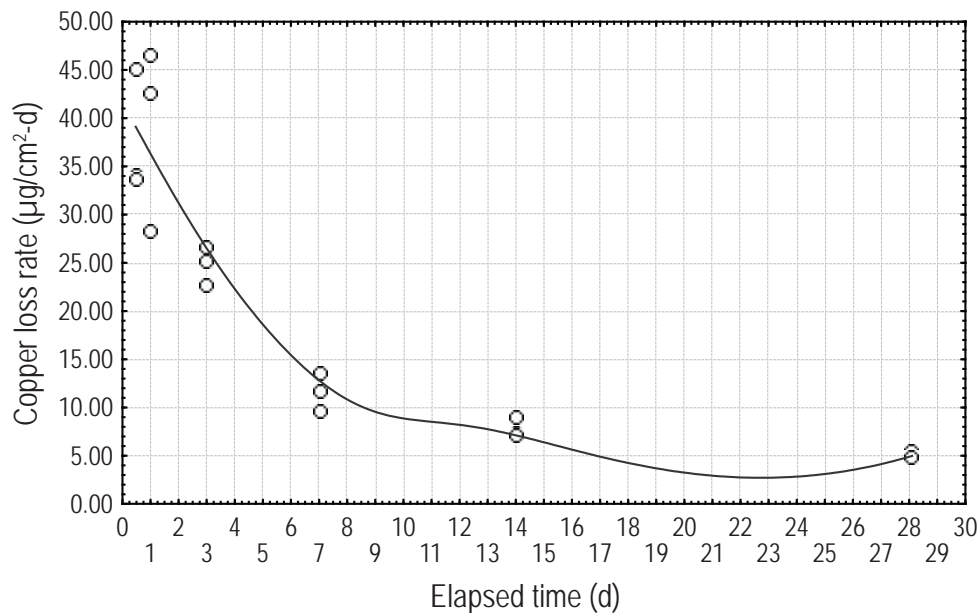


Figure 7.25 Copper loss rates from Douglas-fir piling treated to a retention of 2.38 pcf with ACZA preservative and immersed in a dynamic test using 29 PSU seawater for 28 d.

the ACZA-treated Douglas-fir piling. The copper concentration of 16,000 µg/L in this static test was 27 times higher than the highest copper concentration in the static test of CCA-C described above.

Brooks (2007) conducted additional static testing of different sections from the same Douglas-fir piling used in the dynamic test described in Figure 7.25. The results of this static test were very different from all other tests using ACZA preserved piling. The piling were large in comparison with the volume of static diluent, which contained up to 100,000 µg Cu/L after 7 d and as much as 325,000 µg Cu/L at the end of 28 d. Copper loss rates were constant at ca. 60 µg Cu/cm²-d during the entire 28-d period. An explanation for this may be found in the BMP procedure developed by a Canadian treater, who exposes ACZA-treated piling to rainfall for several weeks to allow unfixed preservative to move from surficial cells to the surface of the wood, creating a deep turquoise patina. The producer then returns the piling to a retort where it is bathed in dilute ACZA, which dissolves the surface deposits, leaving an exceptionally clean product that does not subsequently lose significant copper in a first flush. In this static study, diluent copper concentrations very quickly exceeded 20 to 30,000 µg Cu/L and it is hypothesized that these concentrations were sufficient to dissolve ACZA in surficial layers of wood, leading to the continued high loss of copper.

7.2.3.5 Harmonization of the results of CCA-C and ACZA leaching studies

The point in this discussion is that static testing of Douglas-fir piling treated with ACZA preservative has given inconsistent results. The report of Stanley (1994b) suggested no copper losses after 45 d of immersion, whereas Brooks (2007) found high and sustained copper losses. The cause of these differences has not been rigorously determined. However, it is hypothesized that the low to negative loss rates reported by Stanley (1994b) in a static test were associated with copper concentrations in the diluent of 16,000 µg Cu/L. An opposite effect was observed by Brooks (2007) wherein copper losses remained constant and very high over the entire 28-d static test. This result is hypothesized to have been caused by diluent copper concentrations that quickly exceeded 20,000 µg Cu/L in the first 12 h and were 100,000 to 325,000 µg Cu/L by the end of the study. The point here is that for CCA-C, which loses little copper, the low final copper concentrations in the static diluent (< 650 µg Cu/L) resulted in little difference in loss

rates determined using static or dynamic testing procedures. However, for Douglas-fir treated to a high retention with ACZA preservative, dynamic testing has given consistent results, whereas static results have been highly inconsistent and unusable for purposes of modeling losses.

7.2.4 Summary and recommendations

This report is the first to assess the appropriateness of TCLP, AWWA E11-97, and static and dynamic tests of commodity-size samples for the specific purpose of evaluating preservative loss rates to aquatic environments. The results and analysis reported herein support the following conclusions and recommendations.

7.2.4.1 TCLP and SPLP

Townsend et al. (2003), Dubey et al. (2005), and Nelson et al. (2001) used TCLP and SPLP test protocols in an attempt to assess the environmental response to the use of pressure-treated wood. Each of these protocols was written to answer specific questions. None of these protocols was designed to evaluate preservative loss rates to aquatic environments from immersed pressure-treated wood. The results presented above indicate that TCLP testing of CCA-C-preserved southern pine reduced to 0.7 cm cubes led to an initial loss rate of 21.55 µg Cu/cm²-d. Long-term losses are not determinable using this test. The TCLP does not specify how the tested material should be reduced and these results indicated significantly higher concentrations of copper (18,200 ± 100 mg Cu/L) in the diluent exposed to ground CCA-C treated wood when compared with the 0.7 cm cubes (12,300 ± 1,800 µg Cu/L). The 18-h loss rate of 21.55 µg Cu/cm²-d observed in the 0.7 cm cube test is approximately one order of magnitude higher than observed in either static or dynamic tests of commodity-size products. The higher TCLP losses are likely associated with fracturing of the wood's cellular structure during grinding, to exposure of unsealed end grain, and the low pH (4.9) of the diluent. The TCLP and SPLP tests were not intended for evaluating preservative loss rates to aquatic environments and they are not recommended for that purpose.

7.2.4.2 AWWA E11-97

This 14-d test of 19 mm blocks of pressure-treated wood resulted in an initial (day 0.5) loss rate of 28.07 µg Cu/cm²-d and a long-term loss rate of 2.6 µg Cu/cm²-d. These loss rates were also approximately an order of magnitude

higher than observed in static or dynamic studies of CCA-C-treated, commodity-size samples. The higher loss rates are likely associated with the unsealed end-grain defined by the protocol. In addition, the study reported herein cut the 19 mm cubes from boards that had previously been treated. The E11 protocol requires treatment of the cubes after cutting. Increased uptake of preservative is anticipated into cell lumens exposed across the end-grain cuts. This would likely result in even higher copper loss rates during subsequent testing. Both the TCLP and E11 procedures are conducted using deionized water, which further exacerbates metal losses. The AWPA E11-97 procedure was developed in support of assessing preservative efficacy. This procedure is not recommended for estimating the loss of active ingredients from pressure-treated wood to aquatic environments.

7.2.4.3 Static testing of commodity size products

The static test, with internal circulation using well water with a hardness of 75 mg CaCO₃ and pH = 6.8, resulted in an initial predicted loss rate of 2.51 µg Cu/cm²-d, followed by an exponential decline to a predicted long-term loss rate of 0.33 µg Cu/cm².

These values were similar to those reported for dynamic testing of commodity-size samples from the same stock of wood. Several points should be noted:

- The relatively large size of these samples, 3.8 cm × 13.9 cm × 60 cm, is considered important to averaging the small-scale differences observed by Breslin and Adler-Ivanbrook (1998).
- The surface area to diluent volume in this test was 0.65:1.
- The end-grain was sealed with two coats of fiberglass resin in these static tests.
- Water was recirculated within the leaching tanks at 450 L/h to break-down diffusion gradients and to insure water renewal in wood checks.
- CCA-C loses little copper and concentrations in the diluent did not exceed 657 µg/L.

Other studies reviewed in this discussion suggest that for preservatives having higher copper loss rates, static testing may lead to underestimates of long-term loss rates in some instances and exceptionally high loss rates and lack of predictability in other instances. These results suggest that the use of commodity size samples with sealed end-

grain and low leaching surface area to diluent volume may be appropriate for some species and preservatives. However, in some cases static tests may produce misleading results.

7.2.4.4 Dynamic testing of commodity size samples

Dynamic tests have been specifically designed for evaluating preservative loss rates to surface waters. The tests use ground- and/or surface waters that do not compromise bioassays and that do not subject the samples to unnatural diluents. The use of end-sealed commodity-size samples with vigorous internal circulation of the diluent has resulted in reproducible results useful for developing algorithms supporting computer models for predicting risk. The dynamic nature of the tests allows researchers to modify flow rates to maintain the concentration of preservative active ingredients above method-detection limits, but below concentrations that will inhibit further migration of preservative from the treated wood. The dynamic testing system described in this chapter also allows for the maintenance of pH and temperature in the diluent entering the test chambers. Southern pine and hem-fir have been shown to be effective at buffering diluents toward neutral. Static test diluents will therefore change pH toward neutral during testing, requiring periodic addition of acid or base to the chambers in which the tests are conducted. In contrast, the dynamic tests continuously modify the pH prior to introduction of diluent to the tanks, providing a more continuous pH environment.

7.2.4.5 Recommendation for assessing preservative loss rates from immersed pressure-treated wood

These results indicate that SPLP, TCLP, and AWPA E11-97 or other tests using small blocks of wood with unsealed end grain are inappropriate for assessing the loss of wood preservative active ingredients to surface waters. Static testing may provide acceptable results for some preservatives in some conditions. However, in other cases, static testing may significantly bias the results. Dynamic testing allows the testing of commodity-size samples of pressure-treated wood under continuously controlled pH, temperature, and concentration of active ingredients and this procedure is recommended for assessing the loss of preservative to surface waters. The use of samples that have leaching surface areas of several thousand square centimeters with end-grain sealed is recommended, as is the recirculation of water within the leaching chambers.

