

**Assessment of the
Associated With the
Products**

**Literature Review and
Environmental Risks
Use of ACZA Treated Wood
in Aquatic Environments**

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ACZA Treated Wood Products in

Aquatic Environments

Introduction

Ammoniacal Copper Zinc Arsenate (ACZA) is an improved formulation of Ammoniacal Copper Arsenate (ACA). ACZA is licensed and being produced in the United States. This product has essentially replaced ACA for the protection of poles, piling and timber. In ACZA, 50% of the arsenic found in ACA is replaced with zinc in the form of ZnO. The proportions of copper, zinc and arsenic in ACZA are 50%, 25% and 25% respectively. Wood is treated to a retention (in the treated zone) of 15.6 kg m⁻³ (1.0 lbs. ft⁻³) ACZA for fresh water applications and to 24.0 kg m⁻³ (1.5 lbs. ft⁻³) for marine use.

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 treated wood does not create unacceptable environmental risks. 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. This paper is intended to provide a more quantitative analysis of the environmental risks associated with the use of ACZA treated wood in aquatic environments.

Background Levels and Sources of Arsenic, 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. Clayton and Tanner (1994) report a median, worldwide concentration of 6 ppm arsenic in soils with a typical range of 0.1 to 40 ppm. Natural levels as high as 4,600 ppm have been reported in soils near mineralized veins in British Columbia (Warren *et al.*, 1964). Bhumbra and Keefer (1994) report average crustal concentrations of 4.1 and 14.4 ppm arsenic in sandstone and shale. Woolson (1983) discussed the arsenic cycle and suggested 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 ppm in highly impacted areas like Elliott Bay. Carpenter (cited in Penrose and Woolson, 1974) reported arsenic levels of 3 to 15 ppm in sediments of Puget Sound and deep sea locations. He also reported levels of 290 to 980 ppm arsenic 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

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 from 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.

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 sources. Bhumbla and Keefer (1994) report the natural transport of 5×10^{11} grams of arsenic from land and the atmosphere to earth's oceans. Anthropogenic activities (mining and smelting) add an additional ten percent (5×10^{10} grams). Bhumbla and Keefer (1994) report reduced use of arsenic in pesticides. However, they note that erosional sediments associated with arsenic contamination can contain substantial (100 to 300 ppm) total arsenic and acid mine drainage > 2000 ppm arsenic.

Woolson (1983) suggested that the natural arsenic cycle is not greatly disturbed, on a global basis, by man's activities. He reported that natural sources contribute 7.8×10^{10} grams/year. Anthropogenic sources add between 10% and 25% to the total global loading. Iron, steel, lead, zinc and copper production contribute 82% of the anthropogenic emissions of 2.36×10^{10} grams/year. Pesticides account for 2.0×10^8 grams/year or less than one percent of total anthropogenic input.

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.

Total arsenic concentrations of 10 to 30 ppm 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 ppm. 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 lenitic fresh waters. It appears that perhaps five percent of the total arsenic load is in the toxic arsenite form in fresh water and fully

marine environments. The arsenic population in highly productive estuarine environments may contain ten to forty percent arsenite.

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 to 10 ppm.

Johnson and Hopkins (1994) reported a median copper level of 1.7 ppb in unfiltered Lower Columbia River water. Pelletier (1994) reported mean dissolved copper levels of 0.7 to 0.8 ppb in the Spokane River in eastern Washington and Johnson (1994) reported median dissolved copper levels of 0.33 to 1.0 ppb in four Washington rivers. All of these values are less than Washington State chronic water quality criteria of 2.5 to 9.5 ppb copper (criteria depend on hardness expressed as equivalent CaCO_3). An exception is the Puyallup river where Johnson (1994) measured mean copper levels 17 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 ppm will be assumed for unpolluted sediments and 350 ppm in sediments near industrialized areas. Dissolved copper concentrations in Washington State rivers are generally within the range of 0.33 to 2.2 ppb.

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 ppm in pristine areas and greater than 700 ppm in industrialized areas like Elliott Bay. Lu and Chen (1977) reported zinc levels of 30 to 35 ppm 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.

Dissolved zinc median concentrations of 1.0 to 1.8 ppb were reported by Johnson (1994) in four Washington State rivers. The highest metal concentrations occurred during winter and were well correlated with Total Suspended Solids (TSS) and flow rate.

In contrast, Pelletier (1994) found zinc levels of 80.9 to 164 ppb in the Spokane River in eastern Washington. These values exceed Zn water quality standards (24.1 to 79 ppb at the reported total hardness) during all seasons. The major sources of Zn were found to be nonpoint from historical mining practices.

Johnson and Hopkins (1991) reported zinc concentrations in unfiltered Lower Columbia River water of <0.33 to 1.7 $\mu\text{g}/\text{L}$.

