# Literature Review and Assessment of the Environmental Risks Associated With the Use of CCA Treated Wood Products in Aquatic Environments

Prepared for:

**Western Wood Preservers Institute**
**7017 NE Highway 99, Suite 108**
**Vancouver, WA 98665**

Prepared by:

**Kenneth M. Brooks, Ph.D.**

**Aquatic Environmental Sciences**
**644 Old Eaglemount Road**
**Port Townsend, WA 98368**

**August 1, 1997**

*Table of Contents*



*Table of Contents (Continued)*

## *List of Tables*

## ***List of Figures***

# Literature Review and Assessment of the Environmental Risks Associated With The Use Of CCA Treated Wood Products in Aquatic Environments

## Introduction

Chromated-copper-arsenate (CCA) is a formulation of copper, chromium and arsenic, dissolved in an aqueous solution. In was first developed in 1933 and has been widely used throughout the world as a wood preservative for 60 years. The metals in CCA treated wood undergo chemical change after impregnation resulting in their being bonded or fixed to wood fibers. These formulations combine the fungicidal properties of copper with the insecticidal properties of arsenic pentoxide. In CCA, the fixation of arsenic and copper is dependent on the presence of chromium. A number of formulations, using different forms of the metals and marketed under a variety of trade names, are available. The American Wood Preservers Association (AWPA) classifies these formulations as CCA Types A, B and C. Each type may behave slightly different in aquatic environments. However, these differences are small and only the most commonly used formulation, CCA-C will be considered in this review.

Ammoniacal Copper Arsenate ACA has recently been improved by the replacement of some of the arsenic with zinc. The current formulation of Ammoniacal Copper Zinc Arsenate (ACZA) contains 25% zinc as zinc oxide, 50% copper as cupric oxide and 25% arsenic as arsenic pentoxide. Ammonia in this formulation catalyzes the fixation of copper, arsenic and zinc to the wood fibers.

Both arsenic and chromium are heavy metal poisons. Both have chronic and acute environmental health risks associated with them. Copper does not generally constitute a human health risk. However, low concentrations of copper, in certain ionic forms, are highly toxic to marine fauna and flora. The known toxicity of arsenic and chromium to humans has resulted in concern about the possible introduction, into the environment, of large amounts of these metals in treated wood products.

Several reviews assessing the environmental risks associated with treated wood have been compiled by Hartford (1976), Konasewich and Henning (1988), Stranks (1976), Ruddick and Ruddick (1992) and the U.S. Department of Agriculture (1980). The conclusion reached in these papers is that the use of treated wood causes no significant hazard to the environment. However, all of these reviews suffer from lack of quantitative analysis, leaving some doubt about the risks associated with using treated wood in aquatic environments. Cooper (1990) discusses the considerable confusion created by contradictions in the technical literature regarding the leaching of metals from CCA treated wood products.

This paper is intended to provide a more quantitative analysis of the environmental risks associated with the use of CCA treated wood in aquatic environments.

## Background Levels and Sources of Arsenic, Chromium, Copper and Zinc in Aquatic Environments.

The metals used in wood preservatives are naturally occurring elements. The purpose of this chapter is to gain an understanding of the background levels of these materials and the natural and anthropogenic sources that contribute to present environmental levels.

**Arsenic** is found in rocks and soil from concentrations of less than 1,000 ppb to several hundred thousand ppb. Andreae (1978) found background levels of arsenite (arsenic III) to be less than 0.9 ppb in sea water and total inorganic arsenic (primarily arsenate or arsenic V) was less than 1.5 ppb. Penrose (1974) reported arsenic levels of 2.3 to 8.3 ppb in the Caribbean and 0.8 to 4.5 ppb in the Gulf of Mexico. The U.S. EPA (1985) reported arsenic levels of 1.5 ppb in Puget Sound water. Brooks (1991, unpublished data) found arsenic levels of 19 ppb in marine water samples in Little Skookum Inlet, South Puget Sound. There is a consensus among other authors (Waslenchuk, 1977, 1978 and Sanders, 1980) that total arsenic concentrations in marine waters generally range between 1 and 1.5 ppb.

Andreae found significantly more reduced arsenic (arsenite) than would be expected in highly oxygenated water where chemical equilibrium models suggest that most of the arsenic should be in the less toxic arsenate form. The ratio of arsenite to arsenate is correlated with chlorophyll $\alpha$ production suggesting that the speciation of arsenic in natural waters is highly influenced by biological activity. Sanders and Windom (1980) estimate that as much as 15-20% of total arsenic is reduced by phytoplankton during the spring and fall blooms on the continental shelves.

Woolson (1983) suggested that the natural arsenic cycle is not greatly disturbed, on a global basis, by man's activities. He reported that volcanoes constitute the major natural source, and estimated their contribution at $70 \times 10^9$ grams/year. All other natural sources contribute only $8 \times 10^9$ grams/year. Anthropogenic sources add nearly 25% to the total global loading. Iron, steel, lead, zinc and copper production contribute 82% of the anthropogenic emissions of $23.6 \times 10^9$ grams/year. Pesticides account for $0.20 \times 10^9$ grams/year or less than one percent of total anthropogenic input.

Woolson discusses the arsenic cycle and suggests that the final environmental fate of all arsenic is incorporation into oceanic sediments. Characteristic levels of arsenic in Washington State marine sediments are presented in Table 1. Values range from less than 10,000 ppb in reference areas to greater than 70,000 ppb in highly impacted areas like Elliott Bay. Carpenter (cited in Penrose and Woolson, 1974) reports arsenic levels of 3,000 to 15,000 ppb in sediments of Puget Sound and deep sea locations. He also reports levels of 290,000 to 980,000 ppb in sediments near a Puget Sound smelter.

**Table 1. Metal levels in sediments of Puget Sound reported in the 1992 edition of the Puget Sound Environmental Atlas.**

| Area | Arsenic | Copper | Zinc |
|---|---|---|---|
| Straight of Georgia | <10 ppm | < 50 ppm | < 100 ppm |
| San Juan Islands | <10 ppm | < 50 ppm | < 100 ppm |
| Bellingham Bay | <30 ppm | > 350 ppm | < 300 ppm |
| Strait of Juan De Fuca | <10 ppm | < 50 ppm | < 100 ppm |
| Penn Cove | <10 ppm | < 50 ppm | < 100 ppm |
| Everett | <70 ppm | > 350 ppm | > 700 ppm |
| Dyes Inlet | <70 ppm | < 150 ppm | < 300 ppm |
| Elliott Bay | >70 ppm | > 350 ppm | > 700 ppm |

The U.S. Department of Agriculture (1980) reports extreme variation in the amount of arsenic found in fresh surface and ground waters of the world (undetectable to 276,000 ppb). Table 2 provides a cross section of the data. Whanger, *et al.*, (1977) found similar levels in Oregon waters. Oregon spring water typically contains several hundred (133-900) ppb arsenic while lake water is significantly lower (<1-9 ppb).

**Table 2. Typical arsenic levels observed in fresh water.**

| | |
|---|---|
| Glacial ice in Sweden contains | 2.0 to 3.8 ppb |
| Thermal waters in Western U.S. States | 20.0 to 3,800 ppb |
| Columbia River, Washington State | 0.2 to 86.9 ppb |
| Yellowstone River | 4.5 ppb |
| California Well water | 10.0 to 2,000 ppb |
| Washington well water | 5.0 to 6.0 ppb |
| Oregon well water | 0.0 to 1,700 ppb |
| California lakes | 0.0 to 100 ppb |
| Wisconsin lakes | 4.0 to 117 ppb |

**Arsenic Summary.** These data suggest that on a global scale, little arsenic is contributed to aquatic environments by pesticide use. However, local arsenic levels may be highly influenced by anthropogenic inputs. Typical arsenic levels in marine water are in the low ppb range. This report will assume that marine levels of total arsenic are 1.5 ppb and that the ratio of arsenite to arsenate is approximately 1:4.

Total arsenic concentrations of 10,000-30,000 ppb appear reasonable for sediments in reference areas. Further analysis in this report will assume that sedimented levels in industrial areas are on the order of 70,000 ppb.

Arsenic levels in fresh water appear to be higher than in marine waters. For purposes of further analysis, an average total arsenic loading of 50 ppb will be assumed for lotic and lentic fresh waters.

**Chromium.** Eisler (1986) has reviewed chromium hazards to aquatic species. He reports that the earth's crust contains a mean of 125,000 ppb chromium. Natural weathering processes release an estimated 32 thousand tons of chromium per year. The annual world production of chromium is estimated at 7 million metric tons and industrial inputs can be significant. Storm water, sewage treatment plants, metal plating, leather tanning and mining industries contribute significant amounts of chromium to aquatic environments. Untreated industrial effluents contain up to 5,000,000 ppb and electroplating waste streams contain up to 1,290,000 ppb.

Background levels of 0.0 to 5 ppb chromium were reported by Eisler (1986) for uncontaminated seawater. Freshwater levels are somewhat higher at 1.0 to 10 ppb. The U.S. EPA (1983) summarized chromium levels in surface waters of the United States. Values range from undetectable in some California well water to 2790 ppb for water near a cooling tower. Average values are between 4 and 20 ppb with a range of <1 to 112 for U.S. surface waters. The U.S. EPA does not list chromium as a metal of concern in Puget Sound.

Turekian and Scott (1967) report suspended loads of chromium in North American rivers ranging from 37,000 to 460,000 ppb. They estimate that 870 tons of chromium are transported by the Susquehanna River each year. Rivers located east of the Mississippi have higher concentrations of many metals than do western rivers. However, all of these lotic systems transport significant amounts of chromium to the estuaries at their mouths. Eisler (1986) reports that marsh sediments receiving fertilizers containing sewage sludge for seven years contained between 2,150,000 and 4,750,000 ppb chromium. Sediments associated with industrial outfalls had as much as 54,300,000 ppb chromium. Sediments from reference areas contained 50,000 to 54,000 ppb chromium.

**Chromium Summary.** Uncontaminated seawater contains very low levels of chromium. This review finds that anthropogenic inputs of chromium are significant. This is particularly true in localized areas near urban or industrial centers because the metal is readily incorporated into sediments. Further analysis in this report will assume a background level of 3 ppb in marine water and 12 ppb in freshwater. Based on values in the literature, sediments in unpolluted areas will be assumed to have 52,000 ppb chromium and a level of 1,000,000 ppb will be assumed for industrialized areas.

**Copper.** Copper levels of 1 - 10 ppb were reported by Boyle (1979) from unpolluted waters of the United States. However, concentrations downstream of municipal and industrial outfalls may be much higher (Hutchinson, 1979). The U.S. EPA (1985) reports low levels (0.25 ppb) of copper in the waters of Puget Sound.

Copper levels in Washington sediments (Puget Sound Environmental Atlas, 1992) are summarized in Table 1. Lu and Chen (1977) reported copper levels in San Pedro Bay (a reference area) sediments of 5,000 to 10,000 ppb.

**Copper Summary.** Based on available information, this report will assume that background water column levels of copper are < 2.0 ppb in marine environments and 5 ppb in lotic and lenitic freshwaters. A value of 10,000 ppb will be assumed for unpolluted sediments and 350,000 ppb in sediments near industrialized areas.

**Zinc.** Little information was obtained on either sources or background levels of zinc. Levels observed in Puget Sound are reported in Table 1. Zinc values in sediments were less than 100,000 ppb in pristine areas and greater than 700,000 ppb in industrialized areas like Elliott Bay. Lu and Chen (1977) reported zinc levels of 30,000 to 35,000 ppb from reference sediments in San Pedro Bay. The U.S. EPA (1985) reports typical zinc levels of 0.50 ppb in the marine waters of Puget Sound.

**Zinc Summary.** For further analysis in this report, it will be assumed that unpolluted sediments contain 35,000 ppb zinc; polluted sediments contain 700,000 ppb zinc and that marine waters contain 0.50 ppb zinc.

## Cycling and Fate of Arsenic, Chromium and Copper in

## Aquatic Environments

**Zinc** was not included in this discussion because of the paucity of information and its low toxicity to aquatic organisms.

**Arsenic.** The chemistry of arsenic in water is complex and the form present in solution is dependent on such environmental parameters as pH, organic content, suspended solids and sediment characteristics. Thermodynamic considerations predict that at neutral pH, and relatively high levels of dissolved oxygen, most arsenic should be oxidized to arsenate. However, Penrose (1974) notes that most inorganic arsenic in the sea is in the form of arsenite. Johnson (in Penrose, 1974) found that marine bacteria can reduce arsenate to arsenite. This biological transformation may be responsible for the 2:1 ratio of arsenite to arsenate observed in some marine water by Johnson. In contrast, Onishi (in Andreae, 1978) reports that arsenic III (arsenite) represents only about 20% of the total arsenic found in seawater.

In addition to inorganic arsenic, a number of authors (Johnson, 1972; Lunde, 1977; Penrose, *et al.*, 1977; Andreae, 1977) have demonstrated that bacteria, phytoplankton, marine invertebrates and vertebrates can biotransform arsenic into relatively less toxic organic compounds. These reactions involve methylation and reduction to produce methylarsonic acid and dimethylarsinic acid. The low toxicity of these organic compounds allows high body burdens of arsenic which are eventually incorporated into the sediments. However, significant amounts of arsenate may be regenerated in the water column from phytoplankton that sink below the photic zone and perish. Thus, there is an arsenic cycle which involves a cycling of arsenic through its various inorganic and organic forms. The relatively high levels of arsenic found in sediments, compared to the water column suggests that the ultimate fate of arsenic in aquatic environments is incorporation into sediments.

**Chromium.** Two species of chromium are prevalent. Chromium (III) is less toxic than chromium (VI). Most of the chromium (VI) found in nature is a result of domestic and industrial emissions (Steven et al., 1976). Interaction of chromium (VI) molecules with organic compounds can result in reduction to a comparatively less toxic trivalent form. However, in aerobic marine environments, chromium (VI) is the more abundant species. Chromate, hydrochromate and dichromate are soluble in water and are therefore mobile in aquatic environments.

The ultimate fate of chromium VI appears to be incorporation into fine grained sediments with high organic and iron content. Adsorption of chromium VI onto sediments is dependent on salinity and is greatest at salinities of 0.1 to 1.0 ppt (Mayer and Schick, 1981). However, its fairly high solubility allows easy migration into and out of the water column over aerobic sediments. Observed concentrations in European estuaries ranged from 3,900 ppb in intertidal sands to 162,000 ppb in anaerobic mud's (Rehm *et al.* 1984).

Chromium III forms stable complexes with negatively charged inorganic and organic compounds. It is rarely found in waters with decaying plant or animal tissues or silt and clay particles. Precipitated chromium hydroxides remain in the sediments under aerobic conditions. With low pH and anoxic conditions, chromium III hydroxides may solubilize as ionic chromium III. However, Lu and Chen (1976) found that chromium was not significantly released from sediments into seawater under either oxidizing or reducing conditions.

**Copper.** Copper occurs in natural waters primarily as the divalent cupric ion. In may be found as a free ion or complexed with humic acids, carbonate, and other inorganic and organic molecules. Copper is an essential element in the normal metabolism of both plants and animals.

Therefore, a significant portion of the copper found in both fresh and marine systems may be taken up by the biota. The ultimate fate of much of this copper is sedimentation.

Harrison, *et al.* (1987) found very low copper levels (< 12 ppb) in sandy substrates associated with power plant effluents and suggested that the lack of organic matter in these sediments was responsible for the low copper content.

Clarke (1974) noted that iron sulfide will render copper insoluble in anaerobic sediments. These reports suggest that copper accumulation in sediments is highly influenced by sediment chemistry and physical characteristics. Fine sediments, coupled with poor water circulation could be expected to accumulate more copper than coarse sediments in highly oxygenated areas. Copper accumulations in fine grained, anaerobic sediments are probably not biologically available and therefore these environments may serve as an important mechanism for the removal of excess copper from aquatic environments.

**Cycling of copper from sediments as a function of the REDOX potential.** Lu and Chen (1977) examined the release of copper from sediments as a function of sediment grain size and oxygen availability. Sediment grain size was not a factor in the amount of copper released to the overlying water column. Three oxidizing conditions were examined (oxidizing, 5 to 8 ppm dissolved oxygen; slightly oxidizing, $\leq$ 1 ppm dissolved oxygen; and reducing, $S(-II)_T$ = 15 to 30 ppm). Small amounts of bound copper were released in the reducing and slightly oxidizing environments (0.2 to 0.5 ppb). Copper releases in the oxidizing environment resulted in significantly higher interfacial seawater concentrations (3.2 ppb). This effect was slightly more pronounced in the coarsest sediment tested (silty-sand sediment). These data imply higher copper releases from sediments in aerobic (healthy) environments. There are two ways to look at this phenomena.

In more coarse grained, highly oxygenated sediments, bound copper is more easily lost to the water column and dispersed over greater distances, until the copper finds anaerobic sediments, where it will likely be buried and eventually incorporated into the lithosphere. These anaerobic sediments support reduced infaunal and epifaunal communities of organisms. Therefore we might expect reduced environmental impacts from copper incorporated into these sediments.

In enclosed bodies of water with coarse grained, aerobic, sediments, this study suggests that copper will not be as tightly bound to the sediments and will migrate into the interstitial and surficial water where it is bioavailable. No data was provided on the copper species released from the sediments and therefore it is difficult to assess the toxicity of the released copper.

The work of Lu and Chen (1977) suggests that caution is appropriate when dealing with copper materials in poorly flushed embayments with aerobic (> 2 to 3 ppm dissolved oxygen) sediments. These arguments suggest that anaerobic sediments are a more efficient trap for released copper and that reduced environmental risks should be anticipated from copper releases associated with anaerobic sediments compared with those associated with aerobic sediments.

The data presented in Lu and Chen are not appropriate for development of an expression describing copper releases from sediments at a variety of sediment concentrations. No attempt will be made in the current model to modify the risk assessment based on this discussion. These effects appear to be subtle and their exclusion should not significantly flaw the risk assessment. This discussion is provided as background for proponents and permit writers. Consideration of these factors may be important when considering the relative risks associated with different wood treatments.

## Bioaccumulation of Chromium, Arsenic and Copper In Aquatic Environments.

Chromium and copper are essential micronutrients for plants and animals. Their uptake and metabolism is a normal biological process. The pentavalent form of arsenic (arsenate) is chemically similar to phosphate and arsenate may be readily taken up by plants and animals in their efforts to sequester phosphate for normal cellular metabolism. This chapter discusses the potential for the bioaccumulation of each of these metals by aquatic plants and animals.

**Arsenic bioaccumulation.** Because inorganic arsenic is a potent toxicant in mammals (including man), there is considerable data describing its bioaccumulation. Penrose, *et al.* (1977) examined the arsenic budget in a sea urchin-alga system and concluded that organic arsenic is rapidly excreted by most organisms and therefore, while there may be significant bioconcentration of arsenic from surrounding waters, there is no apparent bioaccumulation in food chains. Organisms containing high levels of arsenic in their tissues tend to be those that are prone to incidental ingestion of sediment particles while feeding.

Arsenic concentration from ambient water was also reported by Schroeder and Balassa (1966), Lunde (1970, 1972) and Fowler *et al.* (1975). High levels of arsenic in marine animals are reported by USDA (1980) from around the world. Reported levels of arsenic, expressed as a proportion of wet tissue weight, for some typical marine species are provided in Table 3 (USDA, 1980). Woolson (1977) reported that arsenic concentrations are 10 to 100 times higher in marine fish and shellfish than in fresh water species. However, as seen in previous sections, reported arsenic concentrations in marine waters are typically lower (1.5 ppb) than in fresh water (see Table 2). No plausible explanation for this apparent contradiction was offered in the literature.

Penrose (1974) reviews studies by Fernandez del Riego, Seydel and Lunde which suggest that arsenic is not bioaccumulated in food chains. Work by Boothe and Knauer (cited in Penrose, 1974) and Black and Penrose (cited in Penrose, 1974) suggest that arsenic ingested in food is rapidly excreted by marine organisms. Woolson (1974) summarizes his review of arsenical bioaccumulation by noting that:

"arsenic is bioconcentrated by aquatic organisms but not biomagnified. Plants usually accumulate more arsenic than fish, and crustacea accumulate intermediate amounts. Marine organisms normally contain more arsenic than their fresh water counterparts. However, the arsenic contained in the organisms is apparently not toxic to animals or humans, and is readily excreted."