7.3 SUMMARY OF LOSS RATES TO AQUATIC ENVIRONMENTS FROM IMMERSSED PRESSURE-TREATED WOOD

With the noted exceptions of pentachlorophenol and creosote, the following algorithms have been determined using the dynamic leaching system described above.

7.3.1 ACQ-B

This preservative contains 66.7% copper as CuO and 33.3% quaternary as didecyldimethylammonium chloride (DDAC). Brooks (1998a) developed the following algorithms for predicting environmental concentrations of copper and DDAC released from 17.2 cm dia southern yellow pine posts treated to an average retention of 6.89 kg ACQ-B/m³, using static test data in 1997. Copper loss rates (Equations [7.5] and [7.6]) were found to be dependent on time of immersion and diluent pH. DDAC loss rates were not significantly affected by pH (Equation [7.7]).

$$\text{Copper loss } (\mu\text{g}/\text{cm}^2\text{-d}) \text{ for days } < 4.5 = 265.14 \times \exp^{(-0.924 \times \text{day} - 0.239 \times \text{pH})} \quad [7.5]$$

$$\text{Copper loss } (\mu\text{g}/\text{cm}^2\text{-day}) \text{ for days } \geq 4.5 = 4.25 \times \exp^{(-0.0175 \times \text{day})} \quad [7.6]$$

$$\text{DDAC loss } (\mu\text{g}/\text{cm}^2\text{-day}) = 77.25 \times \exp^{-1.534 \times \text{day}} \quad [7.7]$$

Loss rates for the two components were initially similar; however, DDAC loss rates declined faster and reached undetectable concentrations after 4.5 d of immersion. Brooks (1998a) reviewed available toxicological data for DDAC and proposed a water quality benchmark of 49 μg DDAC/L. This value is an order of magnitude less toxic than

copper in all but the hardest of surface waters, and if copper is managed to be less than or equal to the USEPA copper Water Quality Criteria (WQC), then DDAC should not stress aquatic organisms. For this reason, only copper was assessed in follow-on studies of ACQ-C.

7.3.2 ACQ-C or Alkaline Copper Quat-Type C

This preservative contains 66.7% copper as CuO and 33.3% Quat (alkylbenzyltrimethylammonium chloride). Southern pine decking (3.8 × 14.0 × 60 cm long) treated to between 2.68 and 6.12 kg ACQ-C/m³ with and without water repellent and 8.9 × 8.9 × 60 cm southern pine posts treated to 4.0 to 6.4 kg ACQ-C/m³ were tested in a dynamic freshwater system at pH = 7 and T = 15°C. Copper loss rates for the six ACQ-C treatments are summarized in Table 7.11. Coefficients of determination for these algorithms varied between R²_a = 0.93 and 0.98. Figure 7.26 describes the temporal response curves for three ACQ retentions of 2.5, 4.0, and 6.4 kg/m³. As expected, increased loss rates were associated with higher retentions; however, the degree of these differences diminished toward the end of the study. All of the treatments demonstrated similar temporal responses.

CA-B. Copper Azole – Type B contains 96.1% copper as Cu and 3.9% tebuconazole. Southern pine decking (8.9 × 14.0 × 60 cm) treated to 3.94 kg CA-B/m³ (0.246 pcf) was immersed in the dynamic freshwater test system at three temperatures (5, 15, and 25°C) and three pH values (5.5, 7.0, and 8.5) with 450 gph internal recirculation for 30.5 d. The AWWA standard (C2) for soil and freshwater use is 3.3 kg CA-B/m³ and therefore the decking was slightly overtreated. Long-term loss rates were determined after 414 d of immersion (Table 7.12). There is no AWWA standard for CA-B use in seawater. Effluent samples in the CA-B dynamic study were collected in 250 ml amber Nalgene

Table 7.11 Predicted copper loss rates on days 0.5, 2.0, 20.5 and 365.5 from six ACQ-C treatments. The loss rates in parentheses are those predicted using algorithms developed during the initial 30.5 d study. Preservative and water repellent retentions are in kg/m³.

Preservative and retention (kg/m ³)	Loss rate algorithm Log ₁₀ (copper loss rate)		Predicted Cu loss rates (μg/cm ² -d)				
			Day 0.5	Day 2.0	Day 30.5	Day 365.5	
Code	ACQ-C	Water repellent	Loss algorithm				
Blue lumber	4.95	6.12 UW	1.659 – 0.626*Log ₁₀ (Time)	70.4 (62.1)	29.5 (34.3)	5.37 (3.5)	0.27 (3.5)
Blue posts	7.13		1.815 – 0.637*Log ₁₀ (Time)	101.6 (59.3)	42.0 (48.0)	7.40 (6.6)	0.35 (6.6)
Green lumber	4.24		1.473 – 0.568*Log ₁₀ (Time)	44.1 (47.9)	20.0 (23.2)	4.26 (6.1)	0.28 (6.1)
Red lumber	2.68	4.28 WR2	1.399 – 0.518*Log ₁₀ (Time)	35.9 (33.8)	17.5 (20.5)	4.27 (5.1)	0.36 (5.2)
Red posts	6.40	4.65 WR2	1.659 – 0.440*Log ₁₀ (Time)	61.9 (50.2)	33.6 (37.3)	10.14 (11.9)	1.23 (3.5)
Yellow lumber	3.02	5.92 UW	1.519 – 0.673*Log ₁₀ (Time)	52.7 (35.3)	20.7 (26.0)	3.31 (2.9)	0.13 (2.9)

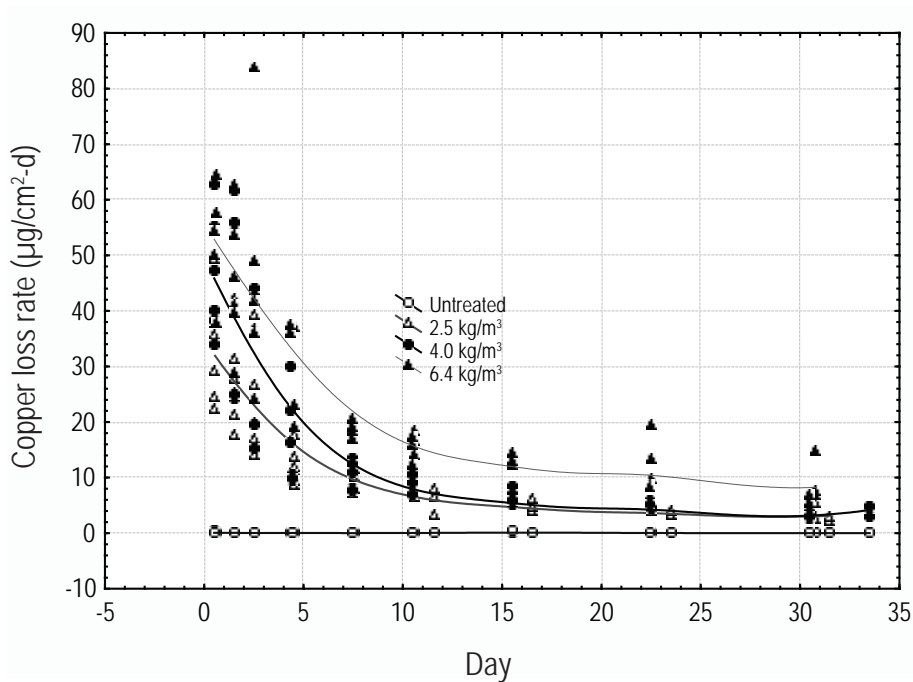


Figure 7.26 Copper loss rates from untreated posts and those treated with between 2.5 and 6.4 kg ACQ-C/m³ observed in a 30.5 d leaching study at pH = 7.0 and T = 15°C.

Table 7.12 Examples of (a) copper loss rates and (b) tebuconazole loss rates on d 0.5 and long term (415 d) from southern pine posts treated to a retention of 0.246 pcf with CA-B preservative. All loss rates are in µg Cu or TEB/cm²-d.

Temperature (°C)	pH	Initial (0.5 d) loss rate (µg/cm ² -d)	Long-term (415 d)
(a) Predicted copper loss rates			
5.0	5.5	43.72	1.14
15.0	5.5	50.61	1.14
25.0	5.5	58.61	1.14
5.0	7.0	32.87	5.11
15.0	7.0	37.36	5.11
25.0	7.0	42.58	5.11
5.0	8.5	19.95	1.84
15.0	8.5	22.88	1.84
25.0	8.5	26.28	1.84
(b) Predicted tebuconazole loss rates			
5.0	5.5	1.47	0.14
15.0	5.5	2.04	0.14
25.0	5.5	2.87	0.14
5.0	7.0	1.06	0.14
15.0	7.0	1.46	0.14
25.0	7.0	2.03	0.14
5.0	8.5	0.78	0.14
15.0	8.5	1.05	0.14
25.0	8.5	1.45	0.14

bottles and stored at 4°C until analyzed by Bayer Industry Services' LanXess Deutschland Laboratory in Uerdingen, Germany. The data were analyzed to produce Equation [7.8] for copper loss rate and Equation [7.9] for tebuconazole (TEB).

$$\mu\text{g Cu/cm}^2\text{-day} = 6.49/(\exp(\text{abs}(\text{pH} - 7.24))) + 203.12 \times \exp^{(-0.14 \times \text{day} - 0.285 \text{ pH} + 0.015 \text{ T})} \quad [7.8]$$

$$R^2_a = 0.89$$

$$\mu\text{g TEB/cm}^2\text{-day} = 0.140 + 4.628 \times \exp^{(-0.164 \times \text{day} + 0.036 \times \text{T} - 0.245 \times \text{pH})} \quad [7.9]$$

$$R^2_a = 0.74$$

The stability of tebuconazole under the study conditions was assessed by spiking 250-ml diluent samples to a concentration of 5,000 µg TEB/L on days 0.5, 15, and 30 of the test. The spiked samples were stored and shipped with the treatment samples. Subsequent analysis revealed concentrations of 5,513.4; 5,067.8; and 4,270.3 µg TEB/L or a mean of 4,950.5 ± 1,565, which was not significantly different from the spiked value of 5,000 µg TEB/L (*t* = -0.136, *p* = 0.90). This test is not very robust with an *N* = 3; however, the results suggest no breakdown of tebuconazole or absorption to the Nalgene™ sample bottles during sample collection, shipment to Germany, and analysis.