Zinc Summary. For further analysis in this report, it will be assumed that unpolluted sediments contain 35 ppm zinc; polluted sediments contain 700 ppm zinc and that marine waters contain 0.50 ppb zinc. Fresh-water dissolved zinc levels are highly variable in Washington State. However, with the exception of the Spokane River, dissolved zinc levels in fresh water of Washington State are less than 2 ppb and are below chronic water quality criteria at all observed values of hardness.

Copper in

Cycling and Fate of Arsenic, zinc and Aquatic Environments

Zinc was not included in this portion of the discussion because of the paucity of information.

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 a significant portion of the 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.

Andreae (1978) also reported 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 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. However, Sanders, *et al.* (1994) conclude that arsenate is the predominant inorganic form of arsenic found in coastal systems. In general, it appears that the less toxic form (arsenate) completely dominates in fresh water and high salinity marine environments. However, in productive estuaries (5 to 15 ppt salinity) 10% to 40% of the total arsenic load may be in the more toxic form (arsenite).

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 3.9 ppm in intertidal sands to 162 ppm 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. It 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, ≤ 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 assessing the relative risks associated with different wood treatments.

and Zinc

Bioaccumulation of Arsenic, Copper In Aquatic Environments.

Copper and zinc 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. Sanders, *et al.* (1994) note that while there is little direct uptake of dissolved arsenic in water by invertebrates or vertebrates, phytoplankton and macroalgae do bioconcentrate arsenic resulting in its introduction into food webs. This is especially true for herbivores (Sanders *et al.*, 1989). However, while bioconcentration in autotrophs may be high, bioaccumulation in higher trophic levels is reported to be low. In studies of arsenic transport from the Baltic Sea, less than two percent of the total dissolved arsenic was incorporated into biotic tissue (Blanck *et al.*, 1989). In feeding experiments with planktonic communities from Chesapeake Bay, Sanders *et al.* (1989) found only 7 to 10% of the arsenic contained within phytoplankton and less than one percent of the arsenic overall was incorporated into invertebrates feeding on the phytoplankton.

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 web 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 (<i>Crassostrea virginica</i>)	600 - 42,750
Lobster (<i>Panulirus borealis</i>)	3,200 - 9,600
Tuna	710 - 4,600

Fresh Water

Trout	69 - 149
Perch (<i>Perca fluviatilis</i>)	600
Bass (<i>Micropterus salmoides</i>)	70 - 930
Channel catfish (<i>Ictalurus punctatus</i>)	0 - 3,100

Copper bioconcentration and bioaccumulation. The 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.

Sorensen (1991) reviewed the literature regarding copper accumulation in teleost fish. She concludes that the teleost liver actively processes and stores large copper loads; whereas, the kidney does not. Unlike zinc, it appears that copper concentrations in tissue are dependent on the Ecomix (Odum, 1960) model. McCarter, *et al.* (1982) and McCarter and Roch, (1983) suggest that copper induces *de novo* synthesis of isometallothioneins in the liver of coho salmon (*Oncorhynchus kisutch*). Metallothionein synthesis appears to be higher and quicker in fish pre-exposed to copper. In addition to isometallothioneins, Lauren and McDonald (1987) report additional hepatic proteins, including acid-soluble thiols and glutathione that are capable of binding copper. Sorensen (1991) suggests that hepatic detoxification of copper may initially involve metallothionein induction which is supported by subsequent displacement of zinc and/or other metals in unspecified high molecular weight hepatic proteins. In any case, the body of literature suggests that copper continues to accumulate and that it is sequestered (as a method of detoxification) in several hepatic protein compartments.

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. While many organisms are known to bioconcentrate copper, there is inadequate information describing the copper's bioaccumulation 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.

Zinc bioconcentration and bioaccumulation. Accumulation of zinc by fish is a factor of exposure time, exposure concentration, size of the organism, water hardness, acclimation, feeding level and trophic level. Sorensen (1991) reviewed zinc accumulation in fish and reported bioconcentration factors of 2.8 to 5.1. Unlike copper, which is sequestered primarily in the liver, zinc accumulation is greatest in the eye, followed in order

by decreasing concentrations found in the kidney, bone, skin, gill and liver. Very little zinc was found in muscle or gonad. Sauer and Watabe (1984) observed significant zinc deposition in the scales of mummichogs (*Fundulus heteroclitus*) exposed to varying concentrations of zinc (210 to 7,880 ppb zinc). Their study suggests that scales take up zinc actively, rather than passively.

Baptist and Lewis (1967) examined zinc bioaccumulation in a four level system composed of phytoplankton, brine shrimp, post-larval fish (*Eucinostomus sp.* or *Micropogon undulatus*) and mummichogs (*Fundulus heteroclitus*). They observed zinc bioaccumulation factors (relative to the amount of zinc in the phytoplankton) of 40 in the post-larval fish fed to satiation on brine shrimp and of 5 in the mummichogs which were fed a reduced diet of post-larval fish.