The available evidence indicates that arsenic does not bioaccumulate in food chains. It appears that arsenic ingested at lower levels of the food webb are converted to organic molecules which may be rapidly excreted at the next trophic level. For purposes of the analysis in this report, it will be assumed that levels of arsenic are dependent on ambient water levels and that they are not bioaccumulated as one progresses to higher trophic levels.

**Table 3. Arsenic content of aquatic animal life (in parts per billion).**

| | |
|---|---|
| **Marine** | |
| Crab | 27,000 - 52,500 |
| Clams (all species) | 900 - 12,720 |
| Oysters (*Crassostrea virginica*) | 600 - 42,750 |
| Lobster (*Panulirus borealis*) | 3,200 - 9,600 |
| Tuna | 710 - 4,600 |

*Table (3) continued.*

**Fresh Water**

| | |
|---|---|
| Trout | 69 - 149 |
| Perch (*Perca fluviatilis*) | 600 |
| Bass (*Micropterus salmoides*) | 70 - 930 |
| Channel catfish (*Ictalurus punctatus*) | 0 - 3,100 |

**Chromium bioaccumulation**. Eisler (1986) reports that algae and higher plants accumulate chromium from seawater by factors of up to 8,600 and from solutions containing 50 ppm chromium by a factor of 18 in 48 hours. Although chromium is abundant in primary producers, there is little evidence of bioaccumulation through marine food chains. Baptist and Lewis (1969; cited in Eisler, 1986) followed the transfer of chromium through an experimental food chain and observed a decline in the concentration of chromium through each of four trophic levels. Comparison of the results of this food chain study with measurements of direct chromium uptake from seawater suggest that direct uptake is a far more important pathway than assimilation through the food chain. Bioconcentration factors (BCF) for numerous aquatic species are given in U.S. EPA (1983). The reported BCF for chromium (VI) in fish muscle is less than 1.0. Values of 125 and 192 were obtained by EPA for chromium (VI) in oysters and blue mussels. The EPA document also gives values for chromium (III) and concludes that they are similar to those given above for chromium (VI). The EPA conclusion was that mean BCF values of 0.5 and 130 are appropriate for fish muscle and bivalve mollusks respectively. These are both relatively low BCFs. It appears that chromium is not bioaccumulated in the food chain and that chromium concentrations at all trophic levels are primarily a function of background levels in the water.

**Copper and zinc bioaccumulation.** National Academy of Sciences (1971) provides copper bioconcentration factors for numerous taxa. These values range from 100x for benthic algae to 30,000x for phytoplankton. Mollusks concentrate copper by a factor of 5,000 in muscle and soft parts. No information was reviewed on the bioaccumulation of either copper or zinc by aquatic organisms. For the purposes of this paper, it will be assumed that copper and zinc accumulation in aquatic organisms is primarily a function of metal concentration in the ambient water and while many organisms may bioconcentrate copper, there is inadequate information describing the bioaccumulation of copper through food webs. The two processes (bioconcentration and bioaccumulation) are not necessarily directly related. Many materials are bioconcentrated, particularly by bivalves. However, many of those bioconcentrated substances are not bioaccumulated because they are either rapidly excreted or metabolized.

**Summary of bioaccumulation potential.** All of the reports on arsenic and chromium indicate that these metals are either not bioaccumulated, or bioaccumulated at very low levels, in the food chain. Arsenic and chromium are bioconcentrated at low levels (70x to 2,000x) and copper and zinc at moderately high levels (100x to 30,000x). Mollusks can be expected to bioconcentrate copper by a factor of 5,000x from background levels (NAS, 1971).

## Toxicity of Chromium, Arsenic and Copper to Aquatic Fauna and Flora.

In order to assess the potential impacts of CCA treated wood used in aquatic environments, it is necessary to determine the minimum levels of these metals causing acute or chronic stress in populations of marine organisms.

**Arsenic toxicity in aquatic environments.** Arsenic is a common environmental metal whose toxic properties have been known for centuries. The toxicology of arsenic may be divided into three general areas: direct inhibition of cellular respiration, mutagenic effects and hemolysis. Baroni *et al*. (1963) and Penrose (1974) note that controlled attempts to attribute carcinogenic properties to the arsenicals have failed. Ferm (1977) has demonstrated the teratogenic nature of sodium arsenate injected into a variety of experimental animals.

Arsenical toxicity is dependent on the oxidation state, chemical form and route of exposure. In general, arsenic acids are least toxic, followed by inorganic arsenate, arsenoxides, inorganic arsenite and the trivalent organic and inorganic arsines are the most toxic.

Eisler (1988) reports acute toxicity levels for a variety of fresh water and marine plants and animals associated with several species of arsenic. Lethal Concentrations which killed 50% of the invertebrate test organisms ($LC_{50}$) are provided in Table 4. In marine water, it appears that arsenic levels in excess of 200 ppb may result in the mortality of juvenile Dungeness crab and an unspecified species of red algae. NTIS (1986) reported acute values of arsenic (III) for twelve saltwater animals. The range of sensitivities was from 232 to 16,030 ppb. Chronic stress is observed at about half these values or 116 ppb. Arsenic (V) was less toxic for the two invertebrates examined with acute values of 2,000 and 3,000 ppb. None of these animals were as sensitive to arsenic as were some algae which showed toxic responses to either arsenic (III) or (V) at values as low as 19 ppb.

Eisler's (1986) data suggest that in fresh water, arsenic levels associated with acute toxicity appear to be a somewhat higher, in the neighborhood of 900 ppb. NTIS (1986) reported acute toxicity associated with arsenic (III) in 16 species of freshwater animals. An acute value of 812 ppb was found for cladocerans. At the other end of the range, the acute level for a midge was 97,000 ppb. From these papers it appears reasonable to assume an $LC_{50}$ of 800 ppb for the more sensitive fresh water species. NTIS (1986) suggests that chronic stress is encountered by all freshwater species at about 21% of their acute values. For the most sensitive species, this value would be 168 ppb total arsenic.

**Table 4. Lethal Levels of Arsenite on Fresh Water Plants and Animals. Unless otherwise specified, values are for the $LC_{50}$ expressed as ppb.**

**Fresh Water**

| Taxa | Arsenite ($As^{+3}$) |
|---|---|
| Algae | 1,700-4,000 ($LC_{100}$) |
| Cladocerans | 1,300 |
| Amphipod | 960 (28-d $LC_{100}$) |
| Goldfish | 490 (7-d $LC_{50}$) |
| Fish | 15,000-35,000 |

**Marine Water**

| Taxa | Total Arsenic (As) |
|---|---|
| Red Algae | 300 ($LC_{100}$) |
| Copepods | 510 |
| Dungeness Crab | 230 |
| Oyster (eggs) | 7,500 (48 hr) |

| | |
|---|---|
| Blue Mussels | 16,000 ($LC_{100}$) |
| Pink Salmon | 3,800 (10-d $LC_{54}$) |

This review indicates that arsenite can cause chronic stress in several marine animals at levels as low as 168 ppb in fresh water systems and 230 ppb in marine systems. For most aquatic organisms, arsenate is far less toxic. However, for the most sensitive marine algae, this review indicates no difference in toxicity thresholds between the two primary valence states of arsenic (+3 & +5) and toxicity thresholds as low as 19 ppb.

**Chromium toxicity in aquatic environments.** The toxicity of chromium to aquatic species can vary by an order of magnitude, or more, depending on a variety of biological and physical factors. These include differences associated with species, age, developmental state, temperature, pH, salinity, length of exposure and interaction with other contaminants. Chromium (VI) is most toxic to the developmental stages of aquatic species in soft, fresh water, with low pH. Eisler (1986) reports a 96 hr-$LC_{50}$ of 200 ppb for salmon fingerlings and 495 ppb for rainbow trout (*Oncorhynchus mykis*) eggs. Most species of fish tolerate >10,000 ppb and Bluegills (*Lepomis macrochirus*) demonstrated a very high toxic threshold at 213,000 ppb in water with 120 ppm $CaCO_3$.

In marine water, chromium (VI) toxicity also varies by orders of magnitude, depending on the taxa. The range is about the same as for fresh water species. Polychaetes and larval crabs (*Callinectes sapidus*) are the most susceptible organisms at 200 and 320 ppb respectively.

**Copper toxicity in aquatic environments.** Copper is an essential element for most living organisms. It is added at a concentration of 2.5 ppb in Guillard's Medium F/2 to sea water for the optimum culture of marine algae (Strathman, 1987). At concentrations slightly above those required as a micronutrient, copper can be highly toxic; especially to the larval stages of marine invertebrates. A single copper fitting in a seawater system may destroy most invertebrate embryos being cultured in the laboratory.

EPA's (1984) Ambient Water Quality Criteria reports that copper toxicity in aquatic environments is related to the concentration of cupric ($Cu^{2+}$) ions. The cupric ion is highly reactive and forms various copper complexes and precipitates which are significantly less toxic than the cupric ion (Knezovich, *et al.,* 1981). Sundra (1987) has proposed a basic mechanism to explain the observed relationship between free ion activities and the bioavailability of metals such as copper. He observed that the complexed species of copper are charged or polar and cannot pass directly across the lipid bilayer of the cell membrane. Thus, transport of these metals across the membrane would require that they interact with specific metal transport proteins in the membrane. Because the free ion activity is a measure of the potential reactivity of a metal, it reflects the ability of that metal to interact with these transport proteins. The many chemical forms of copper in aquatic environments are maintained in a dynamic state of equilibrium that depends on salinity, temperature, pH, alkalinity, dissolved oxygen, sediment characteristics and the presence of other inorganic and organic molecules.

The dual nature of copper as an essential trace element and a potential toxin at very low concentrations demands that organisms strictly regulate copper at internal levels suitable for metabolic requirements. Roesijadi (1980) reports that copper is normally present at relatively high levels in the tissues of marine animals (> 1,000 ppb). Roesijadi (1980), Harrison, *et al.* (1987) and Harrison and Lam (1985) review both the environmental detoxification of copper and the physiological detoxification of copper by *Mytilus edulis, Protothaca staminea, Patella vulgata, Ostrea edulis* and *Littorina littorea*. Copper detoxification and metabolic regulation was associated with copper binding by low and high molecular weight metallothionein-like proteins in the digestive gland and sequestering of copper in lysosomes.

Costlow and Sanders (1987) used a metal-chelate buffer system to regulate the free ion concentration of copper in seawater. They exposed crab larvae to a range of free cupric-ion concentrations and monitored survival, duration of normal development and growth. The authors reported significant reductions in growth correlated with copper accumulation and concluded that when crab larvae are exposed to cupric ion concentrations in seawater that are below ambient concentrations, they are able to regulate bioconcentration of copper. At high concentrations of the cupric ion, copper bioconcentration increases and larval growth was inhibited.

Harrison *et al.* (1987) reported that copper discharged from the San Onofre power plant cooling system was mostly in bound forms under normal operating conditions. Their study found sufficient organic ligands available in ambient seawater to complex most of the copper and expected little or not impact from the discharges. Harrison *et al.* (1987) conducted copper bioassays on a number of aquatic invertebrate and vertebrate species. They found that *Crassostrea gigas* embryos were most sensitive (48-hour $LC_{50}$ =10 ppb) and larval herring the least sensitive. The range of 48-hour $LC_{50}$ values for copper was 10-2,000 ppb. Dinnel, *et al.* (1983) published the results of copper toxicity bioassays on various life stages of a number of marine organisms. They report a very low $LC_{50}$ ( 1.9 ppb) for the sperm of the red sea urchin (*Strongylocentrotus franciscana*). This value seems suspect because it falls within the range normally expected in unpolluted seawater. Reported values from the Dinnel, *et al.*(1983) study are presented in Table 5.

Gametes and the embryos of marine organisms are most sensitive to copper. Based on the previous discussion regarding the metabolic regulation of copper, it seems reasonable to suggest that the susceptibility of embryos to even low copper concentrations is associated with their inability to regulate cellular exposure to the cupric ion. Copper levels maintained at levels low enough to protect embryos are sufficient to insure that toxic effects are not imposed on larvae and adult organisms. With the exception of the sperm of the red sea urchin, environmental levels less than 6 ppb appear reasonable for the protection of aquatic life. In areas where red urchins spawn, additional restrictions should be considered.

Because of the variety of molecular structures containing copper in aquatic environments, and a lack of definitive information about their relative toxicity, no single analytical measurement is ideal for expressing copper concentrations with respect to their potential toxicity to aquatic life. Baldwin (1989), advises that active copper (operationally defined by acidifying the aqueous sample to pH = 4 with nitric acid and measuring the concentration of copper that passes through a 0.45 micron membrane filter is probably the best available measurement.

This review revealed little copper toxicity data which included an analysis of the form of copper used in the bioassay. Most toxicity data are reported on the basis of total or dissolved copper. If bioassays are conducted in distilled water with low complexing capacity, there is significant potential to overestimate the toxicity of copper in the natural environment. If 2 mg of copper sulfate are added to distilled sea water, much of this may become available in its toxic cupric ion form. However, the same amount of copper added to organically rich estuarine waters could result in only a small fraction being present in the toxic form, the majority of the copper being detoxified by adsorption to sediments and precipitation, or complexation with organic molecules. These comments indicate the difficulty in accurately assessing the impact of copper in natural environments. However, because of the potential for detoxification, water quality criteria based on total copper will result in conservative criteria. Further analysis in this review assumes that all copper measured is in a toxic form.

**Table 5. Total Copper Toxicity Measured in Controlled Bioassays. Values are $EC_{50}$ or $LC_{50}$ in ppb.**

| | Taxa | $EC_{50}$ or $LC_{50}$ |
|---|---|---|
| ***Sperm*** | | |
| | Purple Sea Urchins | 34.0 |

| | |
|---|---|
| Oysters | 12.1 |
| Salmon | 44.2 |

*(Table 5, continued)*

| | | |
|---|---|---|
| ***Embryo*** | | |
| | Purple Sea Urchins | 6.3 |
| | Oysters | 6.1 |
| | Mussels | 21.0 - 35.0 |
| ***Larvae*** | | |
| | Crab Zoea | 95.7 |
| | Squid | 309.0 |
| | Cabezon | 95.3 |
| ***Adults*** | | |
| | Sand Shrimp | 898.5 |
| | Shiner Perch | 417.7 |
| | Coho Salmon Smolt | 601.0 |

**Summary of the toxicity of chromium, copper and arsenic.** This review of metal toxicity to aquatic organisms clearly demonstrates that copper is the metal of most concern. From a purely biological point of view, the cupric ion should be maintained below 6 ppb. No Observed Effect Levels (NOEL) for copper in embryos were not found in this review. However, it seems reasonable that these levels would be at least half the 48 hour-$LC_{50}$ level or 3 ppb. Chromium is somewhat less toxic and susceptible species have an $LC_{50} \geq 200$ ppb. Arsenic, which is notoriously toxic to humans and other mammals is highly tolerated by marine animals at levels up to 230 ppb. However, the susceptibility of some species of red algae impose an upper limit of 19 ppb in marine environments where they are present. The most susceptible fresh water species, examined to date, tolerate up to 168 ppb arsenic.

Most potentially toxic substances are regulated at the Federal and State Levels. Therefore, it would be highly presumptuous to suggest that these values should be used when considering the use of treated wood in aquatic environments. Their review is intended to provide insight into the regulatory standards which will be discussed in the following section.

## Regulatory Requirements for Arsenic, Chromium, Copper and Zinc In Aquatic Environments.

**Water column standards.** Washington State, in Chapter 173-201A WAC, defines water quality standards for surface waters. The WAC states that toxic substances shall not be introduced above natural background levels in waters of the state which have the potential either singularly or cumulatively to adversely affect characteristic water uses, cause acute or chronic toxicity to the most sensitive biota dependent upon those waters, or adversely affect public health, as determined by the

Department of Ecology. Table 6 lists criteria established for the protection of aquatic life in Washington State.

**Table 6. Water Quality Standards for Surface Waters of the State of Washington. Values are expressed as parts per billion (ppb). A hardness of 200 ppm was used for values requiring computation. See WAC 173-201A-040 for details.**

| Contaminant | Fresh Acute | Fresh Chronic | Marine Acute | Marine Chronic |
|---|---|---|---|---|
| **Arsenic** | 360 | 190 | 69 | 36 |
| **Chromium (VI)** | 16.0 | 11.0 | 1,100.0 | 50.0 |
| **Copper** | 29.4 | 22.8 | 2.9 | - |
| **Zinc** | 421.3 | 381.6 | 84.6 | 76.6 |

U.S. EPA water quality criteria are presented in Table 7. Direct comparison of the EPA criteria for copper and zinc with the Washington State Standards provided in Table 6 is not appropriate because the latter are variable, and depend on water hardness. Table 7 also compares EPA criteria with existing average metal concentrations in unpolluted areas of Puget Sound.

With the exception of the reported copper toxicity to red sea urchin sperm, both the state and federal criteria are consistent with biological considerations and reflect significant safety factors for the protection of aquatic life. However, there are some activities which bear additional consideration and these will be discussed in the following section.

**Table 7. EPA Water Quality Criteria (U.S. EPA, 1985) and Ambient Concentration of Metals in Puget sound Seawater (ppb).**

| Metal | EPA Water Quality Criteria | Puget Sound Ambient Levels |
|---|---|---|
| Arsenic | 36.0 | 1.50 |
| Copper | 2.9 | 0.25 |
| Zinc | 58.0 | 0.50 |

**Sediment standards.** Washington State has developed Sediment Quality Standards for metals in WAC 173-204-320. These standards are based on Apparent Effects Thresholds (AETs). Different jurisdictions may develop more, or less, stringent standards depending on a number of factors. For purposes of this risk assessment, the Washington State standards will be used as a regulatory standard. A second standard, describing maximum permitted metal levels in an authorized Sediment Impact (dilution) Zone (SIZ) is described in WAC 173-204-420. These sediment levels are provided in Table (8).

**Table 8. Maximum metal concentrations (in PPM dry sediment weight) authorized in Washington State (WAC 173-204).**

| *Metal* | *Sediment Quality Standard* | *Maximum level (SIZ)* |
|---|---|---|

| | | |
|---|---|---|
| copper | 390 ppm | 390 ppm |
| chromium | 260 ppm | 270 ppm |
| arsenic | 57 ppm | 93 ppm |
| zinc | 410 ppm | 960 ppm |

**Environments requiring special consideration.** Because of the high levels of stress associated with the intensive culture of aquatic species for aquaculture and enhancement programs, lower levels of metals must be maintained. The following paragraphs review requirements developed through experience in fish and shellfish hatcheries.

**Fish hatcheries.** Piper *et al.* (1982) have suggested water quality criteria for the optimum health of salmonid fishes in hatcheries. The crowded conditions in fish hatcheries and disturbance by humans during feeding, grading, vaccinating, etc. create stressful conditions, making these young salmonids more susceptible to contaminants. The values for both copper and zinc provided in Table 9 are less than that specified in WAC 173-201A.

**Table 9. Suggested water quality criteria for optimum health of salmonids in hatcheries. Concentrations are in parts per billion (ppb).**

| | |
|---|---|
| Copper | 5 |
| Zinc | 30 |

**Shellfish hatcheries.** Marine invertebrates (primarily shellfish) cultured at high densities in hatcheries require the highest water quality. Table 10 provides recommended shellfish hatchery screening and production levels for the metals of concern. Data for this table were taken from Huguenin and Colt (1989). The special conditions in fish and shellfish hatcheries suggest that the use of treated wood in association with their water supplies requires special consideration.

**Table 10. Preliminary Water Quality Screening and Production Levels for Marine Applications.**

| Parameter | Screening Level | Production Level |
|---|---|---|
| **Chromium** | < 10 ppb | < 25 ppb |
| **Copper** | < 1 ppb | < 3 ppb |
| **Zinc** | < 10 ppb | < 25 ppb |

**Summary statement regarding the sources and toxicity of arsenic, chromium and copper in aquatic environments.** The metals of concern when considering the use of treated wood in aquatic environments are arsenic, chromium, copper and zinc. These metals are natural components of the earth's crust and are found in varying concentrations in both fresh water and marine environments. Copper, and chromium are essential micronutrients. However, high concentrations of arsenic, chromium and copper are known toxicants. Arsenic and chromium are tolerated at moderately high levels by aquatic species. Buchanan and Solomon (1990) concluded that chromium and arsenic concentrations in CCA leachate were deemed sufficiently low as to have little or no effect on $LC_{50}$ determinations.