The portion of Equation [7.8] describing long-term loss rates determined in the dynamic test system after 414 d of immersion may seem unnecessarily complicated and deserves explanation. A scatter plot of the data with the fitted regression is provided in Figure 7.27.

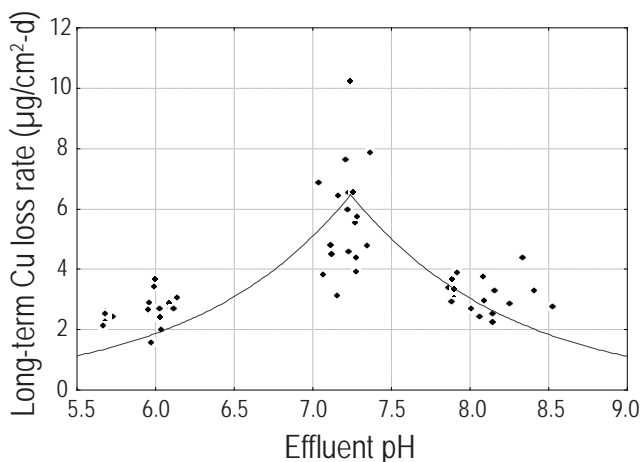


Figure 7.27 Predicted values and actual data describing the effect of pH on long-term copper loss rates from CA-B preserved wood.

Intuitively, one might not expect the observed higher copper loss at neutral pH. The higher loss rates at pH 7.0 were not associated with one or two high values, as would be expected with contamination of the samples. Rather the loss rates were grouped around the three pH values. All of the regression coefficients were significant (*p* < 0.000) and the resulting expression explained 52% of the variation in the data. Dr. Gene Pasek (Arch Treatment Technologies, personal communication, 2002) hypothesized that hydroxide ions suppress copper solubility at pH 8.5. The solubility product (*K*_{sp}) for copper hydroxide can be used to describe an equilibrium copper concentration of 1.6 × 10⁻⁸ moles/liter. At pH = 7.0, the equilibrium value is 3 orders of magnitude higher at 1.6 × 10⁻⁵ moles/liter. These values do not include any contribution from carbonate ions, which can also inhibit leaching as pH increases. Decreased copper losses at the lower pH of 5.5 were likely associated with silicon, which was measured at 13.4 and 12.8 mg Si/L in both the AES and PESC diluent. Pasek's previous work in understanding the fixation of Wolman E (unpublished) indicated that copper silicates were more readily formed at reduced pH. At pH = 8.5, silicate plays a minor or no role in preventing copper leaching from CA-B. However, as the pH declines, silicates become increasingly important, and at pH 5.5, it is likely that copper silicates form inside the wood, inhibiting copper loss.

A simpler approach would be to use the overall mean long-term loss rate of 3.83 µg Cu/cm²-d as a constant describing long-term loss rates. However, because metals are modeled to accumulate in sediments over the life of a project, accurate long-term loss rate determinations are important. In this case, the use of the an overall mean would have predicted loss of 922 g of copper from a 30-cm dia piling immersed in 2 m of water over 35 y. The algorithm, based on actual data suggests that the loss rate at pH = 7.24 would be nearly twice as high at 6.29 µg Cu/cm²-d, resulting in a 35-y copper loss of 1,515 g of copper. As will be seen in Chapter 9, the distribution of this copper and its potential effects on sensitive species depends on current speeds and the nature of adsorption nuclei. The significance of the differences between a simple average and the more complicated, but more accurate, model presented in Equation [7.8] is warranted in light of the conservative approach taken in modeling the environmental response to pressure-treated wood.

The following points were considered important in summarizing this study.

- The appearance of three abnormally high copper loss rates from the same piece of wood on each of the first 3 sample days at 25°C suggested that predictions made by Equations [7.7] and [7.8] may infrequently be exceeded. The fact that these high values occurred early in the study suggests that they were associated with surficial residues or shallow sub-surface conditions and, therefore, the frequency of occurrence of these high loss rates might be reduced or eliminated by the incorporation of appropriate BMPs during production.
- The increased sensitivity to temperature and pH during the first 4.5 d of immersion suggests that these losses may have been associated with poorly bound copper and tebuconazole that was released at higher temperatures or which was more soluble at the lower pH. It appears that once these poorly bound molecules were lost from the wood, the strength of the bonds for better-fixed preservative was greater than the bond breaking forces generated by random energy (temperature) and/or the ability of excess hydrogen ion activity to release them within the range of temperatures and pH values tested.
- Both control and treated samples of southern pine buffered the pH of diluent water toward a nearly neutral value of 7.4. This observation may be important in developing a standardized method for evaluating preservative losses to aquatic environments in the real world as a function of receiving water pH.
- Tebuconazole loss rates were low at all times, pH values and temperatures.
- An increased long-term copper loss rate at pH = 7.0 when compared with pH 5.5 or 8.5. Pasek suggested

that the observed differences were real and were explained by the interaction of silicate and free hydrogen ions with copper.

7.3.3 CCA-C loss to fresh water and seawater

CCA-C contains 47.5% hexavalent chromium as CrO₃, 18.5% copper as CuO and 34% arsenic as As₂O₅. Numerous leaching studies are available describing the loss of copper, chromium and arsenic from CCA-C treated wood. Brooks (2002b) integrated all of the various studies to produce Equations [7.10] (copper), [7.11] (chromium), and [7.12] (arsenic).

Arsenic losses are significantly a function of salinity and immersion time, while chromium loss is a function of

$$\begin{aligned} \text{Copper loss } (\mu\text{g Cu/cm}^2\text{-day}) = & \quad [7.10] \\ (0.036 \times T + 0.021 \times (S + 0.01) - 0.002 \times & \\ R - 0.031 \times \text{pH}) + 6.946 \times & \\ \exp^{0.007 \times R + 0.12 \times T + 0.02 \times S - 0.2839 \times \text{pH} - 1.379 \times \text{day}} & \end{aligned}$$

$$\begin{aligned} \text{Chromium loss } (\mu\text{g Cr/cm}^2\text{-day}) = & \quad [7.11] \\ 0.047 \times \exp^{-0.13 \times R + 0.103 \times T - 1.074 \times \text{day}} & \end{aligned}$$

$$\begin{aligned} \text{Arsenic loss } (\mu\text{g As/cm}^2\text{-day}) = & \quad [7.12] \\ 0.010 \times S + 0.754 \times \exp^{-0.130 \times \text{day}} & \end{aligned}$$

temperature and immersion time. Day 0.5 and Day 100 loss rates for each of the metals are summarized in Table 7.13. The first line in the copper loss-rate algorithm describes the long-term loss rate and the second line describes short-term loss rate as a function of temperature (T), salinity (S), retention (R), and pH, all of which significantly affect copper loss rates.

These results indicate that copper loss rates are higher in 30 PSU seawater compared with fresh water. Long-term

Table 7.13 Day 0.5 and 100 loss rates of copper, chromium, and arsenic from southern pine pressure treated with CCA to retentions of 12.8 kg/m³ (0.8 pcf) for freshwater use and 40 kg/m³ (2.5 pcf) for marine use (30 PSU). Temperature was assumed to be 15°C; freshwater pH = 7.0 and seawater pH = 8.0.

Use	Retention (kg/m ³)	Day 0.5 Loss Rate (μg/cm ² -d)	Day 100 Loss Rate (μg/cm ² -d)
Freshwater copper	12.8	3.51	0.302
Freshwater chromium	12.8	0.11	<0.000
Freshwater arsenic	12.8	0.71	<0.000
30 PSU seawater copper	40.0	5.48	0.841
30 PSU seawater chromium	40.0	0.03	<0.000
30 PSU arsenic	40.0	1.02	0.315

loss rates are among the lowest for all waterborne preservatives. Very little chromium has been observed leaching from fixed CCA-C-treated wood, and arsenic losses have been shown to be low and intermediate between those of chromium and copper.

7.3.4 ACZA in fresh water and saltwater

This preservative contains 50% copper as CuO, 25% zinc as ZnO, and 25% arsenic as As₂O₅. Depending on the species of wood, AWPA Standards require treatment of fresh-water piling to 12.8 or 16.0 kg/m³ (1.0 pcf). The standard for marine piling is 40 kg/m³ (2.5 pcf) in higher hazard waters south of San Francisco and 24 kg/m³ (1.5 pcf) in lower hazard waters in and north of San Francisco. This preservative is used primarily to treat western species such as Douglas-fir and mixed hemlock and true-fir that are difficult to treat with CCA-C. ACZA has proven to be a difficult preservative to model because subtle differences in treating procedures create measurable differences in metal loss rates.

The uncertainties in ACZA metal loss rates as a function of production techniques are described in Brooks (2005c), who examined the efficacy of various treating procedures for minimizing preservative loss from a single 70-ft long Douglas-fir piling that was sectioned and treated to nominal ACZA retentions 16.0 kg/m³ (1.0 pcf) for immersion in fresh water or 24.0 kg/m³ (1.5 pcf) for use in temperate latitude seawater. Three treated samples plus an untreated control were examined in each study. The short-term study was conducted for 30.5 d in a dynamic system. Long-term loss rates were determined in the dynamic system following 429 d of immersion in fresh water. Differences in metal loss rates associated with the eight post-treatment practices will be discussed in more detail in Chapter 9. Copper loss rates to fresh water for three different BMPs are described in Table 7.14, together with predicted short- and long-term loss rates. There are several points that should be emphasized in these results.