Summary of bioaccumulation potential. Based on this review, it appears that arsenic, and zinc are either not bioaccumulated, or bioaccumulated at low levels (70x to 2,000x), in the food chain. Copper is bioconcentrated at moderately high levels (100x to 30,000x) and mollusks can be expected to bioconcentrate copper by a factor of 5,000x from background levels (NAS, 1971). There is insufficient evidence to determine the degree of copper bioaccumulation in aquatic organisms.

Toxicity of Arsenic and Copper to Aquatic Fauna and Flora.

In order to assess the potential impacts of ACZA 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. Zinc was not included in this discussion because levels at which toxic responses are observed are two to three orders of magnitude greater than those associated with ACZA treated wood.

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 and inorganic arsenite. The trivalent organic and inorganic arsines are the most toxic. Sorensen (1991) suggests that two to ten higher levels of arsenate (compared with arsenite) are required to achieve the same level of toxicity.

Acute arsenic exposure to levels exceeding the reported LC₅₀ values can result in immediate death of fish because of arsenic induced increases in mucus production, resulting in suffocation, or degeneration of the gill epithelium. Chronic exposures can result in the accumulation of arsenic to toxic levels. The detoxification role of the liver places this organ at risk. The liver is considered the site of greatest damage associated with acute arsenic intoxication. Renal and splenic tissues also concentrate elevated levels of arsenic because of their roles in urinary and erythrocyte filtration.

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 (LC₅₀) are provided in Table 4 (data from Eisler, 1988 and Sorensen, 1991). 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 and that of Sorensen (1991) 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 LC₅₀ 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 in Fresh Water Plants and Animals. Unless otherwise specified, values are for the LC₅₀ 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)
<i>Salmo gairdneri</i>	25,600 (96-hr. LC ₅₀)
<i>Ictalurus punctatus</i>	15,000 (72-hr. LC ₅₀)
<i>Lepomis microchirus</i>	35,000 (96-hr. LC ₅₀)
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 are necessary to protect the most sensitive species of marine algae.

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 F/2 Medium for the optimum culture of marine algae (Strathman, 1987). At concentrations slightly above those required as a micronutrient, copper becomes 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 (Cu₂₊) 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. 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 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 is 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 LC₅₀ = 10 ppb) and larval herring the least sensitive. The range of 48-hour LC₅₀ 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 LC₅₀ (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 dissolved copper is in a toxic form.

Table 5. Total Copper Toxicity Measured in Controlled Bioassays. Values are EC₅₀ or LC₅₀ in ppb.

	Taxa	EC ₅₀ or LC ₅₀
<i>Sperm</i>	Purple Sea Urchins	34.0
	Oysters	12.1
	Salmon	44.2
<i>Embryo</i>	Purple Sea Urchins	6.3
	Oysters	6.1
	Mussels	21.0 - 35.0
<i>Larvae</i>	Crab Zoea	95.7
	Squid	309.0
	Cabezon	95.3
<i>(Table 5, continued)</i>		
<i>Adults</i>	Sand Shrimp	898.5
	Shiner Perch	417.7
	Coho Salmon Smolt	601.0

Chronic effects of copper in fish. Copper can have more subtle effects on fish. Gardner and LaRoche (1973) reported olfactory damage in mummichogs (*Fundulus heteroclitus*), following even brief encounters (6 hours) with elevated copper levels. Giattina, *et al.* (1982) reported copper avoidance in rainbow trout (*Oncorhynchus mykiss*) at levels of 4.4 - 6.4 ppb in soft water (28 ppm as CaCO₃). However, these same trout were apparently attracted to higher copper levels (334 to 386 ppb). These studies suggest that coho salmon and rainbow trout (two species in the genus *Oncorhynchus*) will avoid areas with copper levels elevated above 4.4 ppb and therefore avoid the stress associated with low levels of copper exposure.

Drummond, *et al.* (1973) observed changes in the feeding behavior of brook trout (*Salvelinus fontinalis*) when exposed to low levels of copper. Feeding was reduced for 24 hours in a constant exposure to 6 ppb copper and for 14 days at 12 ppb. These effects appeared to be transient and McKim and Benoit (1971) reported that normal feeding behavior was resumed within two weeks during a continuous exposure to 9 ppb copper.