Copper is the most toxic metal to aquatic organisms, particularly in marine environments. Copper toxicity, associated with the presence of the cupric ion, is most detrimental to the early life stages of marine invertebrates. These stages are not readily visible and therefore this toxicity is not necessarily apparent to the untrained eye.

It appears that regulatory standards are sufficient to protect aquatic life. There are however, activities, such as the hatchery production of salmonids and shellfish that require significantly higher water quality standards.

Because natural sources of these metals are common, they are abundant in all aquatic environments. Anthropogenic activities, such as the use of treated wood in aquatic environments, can add to background levels of these metals. There certainly exists, the potential to raise ambient concentrations of these metals to levels that are harmful to aquatic life. The appropriate question is then: "How much arsenic, chromium, copper and zinc are added to aquatic environments by treated wood." This question will be addressed in the following chapters.

## Anticipated Environmental Impacts Resulting From the use of Chromated Copper Arsenate (CCA) Treated Wood In Aquatic Environments.

**Introduction.** Depletion of preservatives from treated wood can occur by leaching of water soluble components, physical loss (abrasion) or chemical and biological degradation. In studies of preservative depletion from treated wood, it may be impossible to identify the mechanisms of depletion. When biological or chemical degradation is present, the results from this type investigation will over-estimate the environmental loading. Examination of the surrounding medium (i.e. water or sediments) may fail to account for preservative depletion by biological degradation. Further, it is very difficult to discriminate leached inorganic metals from the background in field studies.

Numerous studies have examined treated wood in the form of sawdust, shavings or small coupons. This is done to speed the leaching process. These studies are valuable for assessing the relative permanence of different wood preservatives and the relative propensity of each metal for leaching. However, their results cannot reasonably be extrapolated to predict leaching from full sized commodities used in the environment. When such extrapolations are made, they will grossly overestimate the potential for environmental contamination. These laboratory studies cannot be substituted for good field studies using full size commodities in natural environments.

**Leaching of arsenic, chromium and copper from CCA treated wood.** CCA was first patented in the United States by Kamesam in 1938. There are currently three CCA formulations registered for use in the United States. Types A, B and C vary in their proportions of chromium, copper and arsenic. Types A and B have generally been replaced by Type C since its introduction in 1968. Type C contains 47.5% hexavalent chromium as $CrO_3$, 18.5% copper as CuO and 34.0% arsenic as $As_2O_5$. This report will focus on CCA, Type C.

The fixation of CCA in wood is a chemically complex process. Pizzi (1982) has provided a comprehensive review of the chemistry and kinetic behavior of arsenic, copper and chromium during fixation of CCA in treated wood. During fixation, following impregnation of the treating solution, chromium undergoes conversion from the hexavalent state to the trivalent state. Most of the preservative (>90%) is chemically bound to the wood fibers by reaction with wood sugars to form insoluble arsenate precipitates. The length of the fixation period is temperature sensitive and can last from several hours at 45°C to two months at 5°C. Studies by Jain and Lagus (cited in Baldwin, 1985) measuring the efficiency of the fixation mechanism, have shown that drying at 21°C will fix 95% of the metals within four days and 99% within five days. Further studies by Alexander (1991) have shown that the rates of fixation in all wood species are significantly inhibited if the wood is allowed to dry extensively during the fixation process. Improper fixation can result in significantly increased leaching of all CCA components. This report will assume that proper WWPI and CITW Best Management Practices for the production of CCA and ACZA treated wood are followed by producers. These BMPs are designed to insure maximum fixation and minimum leaching.

**Factors affecting CCA leaching rates.** Dahlgren (1975) suggests that from the wood treaters' point of view, the most important factors determining the leachability of CCA treated products are the concentration and type of preservative, the drying and storage conditions, and the choice of wood species. Important wood properties are the ion-exchange fixation capacity of copper, the natural pH, and the chemical composition and anatomy of the wood. There are several other factors that cannot be controlled by the wood treater.

**Time after installation in aquatic environments.** Leaching is strongly time dependent. Several authors cited in Cooper's (1990) review suggest that the leaching of CCA metals is most rapid during the first five or six days after installation and that leaching rates are halved on each successive day after immersion in water. Evans (1978) periodically examined the outer 5 mm zone of pine pole sections placed in running water. He found that about 20% of the arsenic in CCA-B and CCA-C treated Scots pine pole sections was lost from this outer zone during the first few months. Additional losses over the ten year test period were not measurable. Copper and chromium losses over the entire exposure period were not detectable.

Teichman and Monkman (1966) tested thin CCA treated wafers and found that metal losses were halved each day during the first three days of their test. Fahlstrom *et al.* (1967) found highest metal losses from CCA treated wood during the first six hours. They recorded 1/5 to 1/10 the initial loss rates after 18 hours and reported losses of 1/100 the initial rates at the end of 24 hours.

Cockroft and Laidlaw (1978) suggested that the rate of preservative depletion varies with the inverse square root of time. Teichman and Monkman (1966) found that arsenic leaching was halved on each successive day over a three day leach period in maple and birch. Fahlstrom *et al.* (1967) found that the rate of leaching was highest in the first six hours of exposure of small blocks to water; leaching was reduced to 10 to 20% of the initial rate after 18 hours and was only 1.0% of the initial rate after 24 hours.

In the United States, the most frequently treated wood is southern yellow pine. Putt (1993) conducted a careful study of metal loss from commodity size, CCA treated southern yellow pine in marine water. Fixation was assured in these studies by application of the chromotropic acid test. Summary results produced in that study are presented in Figure 1.

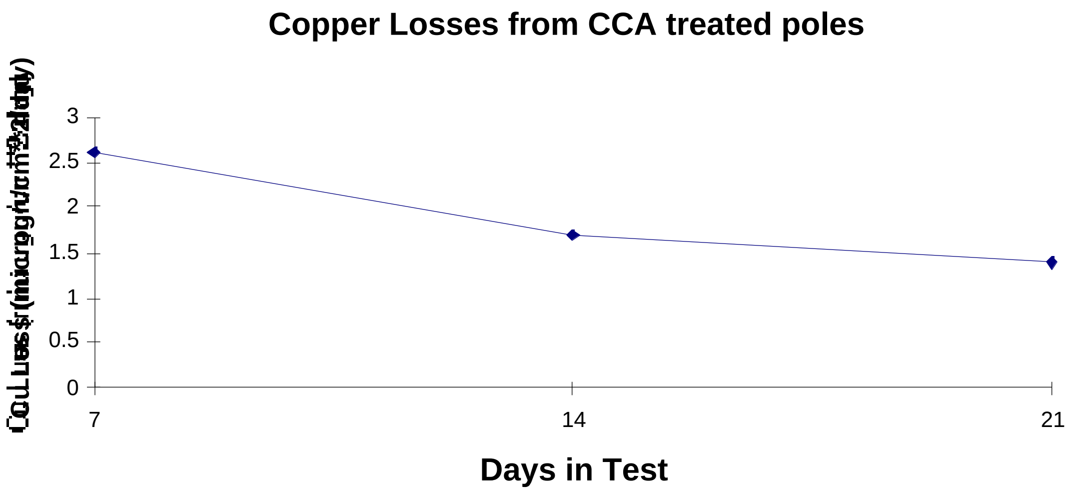


**Figure 1. Copper losses from CCA treated, southern yellow pine, piling as a function of time reported in Putt (1993).**

Non-linear regression techniques were used to evaluate the temporal behavior of copper leaching. The resulting regression is presented in equation (1). The temporal factor ($\exp^{-0.048 \text{ x time (days)}}$) will be used in this model to predict decreases in copper leaching as a function of time. This factor will decrease copper leaching rates to 24% of initial rates within 30 days and to 1% within 90 days. The regression was highly significant with 97% of the variation explained by this relationship. This exponential decrease is conservative from the environments' point of view when compared with previously described temporal declines.

**Equation 1.** $$\textbf{Copper Loss}_{(\text{time = t})} = 3.566 \exp^{-0.048 \text{ x time (days)}}$$

**Environmental pH effects.** Dahlgren (1975) examined the relative leaching of copper as a function of pH and found that leaching rates exceeding 9% at pH 4.0 were reduced to very low values (<0.5%) at pH 6.8. Cooper (1990, 1991) also examined pH effects on the leaching of CCA treated wood. He cautions that when treated wood is exposed to acidified water, maintained at a low pH, the CCA losses are increased compared to more neutral water. He goes on to clearly 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) acknowledges 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.

The material reviewed in this section suggests that more copper and chromium will be leached from CCA treated wood at low pH. Arsenic leaching does not appear to be as sensitive to pH. The data suggest that normal pH values (>4.5) expected in open aquatic environments do not exacerbate leaching rates. However, the leaching of CCA treated wood in direct contact with organic soils found in many wetlands of the Pacific northwest requires further study because of their low pH and humic acid content. Carson and Carson (1972) found that complexing of copper in humic acid and lignosulphonate reduced the acute toxicity of this metal to *Salmo salar*. At a hardness value of 14 ppm, acute toxicity was 25 ppb. Addition of 5 ppm humic acid raised the acute toxicity level to 90 ppb. The incipient lethal level with 17.6 ppm lignosulphate was 80 ppb.

Therefore, the abundant availability of these complexing molecules in hydric soils apparently reduces the availability of cupric ions, reducing the toxicity, and ameliorating the increased leaching rates.

The literature clearly demonstrates increased copper losses from CCA treated wood at very low pH values (<4.5). However, pH values this low are not commonly found in open aquatic systems and this model will not incorporate a factor describing pH effects.

**Salinity effects.** 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 at low salinity, sodium chloride has a coagulating effect on the copper, 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 retention's, loss of arsenic is shown to lag behind that of chromium and copper due to complexation of the liberated copper and chromium ions. At lower retention's (< 1.8 lbs/cf.) this trend is reversed and arsenic is more easily leached than copper. Current AWPA standards generally call for retention's of 0.6 lbs/cf. in dimension lumber, 1.0 lbs/cf. for piling used in freshwater applications and 2.5 lbs/cf. in marine environments.

The most complete analysis of salinity effects was found in Irvine and Dahlgren (1976). In the near term (20 weeks in test), they report relatively low levels of copper loss at salinities less than 10 ppt. There is a significant increase to approximately twice this loss at ca. 22 ppt. Above 22 ppt, losses increase slightly as salinity increases to 35 ppt. Most of the leaching data for CCA has been developed in salt water (ca. 30 ppt). In this model we will assign the following salinity factor:

**Equation (2) Relative copper losses**$_{(salinity)}$ $= \mathbf{0.51\ e^{0.02\ (Salinity)}}$

Where salinity is measured in parts per thousand. This relationship is marginally significant ($P < 0.06$) and explained 61% of the variability in the data base. It predicts fresh water copper loss rates at 51% of those observed at 30 ppt salinity. It should be emphasized that this factor is appropriate to describe early metal losses (<20 weeks). Irvine and Dahlgren (1976) did not find significant differences in loss rates at salinities between 0.0 and 25 ppt after 40 weeks of leaching. However, they observed an increase of approximately 50% in copper losses at salinities greater than 25 ppt in the long term (40 weeks). The relationship given in Equation (2) will tend to slightly overestimate losses in areas where the salinity is between 5 and 15 ppt.

**Chemical fixation.** Envirochem Special Projects Inc. (DRAFT, 1992) examined the loss of copper, chrome and arsenic from stickered slings of CCA treated, hem-fir lumber (2' x 6' x14') and cedar piling in simulated rainfall tests. These tests examined three fixation processes; 1) wood that was allowed to fix at ambient temperatures (12 to 18°C) for three weeks, 2) wood that was processed using an accelerated fixation system at Domtar ™, and lumber that received an iron oxide stain without accelerated fixation. Leachate concentrations for the different fixation processes are provided in Table (11) and show that initial (in the first 50 mm of rain) copper losses were significantly reduced by either the accelerated fixation or iron oxide staining process. Less significant differences were evident after 150 mm of rainfall. The data show a rapid decline in copper losses with accumulated rainfall. This is consistent with the model, presented later in this paper, which predicts reduced copper losses with time after emersion. This reduction is most evident in the air dried samples. It could be argued that fixation was not complete in this product at the beginning of the test and that copper loss rates from the ambient air fixed product are converging with the stained and accelerated fixation products as fixation proceeds.

Lee *et al.* (1992) conducted similar studies with southern yellow pine treated to a range (0.25, 0.40, 0.60 and 2.50 pcf) of CCA retention's. Their study elucidates the importance of maintaining high wood moisture content during fixation. In addition, copper losses are reported to be an inverse function of fixation temperature. The found losses of 1.7% at 24°C, 2.3% at 60°C and 3.9% at 82°C.

The Western Wood Preservers Institute and the Canadian Institute of Treated Wood have developed Best Management Practices (BMPs) for the production of a broad spectrum of treated wood products. These BMPs are designed to minimize metal losses from waterborne wood preservatives by accelerated fixation or prolonged air drying of CCA treated products destined for use in aquatic environments. No corrections for incomplete fixation are included in this model. The publication of WWPI and CITW BMPs provides proponents and permit writers' with a valuable tool to insure that only properly fixed material enters aquatic environments.

**Table (11) Initial copper losses from CCA treated lumber as a function of fixation process. Data are from Envirochem Special Projects Inc. (1992).**

| | *Leachate Copper Concentration (ppm)* | |
|---|---|---|
| ***Treatment*** | ***after 50 mm rain*** | ***after 150 mm of rain*** |
| 1. Air dried lumber (12 to 18°C) | 1.30 | 0.60 |
| 2. Accelerated fixation (Domtar) | 0.87 | 0.55 |
| 3. Iron oxide stained lumber | 0.56 | 0.27 |

**Summary.** On a qualitative basis, all of the studies reviewed suggest the following:

i. Leaching rates are dependent on proper fixation.
ii. Leaching rates increase at low pH (<4.5). Higher leaching should be anticipated in the presence of organic acids, particularly with pH less than 4.5.
iii. Leaching is highly dependent on the period of exposure. Most leaching occurs during the first few days or weeks of exposure to moisture. After six months, very little loss of CCA components has been observed.
iv. Initial leaching rates will be higher in salt water than in fresh water.
v. Leaching rates are proportional to water exposure. CCA treated wood, submerged in water, will leach more material than will CCA treated material used as decking or retaining walls and subjected to intermittent rain.

Cooper (1990) provides a hierarchy of severity of leaching exposure. Portions of his hierarchy are presented in Table 12. This report will consider exposure to seawater, fresh water, and rainwater.

**Table 12. Hierarchy of Severity of CCA Leaching Exposure Conditions.**

| Exposure Condition | Typical Applications | |
|---|---|---|
| Complete exposure to **rain water** | Roofing, decking, railings | ***Lower loss*** |
| Exposure to soil | Fence posts, poles, retaining walls | ↓ |
| Exposure to **fresh water** | Cribs, lock gates, fresh water piling | |
| Exposure to **sea water** | Marine piling, piers, cribs | |
| Acidified water and warm water | Cooling towers, acid lakes | ***Higher loss*** |

**Leaching of metals from CCA treated wood used in fresh water.** Cooper (1990) reviewed the available data describing CCA concentrations in leach water. No data were presented for either CCA treated poles or commodity size lumber exposed to fresh water environments. The largest samples for which data was cited were the 5 cm x 5 cm x 1.9 cm blocks used by Warner (1990). Warner found that 5.2% of the copper, 1.0% of the chromium and 18% of the arsenic were lost during a 40 day leach test. Assuming a CCA-C composition of (47.5% $CrO_3$, 18.5% CuO and 34.0% $As_2O_5$), treatment to a retention of 15.6 kg/$m^3$ ( 1.0 pcf) and losses of 5.2% copper, 1.0% chromium and 18% arsenic, it is possible to estimate leaching rates as a function of surface area. The results indicate that elemental losses are 1.62 micrograms copper/$cm^2$/day, 0.52 micrograms chromium/$cm^2$/day and 8.39 micrograms arsenic/$cm^2$/day. This analysis is somewhat crude. However, the assumptions are conservative and provide reasonable estimates of metal losses. Because of the high proportion of end grain in Warner's samples (21.6%), their small size, and large surface area to volume ratio, the calculated values may significantly overestimate losses by a considerable margin.

**Leaching of CCA associated with rain and above water uses.** Several studies have been carried out on shakes and roof boards (Cserjesi, 1976; Evans, 1987 and Hruby, 1990). The reported losses of arsenic, copper and chromium were in the 0 to 7 ppm range. Cserjesi (1976) found that most of the leached chemical was recovered during the first year. He also found that arsenic and copper losses were greater than chromium.

Cooper (1990) reported that run-off water from CCA-C treated poles exposed to natural rain contained 1,800 ppb copper, 400 ppb chromium and 300 ppb arsenic. Similar data for lumber contained 290 to 5,000 ppb copper, 80 to 1,000 ppb chromium and 1,100 to 7,300 ppb arsenic. The fracturing and exposure of wood cells and end grains in sawn lumber obviously contributes to metal losses from these products. Natural rain water collected from ten year old decking contained less than 100 ppb of any of the metals.

Assuming an average rainfall of 89 cm (35"), this data suggests that CCA treated lumber used in the above water construction of piers, docks, floats and bulkheads will, at a maximum, make average daily contributions of 1.2 micrograms of copper, 0.2 micrograms of chromium and 1.8 micrograms of arsenic per square centimeter of CCA treated lumber surface area exposed to the rain.

**Leaching of metals from CCA treated wood used in salt water.** Several studies using small coupons, shavings or sawdust from treated wood are presented by Ruddick and Ruddick (1992). None of these studies present data that is appropriate for the determination of leaching rates from full size treated wood products exposed to aquatic environments during intended uses. Weis *et al.* (1991) and the critique by Breteler (1992), clearly reveal the inappropriateness of small scale leaching tests in attempts to predict environmental results.

Gjovik (1977) examined the loss of CCA-C components from southern pine posts in the marine environment. The posts used in Gjovik's (1977) study had an average exposed wood surface of 3,651 $cm^2$ and CCA retention of 2.42 lbs/cf. Metal losses in Gjovik's study are based on composite analysis of the metals remaining in concentric shells of the treated poles. Gjovik's composite analysis suggested copper losses as high as 32.37 μg/cm$^2$-day.

A re-evaluation of Gjovik's original data suggests arithmetic errors in his composite analysis. In addition, Gjovik (1977) did not analyze replicates during the fifth year. The single fifth year sample suggested a relatively low retention of 1.78 pcf CCA. Replicate samples in year eight indicated an increase in CCA retention to 2.02 pcf CCA. Gjovik's original retention rates are compared with a re-evaluation in Table 13.

**Table 13. CCA retention and resulting copper leaching rates from southern yellow pine poles placed in seawater and analyzed over a period of eight years. The results of Gjovik's (1977) composite analysis are compared with a new composite analysis. Values are presented in pounds CCA per cubic foot of treated pole. Copper loss rates based on the new composite analysis are also presented. Copper losses are expressed in micrograms of elemental copper lost per square centimeter per day with and without year five data.**

| **Analyst** | **Year** | | | | |
|---|---|---|---|---|---|
| | **0** | **1** | **3** | **5** | **8** |
| Gjovik (1977) in pcf | 2.36 | 2.00 | 2.16 | 2.00 | 2.02 |
| Revaluation in pcf | 2.35 | 2.17 | 2.03 | 1.78 | 2.00 |
| New Cu Loss Rates (μg-cm$^{-2}$-day$^{-1}$) | | 10.24 | 1.91 | 1.08 | -0.57 |
| Cu Loss Rates Excluding Year Five Data (μg-cm$^{-2}$-day$^{-1}$) | | 10.24 | 1.91 | | 0.10 |

The increases in CCA retention reported in years three and eight were not explained in Gjovik (1977). CCA retention is dependent on wood characteristics. It is possible that the single sample evaluated in year five was from an area of the pole with high density (knot, heartwood, etc.). The wood preserving industry requires multiple borings for all retention analyses. Copper losses from these poles, based on a corrected composite analysis, and excluding the anomalous year five data, show a steady decline in CCA retention, which is more consistent with expectations.