- In fresh water, short-term (day 0.5) copper loss rates varied by as much as a factor of three between 13.7 and 39.6 µg/cm²-d, depending on how the piling were produced. Long-term copper loss rates were more consistent, varying between 2.32 and 3.30 µg/cm²-d.
- In general, higher loss rates were observed with fast (120 gph) internal circulation of the seawater diluent

than were observed by gently circulating seawater within the dynamic test chambers using air. This was especially true with respect to the long-term loss rates of copper and arsenic and the short-term loss rate of zinc.

- The best-fit regressions developed for copper loss to seawater and arsenic loss to fresh water had the low coefficients of determination (0.62 and 0.10). Arsenic losses were generally low, but less predictable than those for copper or zinc.
- Loss rates of all three metals from ACZA-treated piling were more predictable in seawater than in fresh water.

The following algorithms will be used for purposes of modeling environmental responses to the use of ACZA treated wood:

Freshwater — Douglas-fir or hem-fir treated to 1.0 pcf with ACZA

$$\text{Cu migration } (\mu\text{g Cu/cm}^2\text{-day}) = 1.246 \times \exp^{-0.381 \times \text{Log}_{10}(\text{day})}; R_a^2 = 0.82 \quad [7.13]$$

$$\text{As migration } (\mu\text{g As/cm}^2\text{-day}) = 0.876 - 0.0017(\text{day}); R_a^2 = 0.10 \quad [7.14]$$

$$\text{Zn migration } (\mu\text{g Zn/cm}^2\text{-day}) = 2.67 + 20.59 \times \exp^{-0.609 \times (\text{day})}; R_a^2 = 0.61 \quad [7.15]$$

Seawater — Douglas-fir treated to 1.5 pcf with ACZA

$$\text{Cu migration } (\mu\text{g Cu/cm}^2\text{-day}) = 10^{(0.837 + 0.504 \times \text{EXP}(-0.287 \times \text{Time}(\text{days}))} \quad [7.16]$$

$$\text{As migration } (\mu\text{g As/cm}^2\text{-day}) = 0.54 \quad [7.17]$$

$$\text{Zn migration } (\mu\text{g Zn/cm}^2\text{-day}) = 5.76 \quad [7.18]$$

7.3.5 Pentachlorophenol

Connor (1994) examined pentachlorophenol loss rates to fresh water in a static study using 11 in. long by 10 in. dia sections of two southern pine utility poles treated to 0.5 pcf (8 kg/m³) with pentachlorophenol. This is the AWPA standard for soil and freshwater use of this pre-

Table 7.14 Copper, arsenic, and zinc loss rates ($\mu\text{g}/\text{cm}^2\text{-day}$) and initial (Day <1.0) and long-term (Day ≥ 30.5) loss rates from ACZA-treated piling as a function of end use (freshwater or saltwater immersion); internal diluent circulation rates (slow or fast); and post-treatment air, ACZA bath, ammonia, or kiln-dried BMPs.

End-use	BMP treatment	Water circulation	Loss rate algorithm	Loss rates ($\mu\text{g}/\text{cm}^2\text{-d}$)		
				Day 0.5	Day ≥ 30.5	
Copper loss rates						
Freshwater	1.0 pcf; air	Slow	$\text{Log}_{10} \text{ Loss} = 1.099 \cdot \exp^{-0.423 \cdot \text{Log}(\text{day})}$; $R_a^2 = 0.87$	17.7	2.32	
Freshwater	1.0 pcf; ammonia	Slow	$\text{Log}_{10} \text{ Loss} = 1.422 \cdot \exp^{-0.388 \cdot \text{Log}(\text{days})}$; $R_a^2 = 0.94$	39.6	3.30	
Freshwater	1.0 pcf; kiln	Slow	$\text{Log}_{10} \text{ Loss} = 1.215 - 0.3038 \cdot \text{Log}_{10}(\text{day})$; $R^2 = 0.93$	13.7	2.60	
Prediction using all freshwater data				$\text{Log}_{10} \text{ Loss} = 1.246 \cdot \exp^{-0.381 \cdot \text{Log}_{10}(\text{day})}$; $R_a^2 = 0.82$	25.0	2.90
Saltwater	1.5 pcf; air	Slow	$\text{Log}_{10} \text{ Loss} = 0.837 + 0.504 \cdot \exp^{-0.287 \cdot \text{day}}$; $R_a^2 = 0.62$	18.78	6.87	
Saltwater	1.5 pcf; ammonia	Slow	$\text{Log}_{10} \text{ Loss} = 0.837 + 0.504 \cdot \exp^{-0.287 \cdot \text{day}}$; $R_a^2 = 0.62$	18.78	6.87	
Saltwater	1.5 pcf; kiln	Slow	$\text{Log}_{10} \text{ Loss} = 0.837 + 0.504 \cdot \exp^{-0.287 \cdot \text{days}}$; $R_a^2 = 0.62$	18.78	6.87	
Saltwater	1.5 pcf; ACZA bath	Fast	Not a function of time	15.95		
Saltwater	1.5 pcf; ammonia	Fast	Not a function of time	16.86		
Arsenic loss rates						
Freshwater	1.0 pcf; air	Slow	$\text{Loss} = 0.876 - 0.0017 \cdot \text{day}$; $R_a^2 = 0.10$	0.88	0.20	
Freshwater	1.0 pcf; ammonia	Slow	$\text{Loss} = 0.876 - 0.0017 \cdot \text{day}$; $R_a^2 = 0.10$	0.88	0.20	
Freshwater	1.0 pcf; kiln	Slow	$\text{Loss} = 0.876 - 0.0017 \cdot \text{day}$; $R_a^2 = 0.10$	0.88	0.20	
Saltwater	1.5 pcf; air	Slow	$\text{Loss} = 0.216 + 4.45 \cdot \exp^{-0.0174 \cdot \text{day}}$; $R_a^2 = 0.68$	4.63	2.83	
Saltwater	1.5 pcf; ammonia	Slow	Not significantly a function of time	0.54		
Saltwater	1.5 pcf; kiln	Slow	Not significantly a function of time	0.54		
Saltwater	1.5 pcf; ACZA bath	Fast	Not significantly a function of time	1.81		
Saltwater	1.5 pcf; ammonia	Fast	Not significantly a function of time	5.19		
Zinc loss rates						
Freshwater	1.0 pcf; air	Slow	$\text{Loss} = 0.92 + 28.8 \cdot \exp^{-0.271 \cdot \text{day}}$; $R_a^2 = 0.79$	25.97	0.92	
Freshwater	1.0 pcf; ammonia	Slow	$\text{Loss} = 1.96 + 24.04 \cdot \exp^{-0.770 \cdot \text{day}}$; $R_a^2 = 0.95$	18.32	1.96	
Freshwater	1.0 pcf; kiln	Slow	$\text{Loss} = 1.82 + 8.68 \cdot \exp^{-0.323 \cdot \text{day}}$; $R_a^2 = 0.85$	9.21	1.82	
Prediction using all freshwater data				$\text{Loss} = 2.67 + 20.59 \cdot \exp^{-0.609 \cdot \text{day}}$; $R_a^2 = 0.61$	17.85	2.67
Saltwater	1.5 pcf; air	Slow	$\text{Loss} = 4.12 + 26.83 \cdot \exp^{-0.364 \cdot \text{day}}$; $R_a^2 = 0.79$	18.49	4.12	
Saltwater	1.5 pcf; ammonia	Slow	Not significantly a function of time	6.56		
Saltwater	1.5 pcf; kiln	Slow	Not significantly a function of time	5.76		
Saltwater	1.5 pcf; ACZA bath	Fast	$\text{Loss} = 3.29 + 27.03 \cdot \exp^{-1.79 \cdot \text{day}}$; $R_a^2 = 0.70$	14.33	3.29	
Saltwater	1.5 pcf; ammonia	Fast	$\text{Loss} = 5.46 + 29.13 \cdot \exp^{-0.541 \cdot \text{day}}$; $R_a^2 = 0.85$	24.55	5.46	

servative. Triplicate treated samples and an untreated control were examined in unbuffered fresh water and fresh water buffered at pH 5, 7, and 9 and in an acidic environment (0.1 normal HCl). The temperature varied between 18.3 and 22°C. Samples were collected on days 1, 3, 7, 14, 21, and 30 and analyzed using high performance liquid chromatography (HPLC) The ends of the pole above the water were sealed to minimize evaporation of penta but the immersed ends were not. Connor found that the longitudinal diffusivity (along the grain) was seven times higher than radially (around the growth rings) or tangentially (perpendicular to the growth rings). This observation supports the need to seal the exposed end-grain because

the bottom of utility poles is buried in soil or sediment. Connor’s (1994) failure to seal the immersed end-grain unrealistically exacerbated penta losses in this study. However, the author also did not account for the potential breakdown of penta in the static diluent during the 30-d study and this could have caused an underestimation of the loss rates—particularly in the later stages. However, this is the best data available and it was used by Brooks (1998b) to develop the following algorithm (Equation [7.19]).

$$\text{Penta migration } (\mu\text{g}/\text{cm}^2\text{-day}) = 10.9 \times \exp^{-0.255 \times \text{Day} + 0.355 \times \text{pH} + 0.01}; R_a^2 = 0.73 \quad [7.19]$$

7.3.6 Creosote

Creosote is not an artificially blended mixture, but rather a product of the distillation of coal tar. Sparacino (1999b) identified up to 129 compounds representing >0.5% of North American P1/P13 and P2 creosote oils. Sixteen of the polycyclic aromatic hydrocarbon compounds (PAH) are considered priority pollutants by the EPA. These *parental* PAH have been the focus of most studies of creosote and their physicochemical properties and toxicity characteristics are well known. Sparacino's (1999b) analysis accounted for 92% to 96% of the compounds in raw North American creosote that contained 34.4% low molecular weight PAH (LPAH) and 16% to 17% high molecular weight PAH (HPAH), representing 50% to 51% total PAH (Σ PAH). Much of the remainder was composed of naphthalene (10.8%) and phenanthrene (4.1%) congeners and benzo-furans (4.4%). As demonstrated by Goyette and Brooks (1998), large portions of the naphthalene, acenaphthylene, acenaphthene, and fluorene are lost to process water during the treatment of wood. The proportion of these more soluble compounds observed in raw creosote oil is compared with their concentrations in expressates from 8-y-old weathered piling and piling treated using WWPI/CITW (1996) BMPs in Figure 7.28. This data is presented to emphasize that bioassays and/or leaching studies assessing the environmental response to creosote treated wood must use the actual leachate and not dose water with whole creosote oil if meaningful data are to be obtained. This is particularly true when wood is treated using BMPs.