Baldwin *et al.* (1994) provide metal leaching data from a carefully conducted marine study of commodity size CCA-C treated wood pilings. Fixation of the pilings used in this study was confirmed using the chromotropic acid test. Putt's study examined seawater leachate obtained from a 28-day agitated (to simulate wave action) soaking of freshly treated, CCA-C marine grade southern yellow pine pilings. The poles averaged 74.4 cm in circumference and were 121.4 cm in length giving an average surface area of 9,032.6 cm$^2$. The total leachate volume of 240 liters was renewed every seven days. Average daily metal loss rates per square centimeter of exposed treated wood surface are presented in Table 14. Metal loss rates are less than those found in Gjovik's study. However, Putt's study addresses leaching in a more direct and appropriate way because it evaluated losses as a function of metal in the leachate while Gjovik's study examined metal concentrations remaining in the treated wood as a function of time. Putt's data are compared to copper leaching rates computed from a variety of sources in Table 15. Table 16 describes reported metal loss rates for a variety of environments.

**Table 14. Average daily leaching rates/cm$^2$ of arsenic, copper and chromium observed in large scale, agitated, seawater leaching experiments on CCA-C treated poles. (Putt, 1993).**

| | Leaching Rates (micrograms/cm$^2$/day) | | |
|---|---|---|---|
| **Period** | **Copper** | **Arsenic** | **Chromium** |
| 0 through day 7 | 2.6 | 1.1 | 0.13 |
| Day 7 to 14 | 1.7 | 0.7 | 0.05 |
| Day 14 to 21 | 1.6 | 0.4 | 0.04 |
| Day 21 to 28 | 1.4 | 0.5 | 0.04 |

**Table 15. Copper leaching rates determined from a variety of sources.**

| **Source** | **Test Protocols** | **Copper leaching rate** |
|---|---|---|
| Putt (1993) | (23.2 cm dia. x 121.8 cm long poles, 40.7 kg CCA $m^{-3}$, 31 ppt, 240 liters) | 2.6 μg-$cm^{-2}$ $day^{-1}$ |
| Cooper (1991) | (10 x 10 x 40 mm, 0.0 ppt salinity, ca, 15 kg CCA $m^3$) | 6.5 μg-$cm^{-2}$ $day^{-1}$ |
| Warner (1990) | (47.5 blocks, 0.0 ppt salinity, 15.6 kg CCA $m^{-3}$) | 1.6 μg-$cm^{-2}$ $day^{-1}$ |
| Weis, *et al.* (1991) | (11.3x9x0.6 cm, 25 ppt salinity , 6.2 kg CCA $m^{-3}$, first 7 days, 4,000 ml) | 1.5 μg-$cm^{-2}$ $day^{-1}$ |

**Table 16. Summary of metal loss rates associated with CCA treated lumber and piling used in and above aquatic environments. Data are presented in micrograms/cm$^2$/day.**

| **End Use and Environment** | **Copper** | **Arsenic** | **Chromium** |
|---|---|---|---|
| Submerged in Fresh Water | 1.62 | 8.39 | 0.52 |
| Submerged in Marine Water | 2.60 | 1.09 | 0.12 |
| Above Water & Exposed to 35" Average Rain | 1.20 | 1.80 | 0.20 |

The values for copper are consistent. The Putt (1993) study is the most thorough and recent. For purposes of this model, it will be assumed that CCA treated to 40 kg $m^{-3}$ and submerged in marine environments (30 ppt salinity) will lose an average of 2.6 μg copper $cm^{-2}$ $day^{-1}$ during the first seven days of emersion.

**Preservative retention.** Lee, *et al.* (1993) studied the effects of fixation methods on the leachability of CCA-treated southern pine. In their study, small samples (25 x 25 by 29 mm) of southern pine were treated with CCA preservative to retention's of 3.7, 6.1, 9.3 and 39.8 kg $m^{-3}$. Leaching tests were conducted for 14 days in fresh water. The amount of water in each test was adjusted to provide the same wood sample surface area to water volume ratio. The results are expressed in ppm metal in the leachate. Results of the low temperature, kiln-dried, study are presented in Table 17.

**Table 17. Cumulative amount of copper leached during a 14-day water soak after low temperature kiln drying of southern yellow pine treated to several retention's. Data from Lee *et al.* (1993).**

| **Retention** | | **Copper in leachate (ppm)** |
|---|---|---|
| 3.7 kg $m^{-3}$ | (0.23 lbs-$ft^{-3}$) | 7.77 |
| 6.1 kg $m^{-3}$ | (0.38 lbs-$ft^{-3}$) | 11.23 |

| | | |
|---|---|---|
| 9.3 kg $m^{-3}$ | (0.58 lbs-$ft^{-3}$) | 14.09 |
| 39.8 kg $m^{-3}$ | (2.49 lbs-$ft^{-3}$) | 26.06 |

Lee *et al's* (1993) report did not include information regarding the volume of leachate used in the study. However, these data were normalized to the average copper loss rate found in the first 14 days of the Putt (1993) study (2.2 μg $cm^{-2}$ $day^{-1}$). Regression analysis on this transformed data produced an excellent relationship ($R^2_a$ = 0.998) given in Equation 3. This relationship was then corrected to the initial retention rates in the Putt (1993) paper and will be used to describe copper loss from CCA treated wood in marine environments.

**Equation 3. Initial copper losses (μg $cm^{-2}$ $day^{-1}$) = 0.55 + 0.65 x Natural Log (0.71 x Retention)**
Where retention is measured in kilograms-$m^{-3}$

**Summary of anticipated leaching rates from CCA treated wood.** With the exception of the Putt (1993) study, there is a paucity of data describing metal losses from commodity size products. Data from small scale (wafers, small blocks, shavings and sawdust) have been used to estimate salinity, retention and the time dependence of metal losses in a variety of environments. Data from a variety of sources have been normalized to the conditions found in the Putt (1993) study and the variation associated with salinity, preservative retention and time described. Expressions, used in this risk assessment, describing the loss of copper are provided in Equation 4.

**Equation (1) Temporal Factor** $= \exp^{-0.048 \times \text{time (days)}}$
**Equation (2) Relative copper losses$_{(\text{salinity})}$** $= 0.51 \exp^{0.02\,(\text{Salinity})}$
**Equation (3) Initial copper losses (μg $cm^{-2}$ $day^{-1}$)** **= 0.55 + 0.65Natural Log (0.71Retention)**

**Equation (4) Copper losses = Temporal Factor x Salinity Factor x Initial Loss Rate (30 ppt)**

$$\textbf{Copper Losses} = \exp^{-0.048 \times \text{time (days)}} \times 0.51 \exp^{0.02\,(\text{Salinity})} \times (0.55 + 0.65\,\text{Natural Log}\,(0.71\,\text{Retention}))$$

Where copper losses are measured in μg-$cm^{-2}$ $day^{-1}$

Adequate studies quantifying the loss of copper from submerged, sawn lumber (such as used in bulkheads) was not obtained. Rainfall, leaching studies, such as the DRAFT study produced by Envirochem Special Projects Inc. (1992) for Environment Canada, suggest that CCA treated, 2" x 6" hem-fir lumber looses less copper than does similarly treated cedar piling. In addition, the data in rainfall studies suggests similar, or lower, metal losses from commodity size, CCA treated, sawn lumber in comparison with similarly treated piling. Therefore, until adequate studies are conducted to elucidate metal losses from CCA treated lumber, the Putt (1993) data for piling will be assumed to also represent these losses. It appears, from the available data, that this will slightly overestimate the environmental risks.

Additional factors such as wood species, water pH and proper fixation can affect these values. The relationships described above assume normal pH (>4.5 in fresh water), treatment to AWPA standards, and compliance with WWPI and CITW BMPs for proper fixation. The results are appropriate for southern yellow pine, hemlock and properly incised Douglas fir. They should not be applied to refractory species such as hardwoods, spruce and dense Douglas fir.

## Anticipated Environmental Levels of Copper Resulting From the Use of CCA Treated Wood In and Over Aquatic Environments.

The leaching rates estimated by Equation (4) provide a means of estimating the final environmental concentrations of metal contaminants associated with the use of CCA treated wood products. Two Microsoft EXCEL™ based spreadsheet models are presented in the following sections. The first describes anticipated levels of copper resulting from the use of CCA treated piling and the second predicts water column and sediment levels of copper associated with large surface area CCA treated wood structures such as bulkheads. The following assumptions have been made in constructing the model.

*i.* we will assume that the volume of the receiving water is large in comparison with the total amount of preservative being considered. In marine environments, the surface area of the receiving water should be greater than 259 times the immersed area of CCA treated structure.

*ii.* we will assume that detoxification processes due to natural chelation, complexation and sedimentation are long compared with the speed of the current and uptake by aquatic organisms In fact, leached metals may very quickly by detoxified by natural processes.

*iii.* for determining sediment concentrations of copper, we will assume that released copper adsorbs to the silt (3 to 63 micron) fraction of the suspended particulate load.

*iv.* we will ignore the potential for recycling of copper from aerobic sediments back into the interfacial water. Washington State sediment standards are based on Apparent Effects Thresholds and it is assumed that bioassays, upon which these standards are based, naturally account for cycling of sediments from aerobic sediments.

With these assumptions as background, the following derivations are provided to give the reader some insight into the model. That insight is valuable in interpreting the results. The models were designed to provide the analyst with a worst case analysis. Predicted copper levels in the water column are the maxima observed within half an hour of slack tide. At all other times, the metal levels will be significantly reduced.

**Sedimentation of adsorbed metals.** The following paragraphs describe physical phenomena which are important to the distribution of copper adsorbed to silt-clay sediments.

**Sediment Grain Size (SGS) considerations.** The silt-clay (< 63 micron) fraction sequesters metals more efficiently than do coarse grained sediments. In addition, sediments containing high proportions of silt and clay are characteristic of low energy, depositional sites. Therefore a simple sieve and pipette analysis to determine the sediment grain size (SGS), can give a subjective assessment of local water circulation and sedimentation. Coupled with Total Organic Carbon (TOC) and the Redox Potential Discontinuity (RPD), SGS may provide important information regarding deposition of fine grained material (and adsorbed metals) in localized areas.

This model is based on the deposition of copper by following the fate of the silt to which it is adsorbed. A quantitative assessment of silt deposition can be obtained through the application of Stokes Law for the settling velocities of small particles (Shepard, 1963). This law is expressed in Equation (5).

**Equation (5) Stokes law for the settling velocities of small particles:**

$$\varpi = \mathbf{g\, D^2(\rho_s - \rho_w)/18}\ \mu$$

Where: g = gravitational constant

D = particle diameter

$\rho_s$ = particle density
$\rho_w$ = density of water
$\mu$ = coefficient of molecular viscosity

For clay particles or finely divided organic material, the resulting vertical velocities are very small ( $10^{-6}$ cm/sec). In this model we will assume that PAH is adsorbed to silt particles with vertical velocities in sea water ($10^{o}$ C) of $2 \times 10^{-1}$ to $10^{-3}$ cm/sec. An intermediate value of $5 \times 10^{-2}$ cm/sec will be used in computing silt adsorbed copper deposition to the benthos. It should be noted that this is a very conservative number and that actual deposition, particularly in areas where sediments have high total organic carbon or clay fractions, may be significantly lower. The EXCEL Spreadsheet includes provisions for user defined settling velocities.

**Currents.** Tidal currents may be very complex and depend on highly variable factors such as wind velocity, tidal exchange, lunar period, local geography, season and barometric pressure. A very simple tidal model is used in this analysis. We assume that tidal flows are harmonic with a frequency of 12 hours. The instantaneous tidal current can be modeled by the harmonic:

$$V_t = V_{maximum} \operatorname{Sin}(\pi t/12)$$

Integrating this equation from $t = 0$ to $t = 6$ gives: Distance = $V_{max} \int \operatorname{Sin}(\pi t/6)dt$, or:

**Equation (6) Distance = 3.82 (hours) x $V_{maximum}$ = 1.3752 x $10^4$ (sec) x $V_{maximum}$**

where $V_{maximum}$ is measured in cm/hour or cm/sec respectively

$V_{maximum}$ is measured (using either a drogue or a current meter) at a time midway between Mean High Water (MHW) and Mean Low Water (MLW). MHW does not vary significantly from tide to tide. However, $V_{maximum}$ should be measured during a tidal exchange when the low tide is as close to MLW (18.6 year average of all low tides) as possible. Ideally, two velocity measurements should be made at mean water depth One on the ebb tide and again on the flood tide. These two measurements should be averaged to provide a value for $V_{maximum.}$ This procedure will give a crude, but reasonable, estimate of the average, annual, current speed at a site.

The “Distance” developed in this analysis is the average distance which a particle is carried, by the tides, in one direction, before its velocity is reversed and it is carried back toward the point of origin (source). The average tidally driven velocity is $0.64V_{maximum}$ (3.82 hours/6 hours). This procedure will integrate the effects of all currents influencing a site at the time the measurements are taken.

In flowing water, not influenced by tides, a single measurement of water speed will suffice. The measurement should be made during a period of minimum flow. We will refer to this steady state speed as $V_{ss}$.

In situations where local currents are a function of both steady state and tidally driven factors, three current measurements should be taken approximately three hours apart. In addition to the measurements required to determine $V_{maximum}$, the third measurement should be taken at slack tide. This measurement is $V_{ss}$. The appropriate velocity to be used in this model (cm/sec) can then be determined using Equation 7.

**Equation 7. $V_{model} = V_{ss} + 0.64 * V_{maximum}$**

The author acknowledges that during the period of time in which tidal currents are opposed to steady state currents, low velocities may occur, resulting in higher deposition rates in sediments "upstream" from the source. Do to the variety and complexity of potential hydrodynamic interactions, this model will only examine average copper deposition to the sediment.

**Diffusion.** An examination of potential diffusion constants (D) reveals very low values ( $D \sim 1.5 \times 10^{-4}$). Substituting these values into an appropriate diffusion equation, such as Equation 8, suggests that in most open systems, diffusion plays little part in the distribution of copper. The diffusion distances are on the order of a few centimeters per hour which we expect to be small in comparison with currents and turbulence.

**Equation 8.** $\mathbf{C_{(x,t)} = C_o e^{-(x\ exp2)/4Dt}/2(\pi Dt)^{1/2}}$

**Geometrical patterns of copper deposition to sediments.** These patterns may be even more complex than the tidal velocities associated with a site. They depend on many factors such as the interaction of currents with wind driven waves and geomorphologic characteristics of the shoreline, in-water structures, and the benthos. Detailed studies of the distribution of suspended sediments to the benthos are beyond the scope of this analysis and are generally site specific.

In the following analysis, we will assume that copper is adsorbed to silt sediments which are deposited in a circular pattern around the construction site. While this may be viewed as unrealistic, worst case scenarios will be seen to involve very low current velocities associated with backwaters and eddies. In these environments, horizontal mixing associated with wind driven waves may play a significant part in the distribution of suspended material. Therefore, in worst case situations, a circular distribution pattern may very well provide a reasonable assessment of the broad scale distribution of contaminants.

Other distributional geometry's are possible. The model contains a Geometry Factor equal to $1 + V_{model}/10$. This factor tends to concentrate metal deposition into a plume in the direction of the currents. At moderate velocities (50 cm/sec) the Geometry Factor predicts downstream PAH concentrations that are six times those associated with slow speed currents. The following analysis is provided in detail so that additional geometry's can be generated by users. We start with a simple circular geometry and assume that:

(1) $dA = 2\pi(r + R_p)dr$ where: $dA$ = incremental area and
$dr$ = incremental radius
$R_p$ = piling radius
$r$ = radius (measured from the periphery of the pile) where copper is deposited.

(2) $dr = [V_{model}/V_{vert}]dh$ where: $dh$ = incremental piling height and $V_{vert}$ = vertical particle velocity ($5 \times 10^{-2}$ cm/sec for silt)

(3) The distance from the periphery of the pile at which particles impact the bottom is $r = h(V_{model}/V_{vert})$. Therefore:

(4) $dA = 2\pi[h(V_{model}/V_{vert}) + R_p](V_{model}/V_{vert})dh$

Deposition to the benthos of copper migrating from pressure treated wood is then:

(5) Deposition (D) = $M/dA = M/ 2\pi[h(V_{model}/V_{vert}) + R_p](V_{model}/V_{vert})dh$

where: $M$ = Total PAH Migration ($\mu g\ day^{-1}$) = $m2\pi R_p dh$
$m$ = migration rate ($\mu g\ cm^{-2}\ day^{-1}$)

Substituting for M, the relationship becomes:

(6) $D = m2\pi R_p dh/2\pi[h(V_{model}/V_{vert}) + R_p](V_{model}/V_{vert})\, dh$

This expression can be simplified by substituting the relationship, $h = r(V_{vert}/V_{model})$:

**Equation 9.** $\mathbf{D = mR_p/[(r + R_p)(V_{model}/V_{vert})]}$

Where D = deposition rate (excluding degradation factors) measured in $\mu g\ cm^{-2}\text{-}day^{-1}$
m = metal migration rate, measured in $\mu g\ cm^{-2}\text{-}day^{-1}$ (see Equation 4.)
$R_p$ = average piling radius measured in cm
$\mathbf{V_{vert}}$ **=** average vertical velocity of adsorption particles (silt = 0.05 $cm\text{-}sec^{-1}$ )
$\mathbf{V_{model}}$ = Model water velocity = $V_{ss} + 0.64V_{maximum}$
r = the distance from the periphery of the treated wood at which the deposition is measured.

**Surface Area Leaching Ratio.** For closely spaced sawn lumber, backed by earthen fill (bulkheads), minimal copper losses to the aquatic environment can be expected from the protected (landward) bulkhead face. If the boards are not touching, then additional leaching surface is available. For a fully exposed, 2" x 6" board, the total leaching surface per surface area facing the water is 2.54 cm/cm. For a 2" x 6" board in which the front surface and edges are leaching and exposed to the receiving water, the ratio is 1.54 cm/cm. These ratios are somewhat small for 2" x 8" and larger boards. For purposes of this model, we will assume that the entire front face and both edges are exposed to the water and leaching. The model user will input the board width (in centimeters) in User Input 15. The program will correct copper losses for the increased surface area using Equation 10. This equation was developed using non linear regression techniques. It explains 97% of the variation in the data set describing leaching area ratios as a function of board width.

**Equation 10.** **Surface Area Leaching Ratio = 1.84 exp$^{-0.01346 \times \text{Board Width (cm)}}$**

**Water column contamination associated with CCA treated lumber used in Bulkheads.** Significant quantities of CCA may come into contact with marine water in poorly flushed canals. The length of these bulkheads, and low water circulation, suggest that this application may represent a worst case application and deserves special consideration. Copper loss rates from CCA treated wood will be modeled as before. However, in assessing these risks, we assume a newly installed bulkhead of length *l*. The model will assume water is moving slowly along this bulkhead at velocities defined in the same way as was used for the piling model.

**Diffusion** will slowly dilute copper leached from the bulkhead across a concentration gradient. However, diffusion appears to play a minimal part in dispersing leached copper. For instance, given a Diffusion Coefficient (D) = $1.5 \times 10^{-5}$, copper concentrations will be 1% of the concentration next to the treated wood at a distance of only 1.06 cm after 4,000 seconds. For purposes of this model, we will ignore diffusion processes and assume that all mixing is due to turbulence.

**Turbulent mixing** is site specific, and may be very complex. This model will assume that copper is mixed into the water column adjacent to a bulkhead, or other vertical structure, in a time dependent manner given by Equation 13.

**Equation 13.** $$\textbf{Mixing Width} = 2.5 \times 10^{-3} \times (\text{Velocity}_{model})^2 \times \text{Transit time (sec)}$$

Time in this equation can be replaced with an equivalent expression:

$$\textbf{Transit time} = \text{Bulkhead Length}/\text{Velocity}_{model}$$

Substituting this into Equation 13 and simplifying gives Equation 14.

**Equation 14.** $$\textbf{Mixing Width} = 2.5 \times 10^{-3} \times \text{Bulkhead Length} \times \text{Velocity}_{model} \text{ (cm)}$$

This equation predicts that water traveling along a 100 meter long bulkhead at 2.5 cm/sec would be mixed to a width of 62.5 cm. The mixing width of a hydraulic system moving along the same bulkhead at a model velocity of 20 cm/sec would be 5.0 meters.

With the preceding background, it is possible to estimate water column concentrations associated with bulkheads or other structures using sawn lumber in installations with large leaching surface areas. An appropriate expression is of the form:

$$\textbf{Copper Concentration} = \text{Copper Migration Rate } (\mu g \text{ per second}) \times \text{exposure time} \times \text{Leaching Surface Ratio}/\text{Mixing Width}$$

where exposure time = bulkhead length/$V_{model}$

$$\text{Conc}_{(cu\text{-}bulkhead)} = \exp^{-0.048 \times \text{time (days)}} \times 0.51 \exp^{0.02\,(\text{Salinity})} \times (0.55 + 0.65 \text{Natural Log } (0.71 \text{ Retention}) \times 1.84 \exp^{-0.01346 \times \text{Board Width (cm)}}) / (86{,}400) \times (2.5 \times 10^{-3} \times (V_{ss} + 0.64(V_{maximum} - V_{ss}))^2$$

or, after converting this to parts per trillion ( x $10^6$), we obtain Equation 15.

**Equation 15.** $$\text{Conc}_{(cu\text{-}bulkhead)} = 2823.89 \times (\exp^{-0.048 \times \text{time (days)} + 0.02\,(\text{Salinity}) - 0.01346 \times \text{Board Width (cm)}}) \times (0.8462 + \text{Natural Log } (0.71\text{Retention}))/(V_{ss} + 0.64(V_{maximum} - V_{ss}))^2$$

Note that this expression assumes that the water depth out to the edge of the Mixing Width is constant. Vertical mixing would further dilute metal losses associated with bulkheads located on relatively steep shorelines. No vertical mixing is assumed in this model. In addition, no metal losses to sediment are accounted for in the expression. This seems reasonable because the times associated with water transport along even long bulkheads (100 meters) by slow currents (5 cm/sec) are short (2,000 seconds) in comparison with vertical velocities (0.05 cm/sec) for silt and clay. A copper molecule adsorbed to silt would settle an average of 50 cm during transit.

**Sediment concentrations of copper associated with the use of CCA treated lumber in bulkheads.** This model will assume that copper is lost from dimension lumber at the rates previously determined. The lost copper is assumed to adsorb to suspended silt. The fate of the adsorbed copper is then determined by examining the fate of the suspended silt particles. In real environments, significant quantities of the copper may remain solubilized in the water column and/or become adsorbed to clay or particulate organic matter. Copper associated with smaller grain sizes will be distributed over larger areas at much lower concentrations than predicted here. For that reason these predictions are considered conservative from a water quality point of view.

In a previous section, we discussed a concept termed ***Mixing Width.*** In this model we will assume that silt particles are carried down current with a speed equal to the vector sum of the $Velocity_{model}$ + $Velocity_{mixing}$ where we assume that the two vectors are orthogonal. $Velocity_{mixing}$ is determined from Equation 13 and equals:

**Equation 16.** $\mathbf{Velocity_{mixing} = 2.5 \times 10^{-3} \times (Velocity_{model})^2}$

and therefore the vector sum of $Velocity_{model}$ + $Velocity_{mixing}$ is:

**Equation 17.** $\mathbf{|Velocity_{horizontal}| = \{6.25 \times 10^{-6} \times (Velocity_{model})^4 + (Velocity_{model})^2\}^{1/2}}$

An additional correction must to entered into the relationship to describe the aspect ratio of the leaching area to the area of deposition. That factor is given in Equation 18.

**Equation 18. Aspect Ratio Correction Factor (ARCF) =**

$$\mathbf{ARCF = \sin(\tan^{-1}(Velocity_{mixing}/Velocity_{model})) = \sin(\tan^{-1}(2.5 \times 10^{-3} Velocity_{model})}$$

If we assume that the settling copper is distributed over an area equal, to ARCF x $\mathbf{Velocity_{verticle}/Velocity_{horizontal}}$ then we can model copper deposition to the sediments using Equation 19.

**Equation 19.** $\mathbf{Deposition_{copper} = Copper\ Loss\ Rate\ (\mu gm\text{-}sec^{-1}) \times exposure\ time\ (sec) \times Velocity_{verticle} /(Velocity_{horizontal} \times ARCF)}$ or

$$\mathbf{Deposition_{copper} = Copper\ Loss\ Rate\ (\mu gm\text{-}sec^{-1}) \times bulkhead\ length \times Velocity_{verticle} /(|\overrightarrow{Velocity}_{mixing} + \overrightarrow{Velocity}_{model}| \times ARCF)}$$

$$\mathbf{= \exp^{-0.048 \times time\ (days)} \times 0.51 \exp^{0.02\ (salinity)} \times 1.84 \exp^{-0.01346} \times 0.65(0.8462 + Natural\ Log\ (0.71 Retention))/86{,}400 \times bulkhead\ length \times Velocity_{verticle} / \{6.25 \times 10^{-6} \times (Velocity_{model})^4 + (Velocity_{model})^2\}^{1/2} \times Velocity_{model} \times \{\sin(\tan^{-1}(Velocity_{mixing}/Velocity_{model}))\}}$$

Assuming that $6.25 \times 10^{-6} \times Velocity_{model}{}^2$ is << 1 and simplifying Equation 19, we obtain the final form of the sediment deposition model:

$$\mathbf{= 7.06 \times 10^{-6} \exp^{-0.048\ (time) + 0.02\ (salinity) - 0.01346(Board\ Width)} \times (0.8462 + Natural\ Log\ (0.71 \times Retention)) \times bulkhead\ length \times Velocity_{verticle} /(Velocity_{model})^2 \times \{\sin(\tan^{-1}(2.5 \times 10^{-3} Velocity_{model}))\}}$$

**Copper Accumulation.** The accumulation of copper in sediments is more difficult to model because copper does not degrade, but is eventually buried in accumulated sediments.

Assuming that sediment accretion rates are slow compared with either the copper loss rate or the time during which copper is migrating at significant rates, then we can assume that essentially all of the copper lost from a CCA treated structure will remain in the top two centimeters of the sediment. The rate of accumulation will decrease as predicted by the temporal factor in Equation 19. If we integrate that temporal factor from $t = 0$ to $t = \infty$ we find an expected total copper deposition equal to:

$$\textbf{Accumulation} = \int_{t=0}^{t=\infty} \exp^{-0.048 \times time}\, dt = 20.83$$

Therefore we can expect total accumulations equal to 20.83 times the initial daily accumulation.

**Correction for deep water deposition.** Where average water depths in the Mixing Width are greater than 0.025 x Bulkhead Length/$Velocity_{model}$ , copper will be deposited at the center of the bulkhead on either the ebb or flood tides, but not on both. For a bulkhead that is 100 meters in length next to water flowing with $Velocity_{model}$ = 2.5 cm/sec, copper deposition on both tides would occur only in water depths less than 100 cm deep (1 meter). In water depths greater than 1 meter, this model will result in overestimates of copper accumulations. The model contains and if-then statement that corrects sediment copper accumulation for this phenomena. Combining these factors with Equation 20, we obtain the final form of the copper accumulation model.

**Equation 20. $\textbf{Accumulation}_{(copper\ in\ sediments)}$ =**

$$1.47 \times 10^{-4} \exp^{-0.048\,(time) + 0.02\,(salinity) - 0.01346(Board\ Width)} \times (0.8462 + \text{Natural Log}\ (0.71\text{Retention}))$$

$$\times \text{ bulkhead length} \times Velocity_{verticle}$$

$$/\ (Velocity_{model})^2\ \{\sin(\tan^{-1}(2.5 \times 10^{-3}\ Velocity_{model}))\}$$

$$\times 1.0 \text{ \underline{if} Average Water Depth} \leq 0.025 \times \text{Bulkhead Length}/\ Velocity_{model} \text{ or}$$

$$\times 0.5 \text{ \underline{if} Average Water Depth} > 0.025 \times \text{Bulkhead Length}/\ Velocity_{model}$$

## Predicted concentrations of copper in the water column and sediments associated with the use of CCA treated wood.

The results of the preceding analysis have been incorporated into two *Microsoft EXCEL for Windows*™ (Version 5.0) spreadsheets. Copies of the files are enclosed in the pocket at the back of this document. The file names are A:\CCAprisk (for piling calculations) and A:\CCAbrisk for bulkhead calculations. The following paragraphs provide specific definitions and instructions.

**User Entries.** Sixteen entries, in the following format, are required to run the models:

| User Entry | Value |
|---|---|
| 1. Retention In Kilograms/Cubic Meter | 40.0 (marine); 6.2 (fresh) |
| 2. Average Piling Radius (Centimeters) | |
| 3. Treated Wood Age In Days | |
| 4. Salinity (parts per thousand, ppt) | |
| 5. Settling Velocity (0.05 for silt; 0.0005 for clay) | 0.05 |
| 6. Average Maximum Tidal Speed (cm/sec) | |
| 7. Steady State Current Speed (cm/sec, measured at slack tide) | |
| 8. Marine Sediment Copper Quality Standard (ppm) | 390 ppm |
| 9. Maximum Marine Sediment Impact Zone Cu Standard (ppm) | 390 ppm |
| 10. Fresh Water, Chronic, Copper Standard | $\exp^{(0.8545*\lvert \ln(\text{hardness})\rvert - 1.465)}$ |
| 11. Water Hardness (ppm $CaCO_3$) | |
| 12. Marine Water Copper Standard | 2.9 ppb |
| 13. Sediment Density (grams/cubic centimeter) | 2.2 grams-cm$^{-3}$ |
| 14. Length (cm) Of A Bulkhead Or Other Vertical Surface | |
| 15. Bulkhead Board Width (cm) | |
| 16. Average Water Depth (cm) | |

Notes:

**1. Treated wood retention in kilograms-m$^{-3}$.** AWPA defines minimum CCA retention's to insure adequate performance. Treaters' have excellent control over retention rates and assay each charge of piling and or lumber and report the average retention. AWPA Standards (1992) require retention's of 40 kg-m$^{-3}$ for piling and lumber submerged in marine environments and 6.2 kg-m$^{-3}$ for southern yellow pine and hemlock-fir used in direct contact with fresh water.

**2. Average piling radius ($R_p$ in centimeters).** Enter the average radius of the submerged portion of the piling in centimeters. This can be easily found from the relationship:

Circumference = $\pi$*2r or $R_p$ = circumference/2$\pi$. (one inch = 2.54 cm)

Typical piling radii will range between 12 and 22 centimeters for piling.

**3. Treated wood age in days.** Enter the time since emersion, in days. For newly constructed projects, this should be 0.0. Predictions of water column copper concentrations will be for the period within half an hour of slack tide on the day identified in this entry.

**4. Salinity (parts per thousand).** Salinity in open ocean environments is typically 34 ppt. In areas like Puget Sound it is lower at 28 to 30 ppt. Fresh water has a nominal salinity of 0.0 ppt. Salinity in estuaries influenced by major rivers can vary significantly between 3 or 4 ppt and 24 to 26 ppt. Contact your local Sea Grant Office for an accurate estimate. In estuaries, the appropriate value may be very site specific. For preliminary evaluations use the following values:

**Fresh Water** **Salinity = 0.0 ppt**
**Marine Water** **Salinity = 30 ppt**

**Estuarine Water        Salinity = 15 ppt**

**5. Settling Velocity** refers to the vertical velocity of suspended sediment to which metals are likely to adsorb (silt and clay). This model assumes that metals are adsorbed to silt and that the settling velocity is 0.05 cm/sec. If a sediment grain size analysis shows a significant clay content (>60%) and high total organic carbon (TOC), then it might be appropriate to reduce the value to 0.0005. However, very slow settling velocities result in wide spread deposition of the released metals and **very low sediment concentrations.** Unless there is compelling evidence for the use of a lower vertical velocity, it is recommended that the value of 0.05 cm/sec be used. This will give a conservative (from the environment's point of view) estimate.

**6. Average Maximum Tidal Velocity.** Measure the current three hours before, and three hours after, a low tide that is equivalent to (MLW). Mean Low Water is the 18.6 year average of both low tides on each day. It will be somewhat greater than 0.0' Mean Lower Low Water (MLLW) used as a datum in tide tables. Contact your local Sea Grant Office for an accurate value for MLW. Otherwise, measure current velocities around a low tide reported as +1.5' in local tide tables.

**7. Steady State Currents (measured at slack tide).** Total water movement at a project site is a result of the superposition of tidal currents on steady state currents associated with riverine transport and the accumulated effects of geography and wind driven currents. For purposes of this model, these steady state currents will be included by measuring water movement at slack tide. Ideally, a current meter should be positioned at mid depth. Readings should be taken continuously from 1/2 hour before slack tide until 1/2 hour following slack tide. The steady state current is the minimum current observed during that period of time.

**8. Marine Sediment Copper Quality Standard (ppm).** Enter the jurisdictional sediment standard for copper in this space. In Washington State the marine sediment standard for copper is 390 ppm (dry sediment weight in the top two centimeters). Sediment standards in fresh water have not been promulgated. Until they are, this model will assume that fresh water standards are the same as marine standards. No entry is required for this parameter to run the model. The Sed. Std. Column in the spreadsheet output is provided as a basis for decision making. Alternate standards can be assigned by the user.

**9. Maximum Marine Sediment Impact Zone Copper Standard (ppm).** In Washington State, a maximum, marine, Sediment Impact Zone (dilution zone) standard has been established. Sediments with contaminant burden's above these levels do not qualify for a Sediment Impact Zone classification and may require active clean-up. For copper, the permitted value is the same as the Sediment Quality Standard (390 ppm). Alternate standards can be assigned by the user.

**10. Fresh water, chronic, copper standard.** In Washington State, fresh water copper standards are designated as chronic or acute. The acute standard cannot be exceeded for more than one hour, once every three years. The chronic standard cannot be exceeded for more than four days, once every three years. The chronic standard is used in this model because significant decreases in copper losses from newly installed CCA treated wood occur within a matter of days, not hours. The chronic standard is a function of water hardness measured as the calcium and magnesium salts present in water. For purposes of this standard, hardness is measured in milligrams per liter of calcium carbonate ($CaCO_3$). The standard is determined using Equation 21.

**Equation 21. Fresh Water Quality Standard =** $\exp^{(0.8545*|\ln(\text{hardness})| - 1.465)}$

**11. Water Hardness.** Water hardness is measured as the calcium and magnesium salts present in a sample of water. It is expressed as ppm $CaCO_3$ .

**12. Marine Water Copper Standard.** In Washington State the Marine Water Quality Standard for copper is 2.5 ppb. The more widely accepted EPA standard is 2.9 ppb. Users may enter alternate values.

**13. Sediment Density (grams-cm$^{-3}$).** This value may vary depending on the composition of the sediment. For estuarine sediments, the given value of 2.2 grams-cm$^{-3}$ will be close. Users may use alternate values.

**14. Length Of A Bulkhead Or Other Vertical Surface.** Enter the length of a bulkhead that is submerged in the water. The depth of submergence is not a factor in this model. However, bulkheads that are submerged less than 30 cm along steep shores (>10% slope) will result is minimal copper concentrations.

**15. Bulkhead Board Width.** This input parameter is used to define the ratio of total leaching surface per square centimeter of exposed bulkhead facing. It assumes that the front face and edges are exposed and leaching. The entry is in centimeters (2"x 6" = 13.97 cm, 2"x 8" = 19.05 cm, 2"x10" = 24.13 cm and 2"x12" = 29.21 cm).

**16. Average Water Depth.** This is the average depth (in centimeters) of water in the Mixing Width at the site. Water depth can be measured three hours before or after a low tide equivalent to Mean Low Water (MLW).

**Table 18. Recommended input parameters during preliminary evaluations or when specific information is unavailable.**

| User Entry | Fresh Water | Marine | Estuarine |
|---|---|---|---|
| 1. Treated wood retention in kg-m$^{-3}$ | 6.2 | 40.0 | 40.0 |
| 2. Average piling radius (centimeters) | 15.0 | 15.0 | 15.0 |
| 3. Piling Age in Years | 0.0 | 0.0 | 0.0 |
| 4. Salinity (parts per thousand, ppt) | 0.0 | 30.0 | 15.0 |
| 5. Settling Velocity (0.05 for silt; 0.0005 for clay) | 0.05 | 0.05 | 0.05 |
| 6. Average maximum Tidal Velocity | 0.00 | 10.0 (north)<br>5.0 (south) | 10.0 (north)<br>5.0 (south) |
| 7. Steady State Currents (measured at slack tide) | (0.0 marine; 20.0 riverine; 2.0 lakes) | | |
| 8. Marine Sediment Copper Quality Standard (ppm) | 390 | 390 | 390 |
| 9. Maximum Marine Sediment Impact Zone Cu Stand) | 390 | 390 | 390 |
| 10. Fresh Water, Chronic, Copper Standard | | | |
| 11. Water Hardness (ppm $CaCO_3$) | 100 | | |
| 12. Marine Water Copper Standard | | 3.1 | |
| 13. Sediment Density (grams/cubic centimeter) | 2.2 | 2.2 | 2.2 |
| 14. Bulkhead Length (cm) | enter the proposed length | | |
| 15. Board Width in cm (2" x 6" = 13.97 cm, 2" x 8" = 19.05 cm, 2" x 10" = 24.13 cm, 2" x 12" = 29.21 cm) | | | |
| 16. Average Water Depth | 150 cm | 150 cm | 150 cm |

## Model Output

**Water column copper concentrations associated with CCA treated piling.** The Microsoft EXCEL ™ spreadsheet accompanying this model presents an algorithm for site specific assessments based on the following model. Worst case scenarios occur within half an hour of slack tide in areas where there are no steady state currents. By integrating Equation (2) from half an hour before slack tide to half an hour after slack tide, we find that the average tidal speed during this period is 0.06451 x $V_{maximum}$. Combining this factor with copper leaching rates (Equation 4), we obtain:

$$\textbf{Concentration (C)} = \exp^{-0.048 \times \text{time (days)}} \times 0.51 \exp^{0.02\ (\text{Salinity})} \times 0.65(0.8462 + \text{Natural Log } (0.71 \times \text{Retention})) \times 2\pi R_p / 24\pi[(1800 \times 0.0651 \times V_{max} + 1800V_{ss} + R_p)^2 - R_p^2]$$

or, after simplifying this expression we obtain **Equation 22.**

$$\textbf{Concentration (C)} = 0.0276 \times \exp^{-0.048 \times \text{time (days)} + 0.02(\text{Salinity})} (0.8462 + \text{Natural Log } (0.71 \times \text{Retention})) R_p / [(1800 \times 0.0651 \times V_{max} + 1800V_{ss} + R_p)^2 - R_p^2]$$

Where:

| | | | |
|---|---|---|---|
| exp | = 2.718 | Natural Log | = logarithm (base exp.) |
| time | = age of the project in days | Retention | = CCA retention (kg-m$^{-3}$) |
| $R_p$ | = piling radius in centimeters | Salinity | = in parts per thousand |
| $V_{max}$ | = Maximum Tidal Current Speed | $V_{ss}$ | = Steady State Current Speed |

This model assumes that the volume of the water body is large in comparison with the total amount of copper lost from the structure. It does not make predictions for small volume, closed water body conditions. Output describing water column concentrations in this model is presented in the following format:

| | |
|---|---|
| Water Column Conc. (pptrillion) | OUTPUT |
| Marine Water Standard (pptrillion) | 2900 |
| Fresh Water Standard (pptrillion) | OUTPUT |

The model predicts that tidally driven water currents of 2.5 cm-sec$^{-1}$ will cause the dispersion of leaching copper into a circle of 586 cm in radius. At 30 ppt, with a retention of 40 kg-m$^{-3}$, a single piling will leach 2.86 µg cm$^{-2}$ day$^{-1}$ or 0.119 µg copper cm$^{-2}$ hr$^{-1}$. Dispersed into the water column from a piling 30 cm in diameter, this material would result in concentrations of 34.0 pptrillion copper within half an hour of slack tide on the day of installation. It should be emphasized that copper levels at all other times will be less than this value, which is approximately 1.17 % of the marine standard (2.9 ppb), giving a safety factor of 85. Additional horizontal mixing and turbulence would, in reality, dilute the contaminants even further. Copper concentrations within half an hour of slack tide can be predicted at other times by changing the user input number three (Treated Wood Age in Days). The resulting output will be for the day identified in this entry. In the preceding example, copper concentrations within half an hour of slack tide would be 8.1 parts per trillion on the 30th day of emersion.