The point in this discussion is that creosote is a complex mixture of organic compounds having different solubilities (32 mg/L for naphthalene to 0.0003 for benzo[ghi]perylene); different binding potentials to organic carbon (Log Koc = 2.97 for naphthalene to 7.19 for dibenzo[a,h]anthracene); and different potentials for evaporation (Pv (mPa) = 11,600 for naphthalene and 0.00001 for ideno[1,2,3-cd]pyrene). Brooks (1995) provides a more complete review of these characteristics. This complexity poses significant challenges in measuring migration rates of creosote from pressure-treated wood because some compounds will dissolve in the water and the hydrophobic HPAH will not. Those that do not will likely adsorb to any available organic moieties, including sample bottles, leaching chambers, etc. Some of the LPAH will evaporate and/or rapidly degrade along photochemical and bacterial pathways. The result is that there are no comprehensive studies providing high quality data describing the loss of creosote oil from pressure-treated wood. With these caveats, Brooks (1997a) developed a model based on the available information. Theoretical considerations suggest that creosote loss from immersed treated wood is a function of preservative retention, wood species, salinity, and water temperature. Empirical data is available describing losses as a function of temperature and salinity from southern yellow pine. Inter-study comparisons are confounded by differing retentions. All of the data were therefore normalized to the average historical retention of 359.1 kg/m³ (22.3 *pcf*) measured in 2200 marine piling produced in the Pacific Northwest.

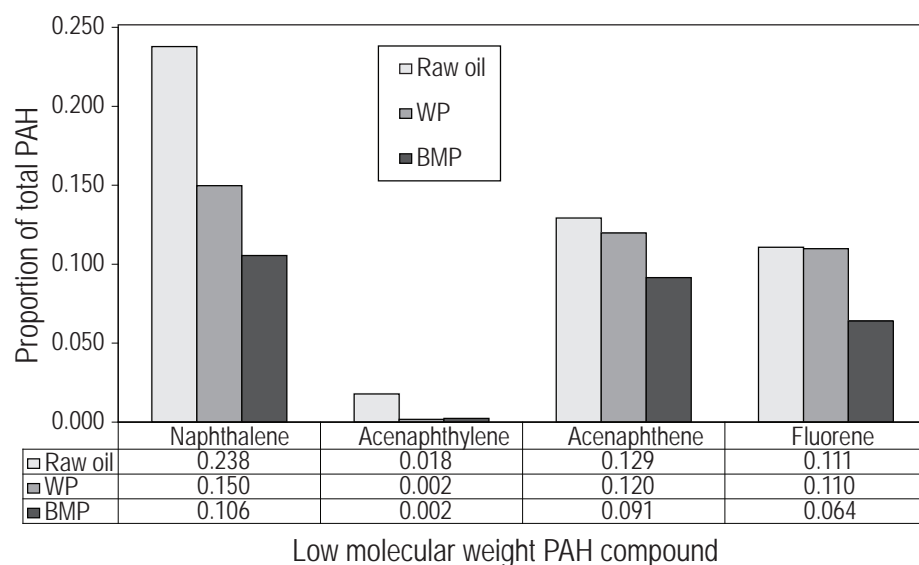


Figure 7.28 Proportion of naphthalenes, acenaphthylenes, acenaphthene, and fluorene in raw creosote preservative and in piling freshly treated using BMPs and in weathered piling (WP) in the Sooke Basin Creosote Evaluation Study (Goyette and Brooks 1998).

7.3.6.1 Temperature and salinity

Miller (1977) immersed three 2-m-long sections of piling, treated to 490.6 kg/m³ (30.7 pcf), in Yaquina Bay, Oregon USA, where water temperatures varied seasonally between 8.8 and 12.0°C, for 8 y. He determined the residual creosote retention within the wood, resulting in data predicting an average loss rate of 30 µg/cm²-d over the 8-y period. The results were highly variable, with two of the piling showing an increase in retention during the first year. That is likely because of the inherent variability in retention over small spatial scales in wood and because the oil continues to migrate within the wood after treatment. The highest quality loss data available are those of Ingram et al. (1982), who immersed whole piling sections in seawater and small blocks of southern yellow pine, treated with marine grade creosote to between 354.3 or 378.4 kg/m³ (22.1 to 23.6 pcf), in fresh and saltwater at temperatures of 20°, 30°, or 40°C. Fifteen parental PAH were observed in the diluent. The study was confounded by degradation of the PAH, which peaked at 72 h and then declined. Brooks (1997a) used regression analysis on data from Ingram et al. (1982), Graham (data from AWPAs with no study specifics provided), and Miller (1977) to determine the basic loss algorithm given in Equation [7.20]:

$$\text{PAH migration (M)} = (24.4 \pm 22.0) + (0.78 \pm 0.70) \times T - (0.58 \pm 0.44) \times S \quad [7.20]$$

7.3.6.2 Temporal changes in creosote migration rates

Baechler et al. (1970) found that creosote losses approached steady state after 6 mo of immersion, and Lebow and Morrell (1988) found no significant losses from creosote-treated panels after the first 3 mo of their 12-mo study. Quantitative data was provided by Ingram et al. (1982), who determined a loss rate of 19.3 µg ΣPAH/cm²-d from newly treated and air-dried piling and 8.0 µg ΣPAH/cm²-d from 12-y-old piling. Brooks (1997a) fitted an exponential model to these data to determine the following temporal characteristic (Equation [7.21]).

$$\text{PAH migration}_{(t=0)}^{\text{(time)}} = \text{Migration}_{(t=0)} \times \exp^{(\text{age in years}/10)} \quad [7.21]$$

It should be emphasized that this algorithm is based on a small database; however, it predicts that creosote loss rates will be halved in 6.9 y and is therefore very conservative in light of other findings (Baechler et al. 1970; Lebow and Morrell 1988).

7.3.6.3 Migration of creosote as a function of preservative retention

Quantitative data describing preservative loss rates as a function of retention were not found. Brooks (1997a) assumed that higher loss rates would occur at higher retentions and used the following algorithm in the absence of data (Equation [7.22]).

$$\text{PAH migration}_{(\text{retention})} = \text{Migration}_{(359.1 \text{ kg/m}^3)} \times \exp^{((\text{measured retention}/359.1) - 1)/2} \quad [7.22]$$

The algorithm predicts an increase of 18% in PAH loss rates at 481 kg/m³ (30 pcf) when compared with loss rates at 359 kg/m³ (22.3 pcf).

7.3.6.4 Combined creosote model

These combined algorithms provide a basis for estimating loss rates from creosote-treated wood to aquatic environments; however, it should be noted, that high-quality data describing PAH loss rates from creosote treated wood are not presently available. In defense of the model, field verification studies have shown that it predicts slightly higher accumulations of PAH in sediments and concentrations in water than are actually observed, making the model somewhat conservative from an environmental point of view. Nevertheless, the predictions have proven surprisingly accurate (Equation [7.23]).

$$\Sigma \text{PAH migration } (\mu\text{g } \Sigma \text{PAH/cm}^2\text{-day}) = (24.4 + 0.78 \times T - 0.58 \times \text{salinity}) \times \exp^{((\text{retention}/359.1 - 1)/2) - (\text{age}/10)} \quad [7.23]$$

where,

T = Temperature in °C

Salinity in parts per thousand (‰)

Age in years

Retention in kg creosote/m³

For purposes of estimating acute toxicity associated with dissolved PAH migrating from immersed, creosote-treated lumber during the first few days of immersion, Brooks (2005d) developed the following model based on the report of Kang et al. (2004). Time is measured in days and flow is the current speed measured in cm/s (Equation [7.24]).

$$\text{Dissolved } \mu\text{g } \Sigma \text{PAH/cm}^2 = \{2.56 \times \exp^{-0.432 \text{Log}_{10}(\text{time}) + 0.279 \text{Flow}}\}^2 \quad [7.24]$$

7.4 DETERMINATION OF PRESERVATIVE LOSS RATES TO RAINWATER

Pressure-treated wood used in overhead portions of structures can release wood preservative active ingredients to aquatic environments in association with rainwater runoff. For instance, a 2-m-wide pier deck that is 10 m long will have a leaching surface area of 291,200 cm² including the vertical faces of 3.8-cm-thick decking. If the deck is supported on 20-cm-dia piling spaced 2 m on center and immersed in 2 m of water, then the 12 piling will have an immersed leaching surface area of 150,796 cm² or about half that associated with the overhead structure.

7.4.1 Methods for assessing the concentration of active ingredients in rainwater runoff

The concentration of wood preservative ingredients in rainwater runoff is dependent on the intensity of the rainfall and its pH, condition of the decking, preservative retention and the total rain that fell on the decking.