**Sediment contamination associated with CCA treated piling projects**. The preceding discussion provides the basis for development of a simple, spreadsheet (Microsoft™. EXCEL Version 5.0), based model to predict near field sediment copper concentrations associated with CCA treated wood projects. Assumptions made in defining this model are:

**1. Copper loss** rates from CCA treated wood are a function of salinity, time after treatment and retention rates. The following algorithm for copper loss rates is used in this model. The output is in μg $cm^{-2}$ $day^{-1}$.

**Copper Losses = $\exp^{-0.048\ (time)}$ 0.51 $\exp^{0.02\ (Salinity)}$ 0.65(0.8462 + Natural Log (0.71Retention))**

**2. Copper Adsorbed Particle Settling Velocities** are measured in cm $sec^{-1}$ and referred to in this model as $\mathbf{V_{vert}}$. For determination of sediment loading, they are predicated on a worst case adsorption of copper to silt particles having a vertical velocity of 0.2 to 0.001 cm $sec^{-1}$. For purposes of this model we will assume an intermediate velocity of 0.05 cm $sec^{-1}$.

$$V_{vert} = 0.05 \text{ cm sec}^{-1}$$

**3. Geometric Correction Factor.** This model assumes a circular distribution of adsorbed copper around the piling or complex of pilings. Justification for that assumption is sought by consideration of the worst case scenarios in which very low levels of water circulation are observed. In these cases, wind driven currents and waves, passing vessels, anthropogenic structures and microgeographic features can play a significant role in creating a complex system of interacting forces which tend to circularize the deposition of suspended sediments (and copper). A Geometry Correction Factor (Equation 17) has been included in this model. The factor will focus copper accumulation in an increasingly narrow plume, downstream from the structure, as current speeds increase.

**Equation 17. Geometry Correction Factor ($1 + V_{model}/10$)**

**4. Copper Deposition (D)** is proportional to the radius of the pile ($R_p$) and the settling velocity ($V_{vert}$). It is inversely proportional to the currents ($V_{model}$) and the radius or distance (r) from the piling at which the contamination is measured. Equation 18 is used to predict copper deposition.

**Equation 18. Deposition (D) = $MR_p/[(r + R_p)(V_{model}/V_{vert})]$**

**Where:**
1. D = Dilution rate is a dimensionless factor
2. $R_p$ = Piling radius measured in cm
3. $V_{vert}$ = silt-clay settling velocity = 0.05 cm $sec^{-1}$.
4. $V_{model}$ = Model water velocity = $V_{ss} + 0.64\ V_{maximum}$
5. r = the distance, in cm from the piling perimeter at which the sediment copper concentration is measured.
6. M = Copper Loss Rate

**Sediment Copper Accumulation (A) Model**. The above parameters are combined in the following, intuitive manner to give the final form of the model.

**Copper Accumulation (A) = Geometry Correction Factor x Copper Deposition**

Substitution of the previously determined values for each of these parameters gives the final form of the Sediment Copper Accumulation model in Equation 19.

**Equation 19.** $(A) = (1 + V_{model}/10) \times \exp^{-0.048\,(time)}\ 0.51 \exp^{0.02\,(Salinity)} \times 0.65(0.8462 + \text{Natural Log}\ (0.71 \times \text{Retention}) \times R_p / [(r + R_p) \times (V_{model}/V_{vert})]$

Where: Salinity is measured in parts per thousand
$V_{model}$ = Model water velocity = $V_{ss}$ + 0.64 $V_{maximum}$
time = project age, in days
$V_{vert}$ = silt-clay settling velocity = 0.05 cm $sec^{-1}$.
Retention = CCA retention, measured in kg-$m^{-3}$
exp = the base for the natural log = 2.7183
$R_p$ = Piling radius measured in cm
r = the distance, in cm from the piling perimeter at which the sediment copper concentration is measured.

There are some limitations to this model. It does not address metal loading to the sediment associated with abrasion of CCA treated wood, which can be water logged, heavier than water, and which will eventually settle to the bottom. The addition of splinters and chunks of treated wood abraded from ferry dolphins and wingwalls could add significantly to copper accumulations in sediments associated with these structures. However, because the metals remain bound to the wood fibers, this material would not be bioavailable.

**Sediment copper accumulation model output for piling.** Output describing sediment accumulation of copper is provided in two formats. Tabular output from the spreadsheet is provided in Table 19. In addition to the tabular output, A:\CCAprisk presents the results in graphical form. A copy of the graphical output accompanying Table 19 is provided in Figure 2. The two horizontal lines represent sediment standards entered by the user at User Inputs 8 and 9. Separate predictions are provided for each of the pilings and the sum of those predictions is also provided. Predicted copper levels can be given in either log or linear scales (user defined by manipulation of Microsoft™ EXCEL). The results of a typical marine piling installation are provided in Table 19 and Figure 2.

**Table 19. Tabular output from the Microsoft EXCEL ™ spreadsheet A:\CCAPrisk. Water column copper concentrations associated with piling.**

**Copper Accumulation in Waster and Sediments Associated with the use of CCA Treated Wood**

| User Entries | | Intermediate Output | |
|---|---|---|---|
| 1. Retention in kilograms per cubic meter | 40.00 | Migration (migr/cm2-day) | 2.72 |
| 2. Average piling radius (centimeters) | 15.00 | Age Factor | 1.00 |
| 3. Piling Age in Days | 0.00 | Retention Factor | 0.99 |
| 4. Salinity (parts per thousand, ppt) | 28.00 | Mixing Width (cm) | 40.00 |
| 5. Settling Velocity (0.05 for silt; 0.00005 for clay) | 0.050 | Model Velocity (cm/sec) | 1.60 |
| 6. Average Maximum Tidal Velocity | 2.50 | Geometry Factor | 1.16 |
| 7. Steady State Currents (measured at slack tide) | 0.00 | | |
| 8. Marine Sediment Copper Quality Standard (ppm) | 390.00 | **Water Column Copper Concentration** | |
| 9. Maximum Marine Sediment Impact Zone Cu Std. | 390.00 | **Associated With CCA Treated Piling** | |
| 10. Fresh Water, Chronic, Copper Standard | 3.62 | | |
| 11. Water hardness (ppm CaCO3) | 25.00 | Water Conc. (pptrillion) | 32.7 |
| 12. Marine Water Copper Standard | 2.50 | Marine Water Standard | 2900.0 |
| 13. Sediment Density (grams/cubic centimeter) | 2.2 | Fresh Water Standard | 3616.6 |
| 14. Bulkhead Length (cm) | 10000 | | |
| 15. Board Width (cm) (2x6 = 14, 2x8 = 19. 2x12 = 29.2) | 13.97 | | |
| 16. Average Water Depth in the Mixing Width (cm) | 250.00 | | |

**Predicted Sediment Copper Levels in micrograms/square cm sediment surface, or ppm**

| Distance | Accumulation P1 (µg cm$^{-1}$) | Accumulation P2 (µg cm$^{-1}$) | Total Cu Acc. (µg cm$^{-1}$) | Cu Conc. (ppm) | Sed. Std. (ppm) | SIZ Maximum (ppm) | # piles | A for # pile |
|---|---|---|---|---|---|---|---|---|
| 200 | 0.14 | 1.54 | 1.69 | 0.38 | 390.00 | 390.00 | | |
| 175 | 0.16 | 0.77 | 0.93 | 0.21 | 390.00 | 390.00 | | |
| 150 | 0.19 | 0.47 | 0.66 | 0.15 | 390.00 | 390.00 | | |
| 125 | 0.22 | 0.34 | 0.56 | 0.14 | 390.00 | 390.00 | | |
| 100 | 0.27 | 0.27 | 0.54 | 0.13 | 390.00 | 390.00 | | |
| 75 | 0.34 | 0.22 | 0.56 | 0.12 | 390.00 | 390.00 | | |
| 50 | 0.47 | 0.19 | 0.66 | 0.15 | 390.00 | 390.00 | | |
| 25 | 0.77 | 0.16 | 0.93 | 0.21 | 390.00 | 390.00 | | |
| 5 | 1.54 | 0.14 | 1.69 | 0.38 | 390.00 | 390.00 | | |
| 25 | 0.77 | 0.13 | 0.90 | 0.20 | 390.00 | 390.00 | | |
| 50 | 0.47 | 0.12 | 0.59 | 0.13 | 390.00 | 390.00 | | |
| 75 | 0.34 | 0.11 | 0.45 | 0.10 | 390.00 | 390.00 | | |
| 100 | 0.27 | 0.10 | 0.37 | 0.08 | 390.00 | 390.00 | | |
| 125 | 0.22 | 0.09 | 0.31 | 0.07 | 390.00 | 390.00 | | |
| 150 | 0.19 | 0.08 | 0.27 | 0.06 | 390.00 | 390.00 | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 175 | 0.16 | 0.08 | 0.24 | 0.05 | 390.00 | 390.00 |
| 200 | 0.14 | 0.07 | 0.22 | 0.05 | 390.00 | 390.00 |

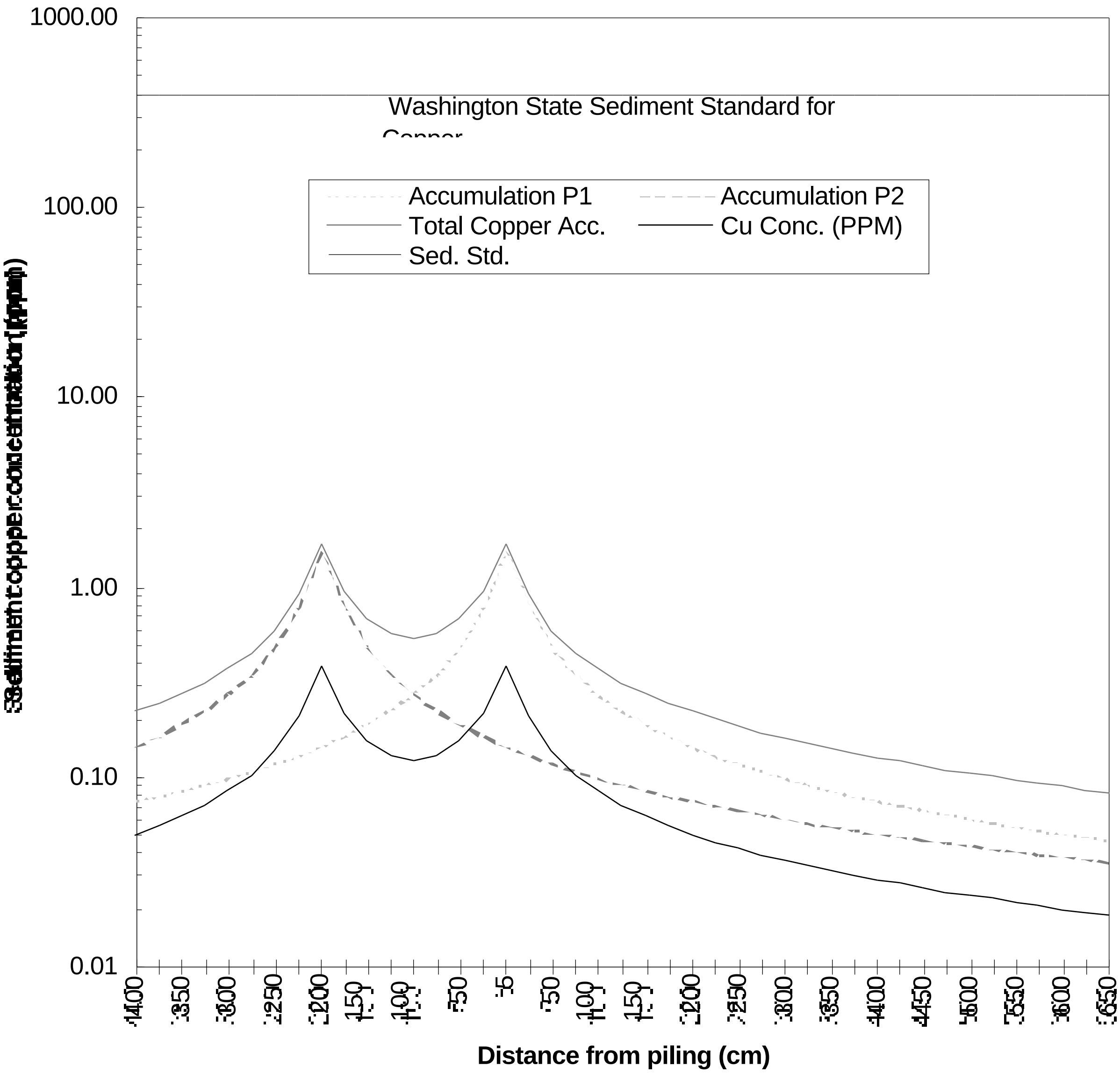


**Figure 2. Copper accumulation in sediments (ppm in the top two cm of sediment) as a function of distance from two piling.**

**Notes for *A:\CCAprisk* output.** The project described in Table 19 is a piling project in which 30 cm (1 foot) diameter piling, treated to a retention of 40 kg $m^{-3}$, is newly installed in a marine environment (28 ppt). The area has poor flushing and a maximum tidal speed of 2.5 cm $sec^{-1}$ was observed. No steady state currents were measured. The EPA marine water quality standard of 2.9

ppb (2900 pptrillion) has been applied along with Washington State's sediment standard of 390 ppm. The predicted water column copper concentration is 32.7 parts per trillion. This is about one percent of the EPA standard. The sediment concentrations of copper associated with this project are 1.53 μg $cm^{-2}$ within 5 cm of a pile decreasing to 0.49 μg $cm^{-2}$ midway between two pilings spaced two meters apart. The sediment copper concentration of 0.35 ppm, found within 5 cm of each piling is about 0.09% of the Washington State standard. The results are presented graphically in Figure 2. Note that in no case does the copper concentration exceed the standard denoted by the horizontal line at 390 ppm. Also note that the solid black line, representing Total Copper Accumulation, should not be used to the left of the 200 cm distance, because no values were provided in column "Accumulation P2" for these distances.

Recall that we integrated the time dependent parameter from $t = 0$ to $\infty$ and found that total copper accumulations will be 20.83 times the day zero accumulation. Therefore sediment copper concentrations predicted by this model assume that all copper delivered to the sediments remains in the upper two centimeters of the substrate. No allowances are made for dispersion due to mechanical disturbances or burial due to high sediment accretion rates. Therefore, these predictions represent a worse case scenario.

**Water Column Conc. (pptr).** This is the water column concentration of copper anticipated from this structure, 32.7 parts per trillion in this case. This is the copper concentration predicted within half an hour of slack tide on the day entered in the "Piling Age in Days" user entry. On day zero, this is the maximum predicted water column concentration. Predictions will significantly decrease after installation.

**Marine Water Standard (pptr).** This is a user entry defined by local, state or federal requirements. In this case we have entered the EPA marine water quality standard of 2.9 ppb (2900 pptr).

**Fresh Water Standard (pptr).** In fresh water, Washington State copper standards are dependent on water hardness expressed in parts per million $CaCO_3$. The algorithm driving this output is dependent on user entry number 11 (Water hardness in ppm $CaCO_3$). In this case, with 25 ppm hardness, the Washington State fresh water standard is 3616.7 parts per trillion copper.

**Distance.** This column contains the values (in centimeters) of (r) for which predictions are made. The distances provided start at 5 centimeters from the edge of the piling and extend outward in increments of 25 centimeters. These distances can be changed by the user.

**Accumulation P1.** Contains predicted total copper accumulation in the sediments associated with the piling or timber described in the input. Values are reported in μg $cm^{-2}$.

**Accumulation P2.** Contains predicted total copper accumulation in the sediments associated with a second piling. In the case illustrated, the pilings are 200 centimeters apart. The distance between pilings can be adjusted by "CUTTING" all values in this column and moving the highest entry in this column to a new interpiling distance. If the pilings in your project were one meter apart, you would "CUT" the values in column "Accumulation P2" and move the highest value (1.54 in this case) down to the row labeled 100 cm (1 meter) in the "Distance" column.

**Total Copper** is the sum of the predictions made for P1 and P2. It is only accurate for distances which include predictions for both P1 and P2.

**Copper Conc (PPM)** contains the results of converting the "Total Copper" values to copper concentrations, in parts per million, in the upper 2 centimeters of the substrate. The upper 2 centimeters were chosen because *Puget Sound Protocols* require that the upper two centimeters of a grab be subsampled for chemical analysis. Because most copper losses occur during the first 90 days following emersion, observed copper concentrations will approach predicted values within three months following installation of the piling.

**Sed. Std.** displays the user defined sediment copper standard required by the appropriate jurisdiction (user defined entry number 8) and allows direct comparison with the predicted copper concentrations.

**Sediment Impact Zone (SIZ) Maximum** is a user entered value (user entry 9) describing the appropriate jurisdiction's definition of maximum allowable copper concentrations in a permitted dilution zone (SIZ). Contaminant levels above 390 ppm are of significant concern and require cleanup or an exemption from the Department of Ecology in Washington State.

**# piles.** This user entry allows for the evaluation of a number of piles at a given distance from each pile. This might occur when it is desired to evaluate sediment copper concentration in the center of a rectangle formed by four, or more, pilings.

**Water column concentrations of copper associated with large surface area projects such as bulkheads.** Significant quantities of CCA may come into contact with marine water in poorly flushed canals with significant lengths of bulkheaded shorelines. The length of these bulkheads, and low water circulation, suggest that this application may represent a worst case application deserving special consideration. A Microsoft EXCEL™ model predicting water column and sediment concentrations of copper associated with large surface area projects is presented in file A:\CCABrisk. Copper loss rates from CCA treated wood will be modeled as before, but converted to losses per second instead of losses per day. The copper concentration predicted by Equation 15 is for water that has transited the entire length of the wood structure. Because it uses average velocities, the predictions are for time integrated and averaged concentrations. This model assumes that the volume of the water body is large in comparison with the total amount of copper lost from the structure. It does not make predictions for small volume, closed water bodies.

**Equation 15.**

$$\text{Conc}_{(cu\text{-}bulkhead)} = 2823.89 \times (\exp^{-0.048 \times \text{time (days)} + 0.02\,(\text{Salinity}) - 0.01346 \times \text{Board Width (cm)}}) \times (0.8462 + \text{Natural Log}(0.71 \times \text{Retention}))/(V_{ss} + 0.64(V_{maximum} - V_{ss}))^2$$

**Small Water Bodies.** The concentration of copper in small bodies of water is difficult to model. Copper losses from CCA treated lumber have already been described. The ultimate fate of the released copper is sedimentation. The rate of sedimentation is dependent on the size and density of suspended material to which the copper molecules adsorb. In determining the risks associated with copper sedimentation, we have conservatively assumed copper adsorption to relatively large particles (silt), which have a high settling velocity (0.05 cm/sec). This was done to address worst case situations in which most of the copper would be deposited near the source, resulting in higher predicted concentrations.

In considering a small body of water, a similarly conservative approach would be to assume adsorption to Particulate Organic Particulates (POM) and clay with settling velocities on the order of $5 \times 10^{-5}$ cm/sec. This model assumes a shallow water depth equal to the depth of water associated with the CCA structure. If we use the marine water copper quality standard of 2.9 ppb copper, then it is possible to show that copper concentrations can exceed the marine standard when the water body surface area is less than 259 times that of the exposed area of CCA treated wood surface.