7.4.1.1 Study design

The studies reported here were undertaken to evaluate concentrations of active ingredients in runoff associated with natural rainfall in the Pacific Northwest over a period of one to two years. Three or four treated replicates and an untreated control were evaluated in each study.

7.4.1.2 Deck samples

The wood used in these studies was standard eight quarter or five quarter decking treated to AWWA standards for aboveground use. The wood was kept under cover after treating and was shipped wrapped in plastic. Control wood, from the same stock of lumber used to create the decking, was wrapped separately. In all cases, retention was measured by an independent agency. Boards not meeting the AWWA standard were rejected for testing. Random boards were taken from each pack for analysis. Approximately 5 cm was removed from one end and then a single, 60-cm-long sample was cut from the board. A one-centimeter-thick dam was constructed around the board from untreated stock of the same species. The space between the dam and the deck sample was sealed with General Electric Silicone I™ silicon seal. A one-centimeter-diameter hole was drilled in one end of the board to allow runoff to enter the sample bottle. An HDPE cap, with a 2.5-cm hole drilled in its center was permanently attached to the underside of each board with a ring of silicone seal and stainless steel screws. The boards were spaced 12 cm apart on a rack attached to a fence in a manner providing 6 mm of fall along the length of the board and 3 mm of fall along the width to direct runoff into the pre-drilled hole. In most cases, a piece of tight fitting Tygon™ tubing was used to line the hole. This is described in Figure 7.29.

The first flush of rainwater runoff was collected, followed by samples taken at 5-inch (12.7 cm) intervals until



Figure 7.29 Example of pressure-treated decking samples evaluated during rainwater runoff studies.

a total of 45 inches (114.3 cm) of rain had fallen on the decking.

Hourly weather information, including temperature, wind, rainfall, and humidity, was recorded during each study using a remote transmitting Davis Vantage Pro™ Weather Station coupled with Weather Link® software. pH was measured immediately after collecting samples on each sampling day using a Thermo Orion Model 290A pH/ISE meter equipped with an Orion™ Low Maintenance Triode probe Model 9107. The meter and probe were calibrated using a three-point (pH = 4.0, 7.0, and 10.0) procedure just prior to use. Rainwater and/or snowmelt were collected separately in a graduated beaker for determination of rainwater pH.

7.4.1.3 Analytical chemistry

Depending on the specific preservative used, a variety of pesticide residues were evaluated in rainwater runoff to include copper, zinc, arsenic, chromium, tebuconazole, propiconazole, and imidacloprid. Analytical chemistry was performed by independent laboratories accredited by at least one state or the federal government. Quality assurance included blanks, duplicates and spiked samples.

Statistical analysis

Analytical results (μg active ingredient/L of runoff) were used to develop algorithms predicting concentration as a function of accumulated rainfall.

7.4.2 Results

The laboratory conducting these studies lies in the rainshadow of the Olympic Mountains in Washington State. Average rainfall between 2002 and 2008 has been 19.7 ± 1.6 in. Most of the rain falls from October through June of each year, with monthly amounts generally varying between 1.2 and 4.4 in. Rainfall is typically light and infrequently exceeds 4 in./mo or 0.3 in./h. During these studies, rainfall pH was 6.8 ± 0.6 . During 2004 and 2005, the minimum recorded rainwater pH was 6.4 and the maximum was 7.3. Figure 7.30 describes copper concentrations in runoff during five sequential rainfall events as a function of accumulated rainfall (cm) on four ACQ-C treatments and one CCA-C treatment. $N = 4$ for all treatments.

Consistent with the immersion studies, a first flush of copper was observed, followed by an exponential decline in preservative concentration. Also note that for the four ACQ-C treatments, there was a direct relationship between the concentration of copper in the first flush and preservative retention in the samples. The addition of water repellants appeared to have little effect on preservative loss rate. Also note that variability within each treatment converged to single values after the first 28 cm of rain had fallen on the decking. It could be hypothesized that preservative concentrations in rainwater runoff from pressure-treated wood cycle seasonally with periods of increasing and decreasing rain. This hypothesis is substantiated by

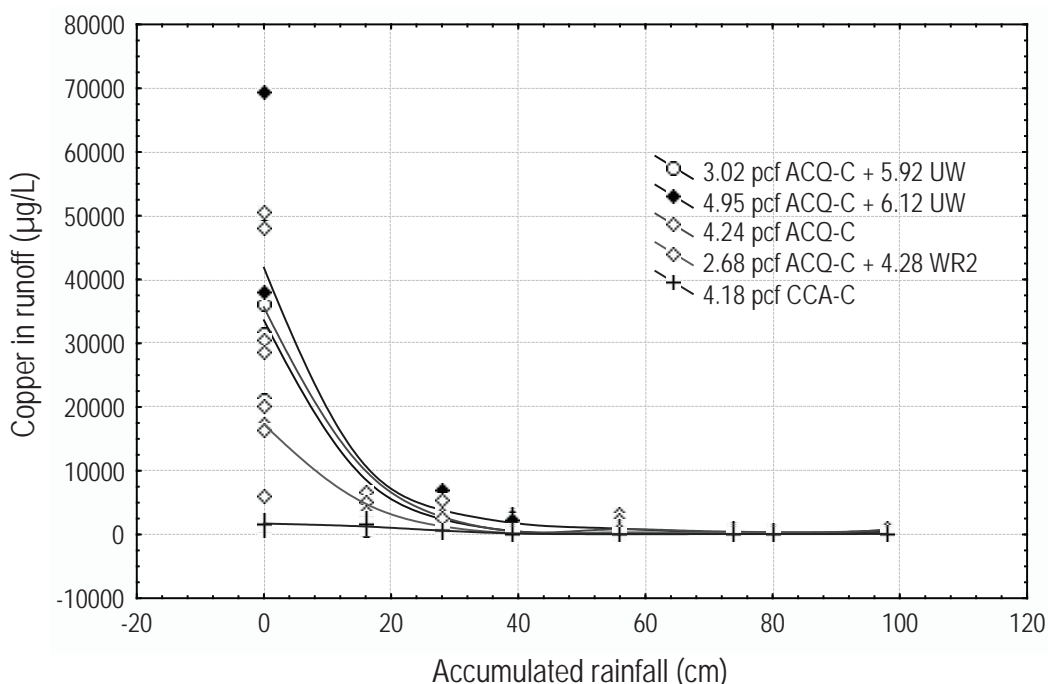


Figure 7.30 Copper concentrations in runoff from southern pine decking treated with ACQ-C and CCA-C copper based preservatives and exposed to rainwater in the Pacific Northwest.

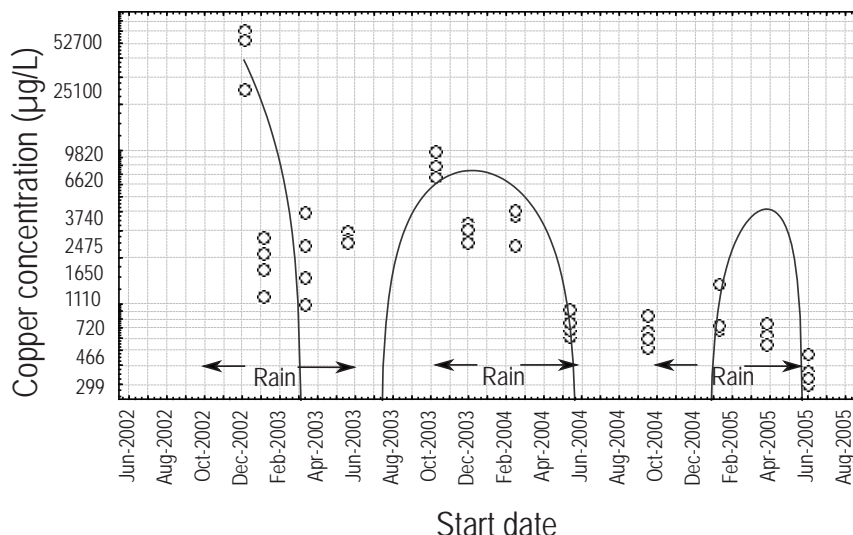


Figure 7.31 Copper concentrations in rainwater runoff from southern pine decking preserved to a retention of 0.10 pcf with copper azole. The October 1 to June 1 rainy season on Washington State’s Olympic Peninsula is highlighted with horizontal arrows.

the data provided in Figure 7.31 demonstrating a periodic cycling of copper concentrations in runoff from copper azole (CA-B) treated southern pine. The fit is a fifth-order polynomial showing a general correlation between increased runoff during the first significant rainfall events occurring in late fall and early winter. However, it should be noted that copper concentrations are presented on a logarithmic scale (y-axis) and that peak copper concentrations declined exponentially from one year to the next over the 3-y study.

Algorithms for predicting the concentration of wood preservative active ingredients in rainwater runoff from pressure-treated decking

Except as otherwise noted, the following algorithms have been developed from data collected using the aforementioned protocols. These algorithms will be used to drive the overhead models described in Chapter 9. Note that AR (measured in inches) is accumulated rainfall.

7.4.2.1 Copper azole-Type B (CA-B)

Southern pine 3.8-cm-thick decking treated to 0.10 pcf. See also Figure 7.31.

$$Cu (\mu\text{g/L}) = 47,414 - 13,671 \times AR + 1,337 \times AR^2 - 55.2 \times AR^3 + 1.008 \times AR^4 - 0.0067 \times AR^5 \quad [7.25]$$

$$\text{Tebuconazole concentration } (\mu\text{g TEB/L}) = 1064.6 \times \exp^{(-0.129 \times AR)} \quad [7.26]$$

7.4.2.2 Copper naphthenate (CuN)

Copper concentrations in runoff from mixed hemlock and true fir 3.8-cm-thick decking treated to 0.44 pcf with CuN were low during the first rainfall event and this event was not included in the analysis.

$$Cu (\mu\text{g/L}) = 1,232 + 38,901 \times \exp^{-0.229 \times AR} \quad [7.27]$$

$$R_a^2 = 0.91$$

7.4.2.3 ACZA

Significant variability among the replicates led to low coefficients of determination and non-significant coefficients on rainfall for arsenic and zinc during the 2-y study of four replicate pieces of Douglas-fir decking treated to a retention of 6.4 pcf with ACZA preservative. The results for this study are summarized in Figure 7.32. Zinc and arsenic losses to rainwater were moderately low and fairly constant throughout the study. The coefficients on accumulated rainfall (AR) were not statistically significant, indicating constant losses. Consistent with the immersion studies, copper loss between replicates was highly variable throughout the study.

$$\text{Copper } (\mu\text{g/L}) = 2465 - 31.2 \times AR \quad [7.28]$$

$$R_a^2 = 0.11$$

$$\text{Arsenic } (\mu\text{g/L}) = 795 \quad R_a^2 = 0.02; \quad [7.29]$$

coefficient on AR NS (p = 0.17)

$$\text{Zinc } (\mu\text{g/L}) = 198; \quad R_a^2 = 0.02; \quad [7.30]$$

coefficient on AR NS (p = 0.19)

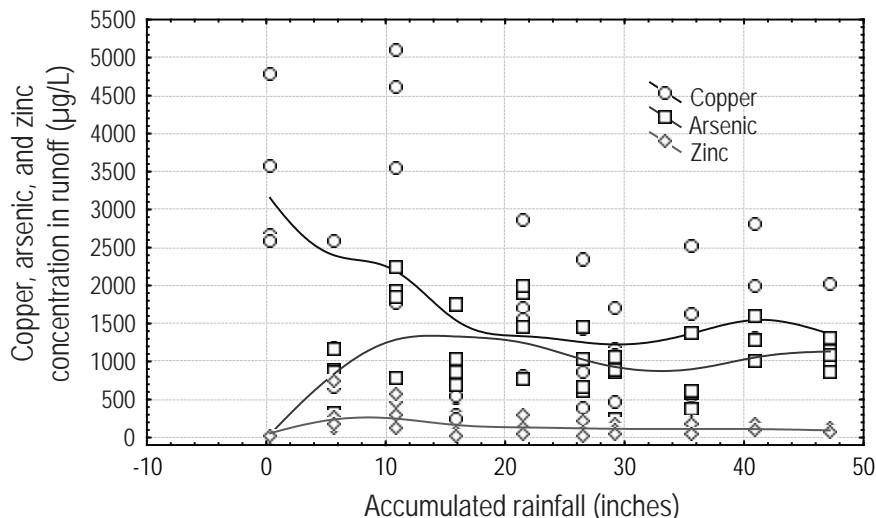


Figure 7.32 Copper, arsenic, and zinc concentrations in rainfall runoff from Douglas-fir boards treated to a retention of 6.4 kg/m³ with ACZA preservative.

7.4.2.4 CCA-C

Like the ACZA results, arsenic and chromium concentrations in runoff at 5 and 10 in. of rainfall were elevated above the initial concentrations in three replicate pieces of southern pine treated to a retention of 4.18 pcf (see Figure 7.24). The concentrations of arsenic were reasonably constant at 500 µg As/L, as was chromium at 100 µg Cr/L (see Figure 7.30) as total rainfall increased.

$$\text{Copper } (\mu\text{g/L}) = 1842 \times \exp^{-(0.037 \times \text{AR})} \quad R_a^2 = 0.66 \quad [7.31]$$

$$\begin{aligned} \text{Arsenic } (\mu\text{g/L}) &= 1595 \times \exp^{-(0.005 \times \text{AR})} & [7.32] \\ R_a^2 &= 0.18 \end{aligned}$$

$$\begin{aligned} \text{Chromium } (\mu\text{g/L}) &= 206 \pm 68 & [7.33] \\ \text{only the constant term} &\text{ was significant} \end{aligned}$$

7.4.2.5 ACQ-C

Four replicate samples of southern pine treated to 4.24 kg/m³ (0.26 pcf) with no added water repellent were evaluated over 75 cm (29.5 in.) of accumulated rainfall. Copper concentrations in the runoff were similar between replicate samples, leading to a reasonably robust algorithm that explained 85% of the variation in the dataset. See also Figure 7.30.

$$\begin{aligned} \text{Copper } (\mu\text{g/L}) &= 1842 \times \exp^{-(0.037 \times \text{AR})} & [7.34] \\ R_a^2 &= 0.66 \end{aligned}$$

7.4.2.6 Wolman AG™

This preservative contains 5% propiconazole, 5% tebuconazole, and 0.5% imidacloprid in a working solution con-

taining 600 mg/L of the active ingredients. It is currently used only above ground, with the AWPA Standard requiring a retention of 0.52 kg/m³ (0.013 pcf) when treated with a water repellent and 0.72 kg/m³ (0.018 pcf) when no water repellent was used. In anticipation of a possible use of this preservative above fresh water, prestained, mixed hemlock and fir decking (3.8 cm × 14.0 cm × 60 cm long) treated to 3.2 kg WAG/m³ (0.20 pcf) was exposed to a total of 49.2 cm (19.4 in.) of natural rainfall in the Pacific Northwest between October 17, 2004 and June 21, 2005. Figure 7.33 describes tebuconazole concentrations in runoff as a function of accumulated rainfall for the four replicates evaluated in this study.

$$\begin{aligned} \text{Log}_{10} \text{Imidacloprid } (\mu\text{g/L}) &= & [7.35] \\ 1.14 + 1.45 \exp^{-(0.174 \times \text{AR})} & \quad R_a^2 = 0.88 \end{aligned}$$

$$\begin{aligned} \text{Log}_{10} \text{Tebuconazole } (\mu\text{g/L}) &= & [7.36] \\ 1.91 + 1.87 \exp^{-(0.249 \times \text{AR})} & \quad R_a^2 = 0.93 \end{aligned}$$

$$\begin{aligned} \text{Log}_{10} \text{Propiconazole } (\mu\text{g/L}) &= & [7.37] \\ 0.93 + 1.81 \exp^{-(0.254 \times \text{AR})} & \quad R_a^2 = 0.88 \end{aligned}$$

7.4.2.7 Pentachlorophenol

Morrell and Simonsen (2004) examined runoff from Douglas-fir lumber pressure treated with pentachlorophenol in P9 Type A oil to a retention of 8.0 kg/m³ (0.5 pcf). Their studies examined 8 replicates in three temperatures between 15 and 35°C and three rainfall rates varying between 0.2 and 1.2 cm/h. Dissolved and solid penta was determined in runoff using high-resolution gas chroma-

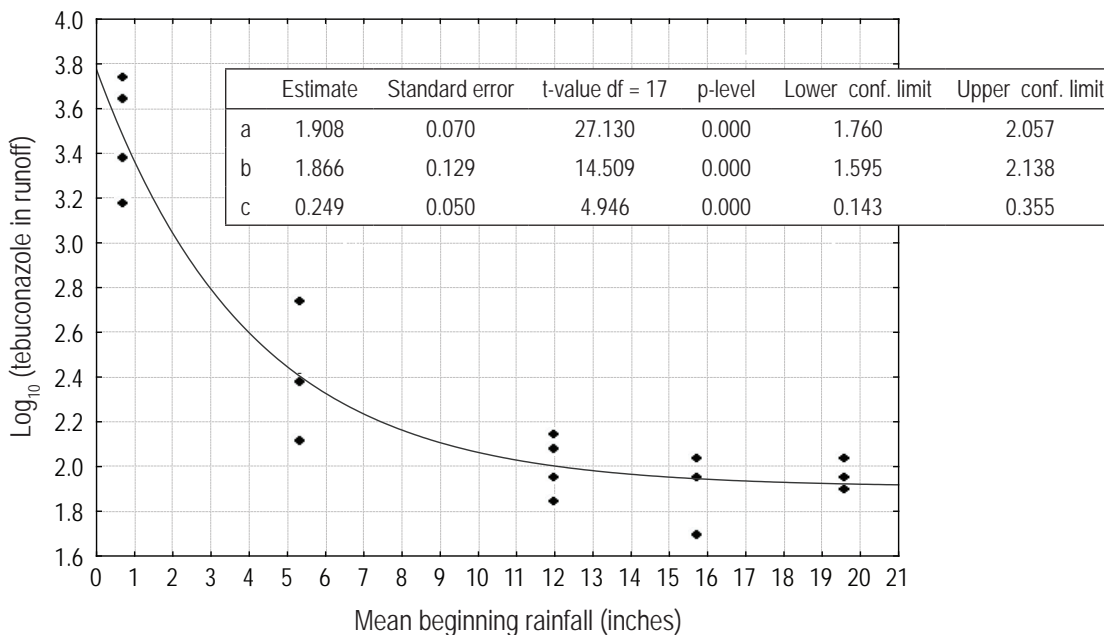


Figure 7.33 Log10 transformed tebuconazole concentrations ($\mu\text{g TEB/L}$) in rainwater as a function of total rainfall. $R^2_a = 0.93$. Model is $V14 = a + b \cdot \exp(-c \cdot V7)$ (WAG Rainwater Study Database). Dep. var.: $\text{LOG}_{10}(\text{TEB})$. Level of confidence: 95.0% ($\alpha = 0.050$).

tography with a low-resolution mass-spectrometer detection system (HRGC-LRMS) having a $0.025 \mu\text{g/L}$ detection limit. Brooks (2003) used this data to develop the algorithm provided below (Equation [7.38]). Penta concentrations were not significantly a function of temperature within the tested range of 15 to 35°C ($p = 0.61$).

$$\text{Pentachlorophenol } (\mu\text{g/L}) = 17.0 \times 10^{-0.020} \times \text{Time (h)} - 0.0104 \times \text{Rainfall (cm/h)} \quad [7.38]$$