For a bulkhead submerged in one meter of water and 30 meters long, the minimum water body surface area would be 0.62 hectares or about 1.5 acres. Bodies of water this small are usually fresh water in which higher copper concentrations are allowed (9.2 ppb at 75 ppm hardness in Washington State). Equations 22 and 23 provide maximum ratios of water body surface area to submerged CCA treated wood areas for marine (Eq. 22) and freshwater (Eq. 23) uses. These ratios are for newly installed projects. Projects could be expanded after initially higher copper losses decrease (approximately 90 days).

**Equation 22. Marine Water Area/CCA Surface Area $\geq$ 259**

**Equation 23. Fresh Water Area/CCA Surface Area $\geq$ 472/exp$^{(0.8545*|\ln(\text{hardness})| - 1.465)}$**

where: ln = natural logarithm
hardness = $CaCO_3$ expressed in milligrams/liter; ie. at 75 ppm $CaCO_3$ enter 75.

At a Hardness level of 75 ppm , Equation 23 predicts that water quality criteria may be exceeded during the early stages of installation of a CCA treated wood project in which the lake surface area is less than 51 times the surface area of the intended project.

**Sediment accumulation of copper associated with large surface area structures treated with CCA.** The accumulation of copper in sediments associated with large surface area CCA treated structures has been predicted using Equation 20.

**Equation 20. Sediment Cu Accumulation$_{bulkhead}$ =**

$$1.47 \times 10^{-4} \times \exp^{-0.048\,(\text{time}) + 0.02\,(\text{salinity}) - 0.01346(\text{Board Width})}$$

$$\times (0.8462 + \text{Natural Log}(0.71\text{Retention})) \times \text{Bulkhead Length} \times \text{Velocity}_{vertical}$$

$$/ (\text{Velocity}_{model})^2 \times \{\sin(\tan^{-1}(\text{Velocity}_{mixing}/\text{Velocity}_{model}))\}$$

**x 0.5 <u>if</u> Average Water Depth $\geq$ 0.025 x Bulkhead Length/ Velocity$_{model}$**

Output describing sediment accumulation of copper is provided in Table 20. The data is for an orthogonal transect midway along the bulkhead. These are the maximum anticipated accumulations. After approximately six months of service, copper losses will be minimal and dynamic processes are expected to disperse the contaminants over a broader area, resulting in lower sediment concentrations.

**Table 20. Tabular output from the Microsoft EXCEL ™ spreadsheet A:\CCABrisk. Water column copper concentrations associated with bulkheads.**

**Copper Accumulation in Water and Sediments Associated With Large Surface Area CCA Treated Projects**

| User Entries | | Intermediate Output | |
|---|---|---|---|
| 1. Retention in kilograms per cubic meter | 40.00 | Migration (migr/cm2-day) | 2.54 |
| 2. Average piling radius (centimeters) | | Age Factor | 1.00 |
| 3. Bulkhead Age in Days | 0.00 | Retention Factor | 0.99 |
| 4. Salinity (parts per thousand, ppt) | 25.00 | Mixing Width (cm) | 80.00 |
| 5. Settling Velocity (0.05 for silt; 0.00005 for clay) | 0.050 | Model Velocity (cm/sec) | 3.20 |
| 6. Average Maximum Tidal Velocity | 5.00 | Geometry Factor | 1.32 |
| 7. Steady State Currents (measured at slack tide) | 0.00 | Mixing Velocity (cm/sec) | 0.008 |
| 8. Marine Sediment Copper Quality Standard (ppm) | 390.00 | | |
| 9. Maximum Marine Sediment Impact Zone Cu Std. | 390.00 | | |
| 10. Fresh Water, Chronic, Copper Standard | 3.62 | **Water Column Cu Conc.** | |
| 11. Water hardness (ppm CaCO3) | 25.00 | **Associated with CCA Bulkheads** | |
| 12. Marine Water Copper Standard | 2.90 | | |
| 13. Sediment Density (grams/cubic centimeter) | 2.2 | **Water Conc. (pptrillion)** | 1578.8 |
| 14. Bulkhead Length (cm) | 10000 | **Marine Water Standard** | 2900.0 |
| 15. Board Width (cm) (2x6 = 14, 2x8 = 19. 2x12 = 29.2) | 14 | **Fresh Water Standard** | 3616.6 |
| 16. Average Water Depth in the Mixing Width (cm) | 100.00 | | |

| | |
|---|---|
| **Predicted Sediment Copper Levels in micrograms/square cm sediment surface** | 16.4 |
| **Predicted Sediment Copper Levels in parts per million (upper 2 cm of sediment surface)** | 3.7 |

**Notes for the output from a:CCABrisk.xls in Table 20.** The basis for the analysis in Table 20 is a newly installed, 100 meter long bulkhead installed in a poorly flushed (maximum water current = 5.0 cm sec$^{-1}$) marine environment (salinity = 25 ppt).

**Predicted water copper concentration.** The model output predicts copper losses on the first day of 2.54 μg cm$^{-2}$ day$^{-1}$. This copper is diluted in a mixing width of 80 cm during transit of the bulkhead. The resulting copper concentration is 1578 parts per trillion in the water column. This is approximately half the EPA water quality standard of 2900. Predictions are valid for the day entered in User Entry Number 3 (Structure Age in Days). Water column predictions for water adjacent to the bulkhead on any given day following emersion can be obtained by entering the day in question in User Entry Number 3.

**Predicted Sediment Copper Levels.** Sediment concentrations of copper will slowly increase over time. A total of 3.7 ppm copper will be added to the upper two centimeters of the sediment column by this bulkhead. This deposition is along the shore to a width equal to the mixing width (80 cm). As in the piling model, sediment concentration predictions are for $t = \infty$. However, measured copper levels will approach predicted concentrations within 90 days.

Waves, bioturbation, and other mechanical disturbances will likely further reduce the sediment burden. In any case, the predicted sediment concentration is less than one percent of that allowed by Washington State sediment standards.

**Treatment of complex structures.** There is an endless variety of placements for CCA treated wood in actual structures. Output from the A:\CCAPrisk.xls model will consider the accumulation from a single pile, along a line between two piling and as the sum of the contributions from a specified number of piling at a point common to all of them. The following paragraphs suggest ways in which the model can be used to predict sediment accumulation of copper associated with complex structures.

**Ferry Dolphins.** Assuming that peripheral piling are tightly bound and that water circulation among interior pilings is minimal, it appears reasonable to suggest that copper lost from interior piles will settle directly to the bottom around those interior piles. Copper accumulation around the perimeter of such a structure can be estimated by inputting the radius of the structure in User Input # 2 (Average pilling radius (centimeters)). A larger (by a factor of $\pi/2$) surface area will be exposed in this instance. This can be accounted for by entering $\pi/2 = 1.57$ in the column labeled "# piles". The anticipated copper accumulation, as a function of distance from the dolphin, can then be read in the last column (A for # piles).

Actual copper accumulation in this instance will probably be negligible in the near-field because of prop wash from the ferry. In this instance, nearfield, estimates will be too high and far field (> 100 meters) estimates too low. However, the model will provide insight into the problem.

**Pier Structures**. PAH deposition is an inverse function of distance and is therefore highest in close proximity to treated wood structures. The effects of several piling can be determined by using the "# piles" user input. For instance, assume you have a rectangular array of piling spaced three meters apart. Heaviest copper deposition will be in the immediate vicinity of the pilings (<25 cm). However, cumulative effects will be highest at a point equidistant from all four piling in any single array. In this case, that point is located 424 cm from each pile. In the example given in Table 19, copper accumulation at the center of this array would be 4 x 0.03 = 0.12 μg cm$^{-2}$ copper.

The contribution from any number of piling at any point on the benthos can be determined in this way. Simply measure the distance of the structural member from the point of interest. Determine the sediment accumulation or concentration from the spreadsheet at the measured distance. The sum of all structural components at that point represents the anticipated sediment levels.

## Testing the Model.

Environmental scale tests of CCA treated wood structures are planned and funded, but have not been completed. The most recently completed studies lending themselves to testing this model come from the work of Weis *et al.* (1991) and Weis & Weis (1992,1993). These studies assess the loss of CCA metals and their subsequent impacts on marine fauna and flora. Data from these studies will be used to test the model reported in this paper.

Weis *et al.* (1991) examined the toxicity of CCA treated wood leachate to several marine organisms. In these experiments, new CCA-C treated wood (0.4 pcf) was blocked and leached for one to three weeks. Fiddler crabs (*Uca pugilator*), alga (*Ulva lactuca*), embryos of the mummichog (*Fundulus heteroclitus*) and gastropods (*Nassarius obsoletus*) were exposed to copper, chromium and arsenic contained in the leachate with the treated wood.

Experiments in which small CCA treated wood blocks were used have little relevance in assessing environmental risks. Replication of metal levels in "Instant Oceans" seawater further distorts environmental responses because complexing molecules (particularly organic compounds) are absent or significantly reduced. It is the cupric ion which is toxic and this ion is known to quickly complex in natural systems, reducing toxicity (Knezovich et al. 1981).

In the crab experiments, small (10 cm x 4 cm x 1 cm), medium (10 cm x 9 cm x 1 cm) and large (20 cm x 9 cm x 1 cm) blocks of wood were covered on all sides with water to a depth of between 2.50 centimeters (for small blocks) and 0.7 cm (for large blocks). Water coverage in the embryo experiments was similarly shallow. The wood volume to water volume ratio in these studies is too high to assess the response of marine taxa to CCA treated wood installed in open aquatic systems. Insufficient data were provided to allow calculation of copper migration rates in these experiments.

There are a series of wood block experiments reported in this article which provide a basis for examining the loss of copper in $\mu g\ cm^{-2}\ day^{-1}$. These snail and alga experiments used a block of wood with a total surface area of 228 $cm^2$ placed in a seawater (25 o/oo) volume of 4,000 liters. Relatively high levels of copper were observed in the CCA leachate. The levels observed are provided in Table 21 as a function of time.

Copper losses predicted by this model were consistent with those observed in the Weis study at all sample times. Furthermore, a paired sample *t* test suggests that the predicted and observed results are not significantly different ($\alpha = 0.05$, $t = -0.6949$, $t_{crit} = 3.182$).

The Weis *et al.* (1991) study reported mortality in *Nassarius obsoletus* at 600 ppb but not at copper concentrations <312.5 ppb which is consistent with reported $LC_{50}$'s for shiner perch (417.7 ppb) and Coho salmon smolts (601 ppb). The results of Weis *et al.* (1991) suggest an $LC_{50}$ of between 250 and 500 ppb copper in *Nassarius obsoletus*. This is greater by a factor of 86,206 than the EPA marine water quality standard of 2.9 ppb upon which risks are assessed in this model.

**Table 21. Copper losses from 228 $cm^2$ CCA treated (6.23 kg $m^{-3}$) wood blocks as a function of time. Blocks were leached into 4,000 ml of 25 ppt seawater and reported in Weis *et al.* (1991). Reported values are the average of two replicates.**

| | Average Day of Leaching Period | | | |
|---|---|---|---|---|
| | 3.5 | 14.0 | 28.0 | 45.5 |
| Copper in leachate (parts per billion) | 600.0 | 312.5 | 125.0 | 265.0 |
| Leaching time (days) | 7.0 | 14.0 | 14.0 | 21.0 |

| | | | | |
|---|---|---|---|---|
| Observed Copper Losses (micrograms centimeters$^{-2}$ day$^{-1}$) | 1.50 | 0.39 | 0.16 | 0.22 |
| Predicted Copper Losses (micrograms centimeters$^{-2}$ day$^{-1}$) | 1.61 | 0.97 | 0.26 | 0.21 |
| EPA marine Cu water quality standard (parts per billion) | 2.90 | 2.90 | 2.90 | 2.90 |
| Environmental Levels (ppb) predicted by this model | 0.92 | 0.58 | 0.30 | 0.13 |

**Environmental levels of copper**. The Weis *et al.*(1991) data were substituted into this model to predict environmental levels of copper. The model predicts a mixing width of 40 cm as the water column passes along a 50 meter bulkhead at an average speed of 3.4 cm/sec. The predicted environmental levels of copper are also provided in Table 21. Environmentally realistic levels of copper associated with the bulkhead in this slowly circulating body of water are 0.918 ppb during the first week. They drop to 0.128 ppb by the seventh week. All of these levels are below the EPA standard of 2.9 ppb. From this, we can conclude that snails and algae will suffer acute stress and die when placed in small volumes of stagnant water containing relatively large blocks of newly treated CCA wood. However, when the copper leaching rates observed in the Weis study are extrapolated to open aquatic systems, the resulting copper concentrations are well below toxic thresholds and EPA standards.

Weis *et al.* (1993) report sediment concentrations associated with a variety of CCA treated wood structures. Their report focuses on the copper concentration as a proportion of the silt clay fraction (grain size < 63 μm). Unfortunately, this report lacks information regarding the size and age of the CCA structures or flushing currents. In the following discussion, we will assume that the bulkhead was new and use low current speeds (worst case).

Washington State regulatory standards (390 ppm total dry sediment) are based on the proportion of copper in the top two centimeters of the sediment column and reflect minimum concentrations at which Apparent Effects Thresholds (AETs) are reached. Weis *et al.*(1993) did not report any control for sediment depth. However, if we assume that they retained the top two centimeters for chemical analysis, then it is possible to compare their results with the predictions made in this model. Most of the sites examined by the Weis *et al.* (1993) study revealed total sediment copper concentrations of less than 100 ppm copper. No information was provided on background levels of copper and therefore it is not possible to determine how much of the observed copper was attributable to the CCA structure. Copper levels in pristine areas are generally < 50 ppm, but often reach 100 ppm in suburban and urban areas. All of the data provided by the Weis *et al.* (1993) study are within this range. Therefore we might conclude that the CCA structures are not contributing a detectable amount of copper to these sediments.

The worst case reported by Weis *et al.* (1993) is for a newly installed bulkhead in Southampton, New York. They reported copper levels of 2000 ppm in the silt-clay fraction of sediments containing approximately 1% fines. The National Oceanic and Atmospheric Administration (1988) summarized sediment chemical contaminants observed from 1984 through 1987. This document includes a discussion of the appropriateness of normalizing contaminant levels to the fine grained fraction of sediments (< 64μm particle size). The discussion concludes that normalization to the fine grain fraction is inappropriate when the fine grain fraction is less than 20% of the total sediment grain size distribution. No justification was given by Weis *et al.* (1988) for normalizing copper to the fine grain fraction which represented only one percent of the sediment in their sample.

Correcting the Weis *et al.* (1988) data to copper concentration in the total dry sediment suggests a copper concentration of 20 ppm. This is typical of the level we would anticipate finding in a suburban area. (NOAA, 1988). This value is significantly less than the 82.6 ppm prediction made by this model. Model parameters for this prediction were: CCA retention = 40 kg-m$^{-3}$; 30 ppt salinity; maximum currents of 2.5 cm/sec; and a bulkhead length of 500 meters. When the Weis *et al.* (1993) data is corrected to copper concentration in the total sediment column, the value of 20 ppm is 25% of the concentrations predicted by this model. This suggests that the bulkhead is creating mechanical disturbances of the sediments and redistributing the copper, which is adsorbed to the fine sediment fraction, away from the bulkhead.

Taken all together, the Weis, *et al.* (1993) study suggests that CCA treated structures do not contribute significant amounts (above background) of copper to sediments. Predictions by this model and the Weis *et al.* (1993) data suggest a positive correlation between sediment grain size and copper binding. Furthermore, these comparisons suggest that dynamic forces, associated with waves, may remove fine material (and bound copper) from sediments adjacent to bulkheads.

Weis and Weis (1992) examined copper levels in oysters residing on CCA treated piling and bulkheads. They reported American oyster (*Crassostrea virginica*) wet tissue weight copper concentrations of 12.59 ppm in a reference area, 27.05 ppm on a piling and 154.3 from oysters growing on a bulkhead in a residential canal. Without adequate information regarding the age of the structures, flushing in the canal and the amount of CCA treated wood immersed in the water, it difficult to predict oyster bioconcentration of copper. The National Academy of Sciences (1991) gives a bioconcentration factor of 5,000 for copper in marine mollusks. Assuming that flushing in the canal is low (2.5 cm/sec maximum) and that the receiving water to bulkhead surface area ratios are greater than 259, we can predict that the initial water column copper concentration along the bulkhead is 6.980 ppb resulting in a tissue concentration of 34.9 ppm. This tissue burden is added to the burden normally found in east coast oysters. Shuster and Pringle (1969) reviewed trace metal levels observed in *Crassostrea virginica* reported in five macrogeographic studies from Maine through North Carolina. They found an average of 144.8 ppm (wet tissue weight) copper in these oysters with a range of 6.83 to 600 ppm. The data provided by Weis and Weis (1993) are well within this range and the oysters from the canal had copper body burdens very close to the average reported by Shuster and Pringle (1969). Based on this review, these observed levels of copper do not appear unusual and while the CCA treated bulkhead is certainly contributing copper to the oyster body burden, that contribution appears small.

**Summary**. Results reported in the Weis and Weis (1991), Weis and Weis (1992) and Weis, *et al.* (1993) studies are difficult to interpret because study sites were not characterized. All environmental scale studies should accurately and thoroughly characterize the study sites to allow proper evaluation of the results. With these caveats, the results of these three studies are shown to be consistent with the model presented in this paper. In addition, when properly extrapolated to real environmental conditions, the data presented in Weis and Weis (1991, 1992) and Weis *et al.* (1993) suggest minimal risks associated with the use of CCA treated wood.

### Generalized Risks Associated With CCA Treated Wood In Aquatic Environments.

While intended as a site and project specific evaluation tool, this model can be used to predict general risks associated with CCA treated wood used in aquatic environments. The results of analyzing a broad set of input parameters in this model suggests that most CCA treated wood projects, particularly piling projects, present minimal environmental risk. There are situations in poorly flushed canals, lined with large amounts of CCA treated wood, where risks become significant. The model allows proponents and permit writers to evaluate these risks and propose project modifications to reduce the risks to acceptable levels. Table 22 provides model output for a range of typical projects. The data are for newly installed structures. Comparing these values with the Washington State surface water standards or the EPA marine copper water quality standard shows that most CCA projects add small fractions of the allowable concentrations. Table 22 also shows that significant risks can be incurred with bulkhead projects in poorly circulated bodies of water.

In all cases, except the 500 meter bulkhead located in a very poorly flushed environment, the resulting copper concentrations are below federal regulatory standards. Water column concentrations at the worst case installation would meet the EPA criteria after 19 days. Mitigation for projects of this magnitude, in poorly flushed environments, can be accomplished in several ways:

a. Projects can be designed to increase water currents.

b. Projects can be designed to increase mechanical turbulence. This model assumes very low values for turbulence.

c. Large projects should be installed during periods of the year when sensitive species are not present or during periods of minimal recruitment of sensitive larval stages.

d. Large projects can be installed in phases with at least 90 days between each phase.

**Table 22. Predicted copper concentrations (parts per trillion) in fresh and marine water associated with newly constructed, CCA treated, wood projects. Fresh water copper water quality standards assume a water hardness of 50 ppm ($CaC0_3$). Values for "Current" are the maximum current speed observed on a tidal exchange to Mean Low Water (MLW) expressed in cm $sec^{-1}$. Salinity is expressed in parts per thousand, CCA retention in kilograms $meter^{-3}$ and copper concentrations in parts per trillion.**

| Project Type | Salinity | CCA Retention | Current Speed | Copper Concentrations Predicted | Copper Concentrations Standard |
|---|---|---|---|---|---|
| 10 pilings (15 centimeter radius) | 0.0 | 6.2 | 5 | 27 | 6540 |
| 10 pilings (15 centimeter radius) | 30.0 | 40.0 | 5 | 89 | 2900 |
| 500 meter bulkhead | 0.0 | 6.2 | 5 | 532 | 6540 |
| 500 meter bulkhead | 30.0 | 40.0 | 5 | 1744 | 2900 |
| 500 meter bulkhead | 0.0 | 6.2 | 2.5 | 2127 | 6540 |
| 500 meter bulkhead | 30.0 | 40.0 | 2.5 | 6979 | 2900 |
| 500 meter bulkhead | 15.0 | 40.0 | 2.5 | 5171 | 2900 |
| 500 meter bulkhead | 30.0 | 40.0 | 10.0 | 436 | 2900 |

**Use of CCA treated wood for decking and support members in structures constructed over aquatic environments.** The information provided in Table 23 allows us to predict the contribution of copper, chromium and arsenic to receiving waters from overhead structures constructed of CCA treated lumber. We will assume that rainwater is mixed to a depth of 15 cm in the receiving water and that a current of 2.5 cm/sec is flowing under the structure. Assuming that there is no horizontal mixing (very unlikely, but conservative), the amount of contaminant delivered is proportional to the length of the structure measured along the current. We will consider construction of a dock, with a dimension of 5 meters in the direction of current flow. The proposed decking is 2" x 6" material with all surfaces of the boards wetted and leaching. Copper, chromium and arsenic levels in the receiving water will be raised by the amounts provided in Table 23 during the first months of exposure. Rates will significantly decline with time (See Figure 1).

**Table 23. Increases in receiving water concentrations of arsenic, chromium and copper resulting from rainwater leaching of overhead structures. Data are for an overhead structure whose width is five meters in the direction of the currents. Current flow is 2.5 cm $sec^{-1}$ and it is assumed that the leachate is mixed to a depth of 15 cm. Average rainfall is 89 cm and is assumed to be spread evenly over the year.**

| | Contaminant in ppb | | |
|---|---|---|---|
| | **Arsenic** | **Copper** | **Chromium** |
| **Predicted increased concentration in the receiving water.** | 0.694 | 0.460 | 0.077 |

**Importance of proper fixation**. Based on the information presented in this report, it is unlikely that normal use of properly treated CCA products in reasonably well flushed marine or fresh water environments will impact marine fauna or flora. These data are based, in part, on the Putt (1993) report in which CCA fixation was assured using the chromotropic acid test. The Western Wood Preservers' Institute (WWPI) and the Canadian Institute of Treated Wood (CITW) have developed, and are implementing, Best Management Practices (BMPs) for the production of a variety of treated wood products intended for use in sensitive environments. The BMPs for CCA treated wood are designed to produce a clean product with no surface residue in which fixation is assured. Project proponents' and permit writers' are encouraged to require the use of these BMPs in projects designed for aquatic environments.

Krahn (1987) reported an incident which demonstrates the potential risks associated with using improperly fixed wood. It is the only documented instance of arsenically treated wood products causing potential environmental damage. In this case the preservative was Ammoniacal Copper Arsenate (ACA). The incident resulted from the use of retreated timber in which proper procedures for fixation were not followed. The timbers were used for support structures and decking on a forestry access bridge across the Chilliwack River in 1986. In early December, 1986, a green chemical stain was observed on rocks beneath the bridge. This stain extended to 0.6 meters below the river surface. Samples of rainwater dripping from the bridge were collected and analyzed for copper and arsenic. Average metal content in the rain runoff was 78 ppm arsenic and 5.4 ppm copper. River water samples taken below the bridge were lower at 0.07 ppm arsenic and 0.006 ppm copper. The arsenic level exceeded the Canadian limit of 50 ppb for the protection of aquatic life. No evidence of biological damage was observed. However, Krahn (1987) concluded that the observed levels of arsenic could potentially exclude fish from this valuable spawning habitat and might kill juvenile fish.

The preceding paragraph is not intended to portend what will happen with the use of treated wood in aquatic environments. Rather, it is included because it is the only reported incident involving arsenically treated wood products which resulted in potential biological damage. It clearly demonstrates the potential for problems if treating protocols are not followed, high industry standards maintained, and effective quality assurance programs followed.

## Summary and Conclusions.

Copper, chromium, arsenic and zinc are ubiquitous in all aquatic environments. Copper and chromium are essential biological micronutrients. However, in localized areas, anthropogenic inputs can increase these background levels above toxic thresholds. The copper, chromium and arsenic metals present in arsenically treated wood products are toxic to aquatic organisms at varying concentrations, most of which are in the low parts per billion range. Based on this review, it appears that copper is the metal of most concern to aquatic organisms in both fresh and salt water environments. Water Quality Standards for Surface Waters of the State of Washington published in WAC 173-201A, and the EPA (1985) copper standard for marine water, provide adequate safety margins for the protection of aquatic organisms.

The environmental risks associated with the use of CCA treated wood products have been evaluated by quantifying the additional metal loading associated with the use of these commodities in aquatic environments and comparing the resulting concentrations with known chronic and acute thresholds and regulatory standards. The model described in this report provides project proponents and regulatory agencies with a tool for evaluating the risks associated with specific CCA projects in specific environments. Analysis of data in Weis and Weis (1991, 1992) and Weis *et al.* (1993) are very consistent with output from the model. However, the model needs to be tested and refined using properly controlled, documented and analyzed data from an environmental scale study. Such a study has been planned and funded, but has not been completed.

Throughout this analysis, very conservative assumptions have been used. Leaching rates from CCA treated products has been shown to decrease exponentially with time. We have used leaching rates observed in freshly treated wood to determine risks. We have assumed minimal mixing in aquatic environments. In all instances we have assumed that the metals leached into the water are in their most toxic form and that there is no detoxification by natural processes. Even with this very conservative approach to assessing the risks involved, this analysis indicates that when used in moderately well circulated bodies of water, the levels of copper resulting from the use of properly treated CCA wood products are normally well below regulatory standards and will produce concentrations far below those causing acute or chronic stress in even the most sensitive taxa. The model does demonstrate the potential for exceeding regulatory standards when bulkheads are installed in poorly circulated or closed bodies of water. Several alternatives to reduce these risks have been discussed.

The predictions and recommendations made in this study presume that wood products are properly treated and fixed. That assumption will only be valid if the treated wood industry continues an aggressive environmental quality control program, and if regulators and the consuming public demand high quality, environmentally sensitive, products for the projects they permit and build. Recently *completed Best Management Practices for the Use of Treated Wood in Aquatic Environments (BMPs)* provide project proponents and regulators with an effective tool to insure that only
well fixed CCA treated wood enters aquatic environments.

The author believes that this Risk Assessment Model, coupled with Best Management Practices for the Production of Pressure Treated Wood, provide proponents, engineers and permit writers with valuable tools allowing us to enjoy the benefits of treated wood in an environmentally sensitive way.

## References


Alexander, D.L. 1991. Effects of temperature and humidity on CCA-C treated pine wood. Proc: Canad. Wood Preserv. Assoc. 12:(in press).

Andreae, M.O., 1978. Distribution and speciation of arsenic in natural waters and some marine algae. Deep-Sea Research, Vol. 25, 391-402.

Baldwin, W.J. 1989. CCA Marine Piling; a review of its safe use. Long Island Coalition to Preserve the Availability of Treated Wood. c/o The Tri-Star Group, Inc. P.O. Box 182 - Carle Place, LI NY 11514.

Baechler, R.H., B.R. Richards, A.P. Richards, and H.G. Roth. 1970. Effectiveness and permanence of several preservatives in wood coupons exposed to seawater. Proc. Amer. Wood Preserv. Assoc. 66:47-64.

Baroni, C., G.J. van Esch and U. Saffiotti. 1963. Carcinogenesis Tests of Two Inorganic Arsenicals. Archives of Environmental Health, Vol. 7. pp. 668-674.

Baxter, J.H. and Company. 1983. A New Wood Preservative - Ammoniacal Copper Zinc Arsenate - Chemonite II. Presentation for the use of the AWPA Treatments Committees. J.H. Baxter and Company, 1700 S. El Camino Real, Post Office Box 5902, San Mateo, California 94402.

Boyle, E.A. 1979. Copper in natural waters. In: J.O. Nriagu (ed.), Copper in the Environment. Part I: Ecological Cycling. Wiley, New York. p.77.

Breteler, R.J. 1992. Critique Provided on Behalf of the American Wood Preservers Institute. The coalition to Preserve the Availability of Treated Wood. C/o The Tri-Star Group, Inc. P.O. box 182 - Carle Place, LI NY 11514.

Carson, W.G. and W.V. Carson. 1972. The lethal action of soluble metallic salts on fishes. Fish. Res. Board MS Report 1181. 5 pp.

Clark, R. McV. 1974. The effects of effluents from metal mines on aquatic ecosystems in Canada, A review. Research and Development Directorate, Freshwater Institute, Winnipeg. Report No. 46. 150 pp.

Cockcroft, R. and R.A. Laidlaw. 1978. Factors affecting leaching of preservatives in practice. International Research Group on Wood Preservatives. Document IRG/WP/3113. 10 pp.

Cooper, P.A. 1990. Leaching of CCA from treated wood. Proc. Canad. Wood Preserv. Assoc. 11:144-169.

Cooper, P.A. 1991a. Leaching of wood preservatives from treated wood in service. Report prepared for Public Works Canada. 79 pp.

Cooper, P.A. 1991b. Leaching of CCA from treated wood: pH effects. Forest Prod. J. 41(1):30-32.

Cserjesi, A.J. 1976. Permanence of preservatives in treated experimental shake roofs. Forest Prod. J. 26(12):34-39.

Costlow, J.D. and B. M. Sanders. 1987. Effects of Cyclic Temperature on Larval Development of Marine Invertebrates: II. Regulation of Growth as a General Indicator of Stress. In: Physiological Responses of Marine Organisms to Environmental Stresses, Ed. by J.V. Dorigan and F.L. Harrison. U.S. Department of Energy, Office of Energy Research, Office of Health and Environmental Research, Ecological Research Division, Washington, DC 20545.

Dahlgren, S.E. 1975. Kinetics and mechanism of fixation of Cu-Cr-As wood preservatives. Part 5. Effect of wood species and preservative composition on leaching during storage. Holzforschung. 29:84-95.

Eisler, R. 1986. Chromium Hazards to Fish, Wildlife and Invertebrates: A synoptic review. Biological Report 85(1.6). 60 pp.

Evans, F.G. 1978. The leaching of copper, chrome and arsenic from CCA-impregnated poles stored for ten years in running water. Int. Research Group on Wood Preservation. Doc. IRG/WP/3122.

Evans, F.G. 1987. Leaching from CCA-impregnated wood to food, drinking water; and silage. Int. Res. Group on Wood Preserv. Doc. IRG/WP3433.

Fahlstrom, G.B., P.E. Gunning and J.A. Carlson. 1967. Copper-chrome-arsenate wood preservatives: a study of the influence of composition on leachability. Forest Prod. J. 17(7):17-22.

Ferm, V.H. 1977. Arsenic as a Teratogenic Agent. Environmental Health Perspectives. Vol. 19, pp. 215-217.

Fowler, B.A., R.C. Fay, R.L. Walter, R.D. Willis and W.F. Gutknecht. 1975. Levels of toxic metals in marine organisms collected from southern California coastal waters. Environ. Health Perspect. 12:71-76.

Gjovik, L.R. and R.H. Baechler. 1977. Selection, Production, Procurement and Use of Preservative Treated Wood. U.S. Dept. Agric., For. Serv. GTR, FPL-15, Madison, Wis. 36 pp.

Harrison, F.L., J.P. Knezovich, D.W. Rice and J.R. Lam. 1987. Distribution, Fate, and Effects of Energy-Related Residuals in marine Environments. In: Physiological Responses of Marine Organisms to Environmental Stresses, Ed. by J.V. Dorigan and F.L. Harrison. U.S. Department of Energy, Office of Energy Research, Office of Health and Environmental Research, Ecological Research Division, Washington, DC 20545.

Harrison, F.L., and J.R. Lam. 1985. Partitioning of copper among copper-binding proteins in the mussel *Mytilus edulis* exposed to increased soluble copper. Mar. Environ. Res. 16:151-163.

Hruby, R. 1989. Analysis of rain water on the surface of CCA pressure treated lumber. B.Sc.F. Thesis. U. of Toronto, Toronto. 20 pp.

Huguenin, J.E. and J. Colt. Design and Operating Guide for Aquaculture Seawater Systems. Developments in Aquaculture and Fisheries Science, 20. Elsevier Science Publishing Company, Inc. 655, Avenue of the Americas, New York, NY 10010, U.S.A. 264 pp.

Hutchinson, T.C. 1979. Copper contamination of ecosystems caused by smelter activities. In: J.O. Nriagu (ed.), Copper in the Environment. Part I: Ecological Cycling. Wiley, New York. p. 451.

Irvine, J. and S.E. Dahlgren. 1976. The mechanism of leaching of copper-chrome-arsenic preservatives from treated wood in saline waters. Holzforschung 30(2):44-50.

Irvine, J., R.A. Eaton, and E.B. Gareth Jones. 1972. The effect of water of different ionic composition on the leaching of a waterborne preservative from timber placed in cooling towers and in the sea. Material u Organismen 7(1):45-71.

Knezovich, J.P., F.L. Harrison and J.S. Tucker. 1981. The influence of organic chelators on the toxicity of copper to embryos of the Pacific oyster, *Crassostrea gigas*. Arch. Environ. Contam. Toxicol., 10:241-249.

Krahn, P.K. 1987. Assessment Report - Leaching of copper and arsenic from ammoniacal copper arsenate (ACA) treated wood used as bridge decking and support timbers. Environment Canada. 11 pp.

Lebow, S.T. and J.J. Morrell. 1993. ACZA Fixation: the Roles of Copper and Zinc in Arsenic Precipitation. Proc. Am. Wood-Preservers' Assoc. (In-Press).

Lee, A.W.C., J. C. Crafton III and F.H. Tainter. 1993. Effect of rapid redrying shortly after treatment on leachability of CCA-treated southern pine. Forest Products Journal.1993:52

Lu, J.C.S. and K.Y. Chen. 1976. Migration of trace metals in interfaces of seawater and polluted surficial sediments. Environmental Science and Technology. 11:174-182.

Mortimer, W. 1991. The environmental persistence and migration of wood preservatives. Canadian Electrical Ass. Report No. CEA 118 D 697. 123pp.

National Oceanic and Atmospheric Administration. 1988. A Summary of Selected Data on Chemical Contaminants in Sediments Collected During 1984, 1985, 1986 and 1987. NOAA Technical Memorandum NOS OMA 44,Rockville, Maryland.

NTIS. 1986. Quality Criteria for Water: ARSENIC, 1986. NTIS #PB 85 227445.

Peden, J.D., J.A. Crothers, C.E. Waterfall and J. Beasley. 1973. Heavy metals in Somerset marine organisms. Marine Pollut. Bull. 4:7-9.

Penrose, W.R. and E.A. Woolson, 1974. Arsenic in the Marine and Aquatic Environments: Analysis, Occurrence and Significance. CRC Critical Reviews in Environmental Control. 465-482

Piper, R.G., I.B. McElwain, L.E. Orme, J.P. McCraren, L.G. Fowler and J.R. Leonard. (1982). Fish Hatchery Management. United States Department of the Interior, Fish and Wildlife Service. 517 pp.

Pizzi, A. 1982. The Chemistry and Kinetic Behavior of Cu-Cr-As/B Wood Preservatives. IV. Fixation of CCA to Wood. Journal of Polymer Science: Polymer Chemistry Edition, Vol. 20, 739-764.

Putt, A.E. 1993. Marine Sediment Toxicity Study with Leachate From CCA-C Treated Wood Pilings on the Benthic Organism, *Amplisca abdita.* Preliminary results on work done at the Springborn Laboratories. Hickson Corporation. Technical Center, 3941 Bonsai Road, Conley, Georgia 30027.

Rehm, E., M. Schulz-Baldes, and B. Rehm. 1984. Geochemical factors controlling the distribution of Fe, Mn, Pb, Cd, Cu and Cr in Wadden areas of the Weser estuary (German Bight). Veroff. Inst. Meeresforsch. Bremerh. 20:75-102.

Ruddick, J.N.R. and J.E. Ruddick. 1992. Development of a Strategy for the Management of Treated Wood in Aquatic Environments. Report prepared for Environment Canada, Environment Protection, 5th Floor, 224 West Esplanade, North Vancouver, B.C. V7M 3H7.

Sanders, J.G. and H.L. Windom. 1980. The Uptake and Reduction of Arsenic Species by Marine Algae. Estuarine and Coastal Marine Sci. 10, 555-567.

Schroeder, A.A. and J.J. Balassa. 1966. Abnormal trace metals in man: Arsenic. J. Chron. Dis. 19:85-106.

Shuster, C.N. Jr., and B. H. Pringle. 1969. Trace metal Accumulation by the American Eastern Oyster. *Crassostrea virginica.* Proceedings of the National Shellfisheries Association. **59**. pp 91 - 103.

Strathman, M.F. 1987. Reproduction and Development of Marine Invertebrates of the Northern Pacific Coast. Univ. of Wash. Press., Seattle, WA. 670 pp.

Sunda, W.G. 1987. Cited in Chapter 2: Physiological Responses of Marine Organisms to Environmental Stresses, Ed. by J.V. Dorigan and F.L. Harrison. U.S. Department of Energy, Office of Energy Research, Office of Health and Environmental Research, Ecological Research Division, Washington, DC 20545.

Teichman, T. and J.L. Monkman. 1966. An investigation of inorganic wood preservatives. I. The stability to extraction of arsenic impregnated hardwood. Holzforschung. 20(4): 125-127

Turekian, K.K. and M.R. Scott. Concentrations of Cr, Ag, Mo, Ni, Co, and Mn in suspended Material in Streams. 1967. Environmental Science and Technology. Vol. 1, No. 11. 940 - 942.

U.S. Department of Agriculture. 1980. The biologic and Economic Assessment of Pentachlorophenol, Inorganic Arsenicals and Creosote. Volume I: Wood Preservatives. USDA Technical Bulletin Number 1658-1. 435 pp.

U.S. EPA. 1983. Health Assessment Document for Chromium, External Review Draft, EPA-600/8-014A, 18 pp.

U.S. EPA. 1984. Ambient Water Quality Criteria for Copper, Aquatic Toxicity, draft, 8/19/83, 49FR 4551.

U.S. EPA. 1985. Water quality criteria. U.S. Environmental Protection Agency, Washington, DC. Fed. Reg., Vol. 50, No. 146, Part II. pp. 30784-30796.

Vogel, M.C., A. Pizzi and W. Conradie. 1983. Comparative leaching tests of Cu, Cr and As from timber treated with CCA types I and II (C and B). National Timber Institute, South Africa Project Report No. TP/43891. 6 pp.

Warner, J.E. and K.R. Solomon. 1990. Acidity as a Factor in Leaching of Copper, Chromium and Arsenic from CCA-Treated Dimension Lumber. Environmental Toxicology and Chemistry. 9:1331-1337.

Washington State Administrative Code. Chapter 173-201A WAC. 1992.

Washington State Administrative Code. Chapter 173-204. 1991.

Weis, P., J.S. Weis and L. M. Coohill. 1991. Toxicity to Estuarine Organisms of Leachates from Chromated Copper Arsenate Treated Wood. Arch. Environ. Conram. Toxicol. 20:118-124.

Weis, J.S. and P. Weis. 1992. Transfer of contaminants from CCA treated lumber to aquatic biota. Journal Exp. Mar. Bio. and Eco. 161:189-199.

Weis, P., J.S. Weis and T. Proctor. 1993. Copper, Chromium, and Arsenic in Estuarine Sediments Adjacent to Wood Treated with Chromated-Copper-Arsenate (CCA). Estuarine, Coastal and Shelf Science **36**, pp. 71-79.

Weis, J.S. and P. Weis (1993) Trophic transfer of contaminants from organisms living by chromated-copper-arsenate (CCA)-treated wood to their predators. J. Exp. Mar. Biol. Ecol., 168, pp. 25 - 34

Whanger, P.D., P.H. Weswig and J.C. Stoner. 1977. Arsenic Levels in Oregon Waters. Environmental Health Perspectives. Vol. 19, pp. 139-143.

Woolson, E.A. 1983. Man's Perturbation of the Arsenic Cycle. In: ARSENIC- Industrial, biomedical, Environmental Prospectives. Edited By: W.H. Lederer and R.J. Fensterheim, Van Nostrand Reinhold Company, New York, New York.

Woolson, E.A. 1975. Bioaccumulation of Arsenicals. In: Arsenical Pesticides, (E.A. Woolson ed.). Amer. Chem. Soc. Symp. Ser. 7), Chapter 7. Am. Chem. Soc. Wash., D.C., pp 97-107.