7.4.2.8 Creosote

Xiao et al. (2001) estimated PAH concentrations in rainwater runoff from commodity-size samples of Douglas-fir treated to $192 \text{ kg P1/P3 creosote/m}^3$ (12 pcf). The wood was heated with a 250-watt halogen lamp to $68\text{--}70^\circ\text{C}$ ($154\text{--}158^\circ\text{F}$) prior to exposure to artificial rain falling at a rate of 10 cm/h for 40 min. Runoff samples were collected 10 min after initiating the rainfall. The runoff was filtered on 2 micron glass filters. The filters were extracted using methylene chloride and both the filtrate and extraction fluid were analyzed using SPME GC. The results indicated that the initial temperature of the wood was quickly reduced by the rainwater and was not a factor in creosote loss rates. They also concluded that solubility of the PAH limited its concentration in the runoff rather than the migration rate

of PAH from the wood. Brooks (2005d) used their data to develop the following algorithm predicting the concentration of PAH in rainwater runoff from creosote-treated wood used in overhead structures.

$$\mu\text{g } \Sigma\text{PAH/L} = 0.302 + 0.420 \times \exp^{-0.032 \times \text{AR}} \quad [7.39]$$

$$R^2_a = 0.90$$

7.4.2.9 Micronized copper preservatives

Total copper, tebuconazole, and propiconazole were measured in rainwater runoff from three replicates of southern pine decking treated to a retention of 0.08 pcf with Wolman Dispersed CA-C™. Total copper concentrations in runoff from southern pine decking preserved with 0.244 pcf with Osmose Smartsense™ preservative were also evaluated in this study which lasted for 2 y, during which 96.5 cm (38 in.) of rain fell on the six samples and an untreated control. The copper data was analyzed in Statistica™ Version 6.1 to obtain Equation [7.40] describing copper concentrations in the runoff as a function of total rainfall and retention. Equations [7.41] and [7.42] describe tebuconazole and propiconazole concentrations in runoff from Dispersed CA-C™ preserved decking. Despite several attempts, no laboratory was found capable of measuring didecylidimethylammonium carbonate (DDACarb) in runoff from the Smartsense™ preserved decking.

$$\begin{aligned} \text{Copper (mg/L)} = & \quad [7.40] \\ 1.26 \times \exp^{-0.069 \times \text{Accumulated rainfall (inches)} + 3.637 \times \text{Retention (pcf)}} & \\ R_a^2 = 0.82 & \end{aligned}$$

$$\begin{aligned} \text{Tebuconazole (\mu g TEB/L)} = & \quad [7.41] \\ 25.95 \times \exp^{-0.220 \times \text{Accumulated rainfall (inches)}}: R_a^2 = 0.89 & \end{aligned}$$

$$\begin{aligned} \text{Propiconazole (\mu g PROP/L)} = & \quad [7.42] \\ 33.56 \exp^{-0.301 \times \text{Accumulated rainfall (inches)}}: R_a^2 = 0.93 & \end{aligned}$$

7.5 SUMMARY

The purpose of the leaching studies described in this chapter is to support computer models designed to predict environmental concentrations of the active ingredients of pesticides used to preserve wood used in and over surface waters. The accuracy of these models can be no better than the loss rate algorithms used to drive them. As shown in Section 7.2., tests designed to evaluate contaminant loss to low pH land-fill environments (TCLP) or to evaluate preservative efficacy (AWPA E-11) will grossly overestimate preservative loss rates to aquatic environments. The comparative studies reported herein also demonstrate the need to seal the ends (cross-grain) of samples. Wood is a natural product and small samples have been shown by Breslin and Adler-Ivanbrook (1998) to vary significantly in their retention of preservative. Therefore, it appears important to either conduct a very large number of leaching studies on small samples or to average the small-scale variation in retention by evaluating commodity-size samples. Most of the work reported in this chapter has been accomplished on 3.8×14 cm lumber, 8.9×8.9 cm square posts, or piling >20 cm dia. All of the samples were 60 cm in length. The number of samples required is likely inversely related to the sample size used. An optimum sample size has not been rigorously determined. Until that work is accomplished, the sample sizes reported herein are recommended.

The studies with ACZA-preserved piling described in this chapter support the need for rigorous circulation or stirring of the diluent to insure that all leaching surface areas, including those inside checks, are continually flushed. In addition, the work described herein indicates that diluent volumes must be designed to maintain the concentration of active ingredients below those that might inhibit further loss from the wood. Both treated and untreated wood have been shown to buffer the pH of diluents

toward neutral—making maintenance of specific pH environments difficult during static testing. These problems can be resolved by using dynamic testing that allows excellent control of preservative concentrations, temperature, and pH in diluents. Inorganic acids or sodium hydroxide are recommended for amending pH in diluents unless the study is specifically designed to assess the environmental response in low pH surface waters containing high concentrations of humic acid.

Immersion and rainwater runoff studies indicate that a *first flush* of preservative should be anticipated during initial exposure to surface or rainwater. For all preservatives but ACZA, loss rates declined exponentially with exposure to water. In addition, the initial variability between replicate samples typically diminishes with time. It is hypothesized that the first flush is associated with surface deposits of preservative remaining after production and with poorly bound preservative in surficial layers of wood. The evaluation of production methods to minimize this first flush will be discussed in Chapter 10. Coefficients of determination have typically been >0.70 , suggesting that preservative loss rates can be used for purposes of modeling environmental responses. ACZA has proven to be difficult to model because of the high variability between samples, which does not diminish shortly after immersion or with accumulating rainfall.

For purposes of evaluating acute toxicity associated with dissolved leachates, it is the highest concentrations of preservative observed during the first one to three days following immersion that are important. These concentrations will be highest within a few centimeters of the wood's surface and they will be diluted as they are transported away from the piling. Environmental effects associated with sedimented active ingredients are a function of their accumulation, and in the case of organic compounds, their degradation. The models will conservatively assume that sedimented active ingredients remain, without further resuspension and downstream distribution, at their point of contact with sediments. Their accumulation in sediments will be determined by integrating the loss algorithms from $t = 0$ to the expected life of the treated wood project, which is normally 35 to 75 y. Therefore, accurate determination of long-term loss rates is important as errors in estimation are compounded by the length of time over which the loss rates are integrated. For instance, the static test of ACZA reported by Stanley (1994b) predicted no losses after approximately 40 d of immersion, versus long-term loss rates of 5.0 to 6.9 $\mu\text{g Cu/cm}^2\text{-d}$ predicted using dynamic

test data. The dynamic test data predicts a 40-y accumulation of 0.07 to 0.1 g of copper for each cm² of immersed treated wood. For a 30 cm dia piling immersed in 2 m of water, that equates to between 1.32 and 1.88 kg of copper. In contrast, use of the static test data from Stanley (1994b) would result in predicting only 8 g of copper lost to the environment during the life of the project—as much as 235 times less. Therefore, the importance of accurate measurement of long-term copper loss rates should not be underestimated, especially when large treated-wood projects are proposed for construction in depositional environments where sediments are not resuspended and dispersed downstream during seasonally high water flows. Long-term preservative loss rates have been shown to continue to decline following initial 30.5 d dynamic testing recommended herein. However, the slope of the decline is shallow and use of 30.5-d data will result in conservative models that overestimate sediment concentrations of preservative. The equations provided in this chapter will be used in Chapter 9 to predict environmental responses to the use of pressure-treated wood in and over surface waters. The Western Wood Preservers Institute and the Canadian Institute of Treated Wood have developed BMPs (WWPI/CITW, 1996) designed to minimize preservative losses to aquatic environments. Additional studies describing preservative loss rates from BMP-produced products will be discussed in Chapter 10.

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APPENDIX 7.1 UNITS OF MEASUREMENT AND ACRONYMS

In general the metric system of units is used in this section. Concentrations are generally expressed in micrograms/L ($\mu\text{g/L}$). The following abbreviations apply throughout the chapter.

Term	Meaning
AWPA	American Wood Protection Association (formerly American Wood-Preservers' Association)
CA-B	Copper azole preservative
CCA-C	Chromated copper arsenate preservative Type C
Cr	Chromium
Cu	Copper
CuN	Copper naphthenate preservative
DDAC	Dimethyldidecylammonium chloride (a surfactant)
DOC	Dissolved organic carbon measured in mg/L
Exp	2.718
Gph	Gallons per hour – applied to the internal recirculation of water in the test chambers
HPAH	High molecular weight polycyclic aromatic hydrocarbons (MW >200)
IMID	Imidacloprid
Ln	Natural logarithm to the base exp (2.718)
Log, Log ₁₀ or Log10	A logarithm to the base 10
Loss rates	Micrograms of active ingredient per square centimeter per day ($\mu\text{g Al/cm}^2\text{-day}$)
LPAH	Low molecular weight polycyclic aromatic hydrocarbons (MW <200)
MicroPro	Osmose Micronized Copper preservative
PAH	Polycyclic aromatic hydrocarbons
ΣPAH	Sum of the measured PAH congeners
Pcf	Pounds per cubic foot
Penta	Pentachlorophenol preservative
PESC	Environment Canada's Pacific Environmental Science Center
pH	Logarithm of the reciprocal of the hydrogen ion concentration.
ppm	Parts per million (mg/kg, ml/L, mg/L, etc.)
PROP	Propiconazole
R	Retention of wood preservative = (kg/m^3) or pounds/cubic foot (pcf) in the treated zone.
R^2_a	Adjusted coefficient of determination which expresses the percent of the variability in the data that is explained by the fitted regression line
PSU	Practical salinity units
SPLP	Synthetic precipitation leaching procedure
TCLP	Toxicity characteristic leaching procedure
TEB	Tebuconazole
T (°C) or (°F)	Temperature
Time	Days (time immersed in water)
Rainfall	Cumulative rainfall measured in inches (in.) or centimeters (cm)
WAG	Wolman AG™ preservative
Wolman MicroPro	Arch Micronized Copper preservative
Zn	Zinc