McPherson (1976) reported impaired migratory ability at copper levels as low as 5 ppb in coho salmon (*Oncorhynchus kisutch*). Lorz and McPherson (1976) exposed ten to eighteen month old coho salmon (*Oncorhynchus kisutch*) to varying levels of copper and then released them into a tributary and observed migratory behavior. Exposure to 5 ppb

copper for 165 days resulted in a 30% reduction in downstream migration. Short term (one to three day) exposure to low levels (<8 ppb copper) were not investigated. However, it appears that copper levels above 5 ppb should be avoided during periods of active salmonid migration. However, based on the work of Giattina, *et al.* (1982), salmonids would be expected to avoid localized areas with copper concentrations exceeding 4.4 ppb.

McKim and Benoit (1971), Gardner and LaRoche (1973) and Scudder, *et al.* (1988) detected a positive copper dose-response effecting hatching time and success in several species of fish. Hazel and Meith (1970) report that copper levels exceeding 100 ppb will kill king salmon (*Oncorhynchus tshawytscha*) eggs. However, no mortality was observed at 8 ppb copper. Other species are more tolerant. Mummichog and silverside fry hatch in ambient levels of up to 5,000 ppb copper (Gardner and LaRoche, 1973).

Reproductive success is negatively influenced by elevated copper levels in numerous levels. The available information is reviewed by Sorensen (1991). Scudder, *et al.* (1988) report 17% premature hatching in brook trout eggs incubated at 32.5 ppb copper. No adverse effects were observed at copper levels less than 17.4 ppb copper. Mount and Stephen (1969) report that while copper concentrations of 18.4 ppb kill half of the fathead minnows (*Pimephales promelas*) used in reproductive studies, survival, growth, and reproduction were normal at 4.4 to 10.6 ppb copper. They did observe higher NOEL (No Observed Effects Levels) in hard water (200 ppm CaCO₃)

In summary, fresh-water species of fish are more sensitive to metals than are marine species. Higher salinity and hardness protect fish from copper poisoning as do factors such as pH, dissolved organic material and alkalinity which increase the potential for Cu⁺² complexation and detoxification. It appears that growth and survival are affected at higher copper levels than is successful migratory behavior, reproduction and survival of larval stages. Copper levels greater than 17.4 ppb can adversely effect the number of eggs spawned, hatchability and larval survival. At intermediate hardness values (ca. 50 ppm CaCO₃) migratory impairment can occur at constant copper levels as low as 5 ppb. This suggests that Washington State regulatory levels for copper are adequate to insure reproductive success with the exception that more strict standards should be imposed (≤ 5.0 ppb) during periods of active salmonid migration.

Summary of the toxicity of copper and arsenic. Most potentially toxic substances are regulated at the Federal and State Levels. It appears that these regulatory levels are sufficient to protect aquatic species. However, long term exposure to copper levels exceeding 5 ppb should be avoided during the time in which anadromous fish are migrating.

Copper is clearly the metal of most concern in both fresh water and marine environments. From a purely biological point of view, the cupric ion should be maintained below 6 ppb in marine environments. Either the EPA limit of 2.9 ppb, or the Washington State marine standard of 2.5 ppb appear adequate to protect marine life.

In fresh water, at hardness values of 50 ppm (CaCO₃), the No Observed Effect Level (NOEL) for copper appears to be 5.0 ppb. Acute effects are observed at significantly higher levels in all fish species studied (50 to 200 ppb). However, reproductive success can be impaired at copper levels as low as 17.4 ppb and migratory behavior (primarily chemoreception) is effected at copper levels greater than 5.0 ppb. Salmonids have been shown to avoid copper concentrations exceeding 4.4 ppb. Therefore, unless the avoidance reaction causes a change in migratory patterns, the Washington State water quality criteria are adequate to protect fresh-water fauna.

Arsenic, which is notoriously toxic to humans and other mammals is highly tolerated by marine animals at water column concentrations 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 tolerate at least 168 ppb arsenic.

Chromium, Copper

**Regulatory Requirements for Arsenic,
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 calculated at 50 ppm hardness (CaCO₃).

Table 6. Water Quality Standards for Surface Waters of the State of Washington. Values are expressed as parts per billion (ppb). A hardness of 50 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	8.0	5.6	2.9	-
Zinc	58.0	52.5	84.6	76.6

United States 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 marine aquatic life. The Washington State chronic copper standard of 5.6 ppb copper at 50 ppm hardness is slightly higher than the minimum level (5.0 ppb Cu) associated with migratory dysfunction in salmonids. Therefore, it may be appropriate to modify this standard to read, "not to exceed 5.0 ppb copper during the period in which anadromous or catadromous fish are migrating."

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

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

Sediment standards. Washington State has published 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 criteria 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).

<i>Metal</i>	<i>Sediment Quality Standard</i>	<i>Maximum level (SIZ)</i>
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 and vaccinating 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 at 50 ppm (CaCO₃) hardness.

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, zinc and copper in aquatic environments. The metals of concern when considering the use of ACZA treated wood in aquatic environments are arsenic, 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. However, and copper are known toxicants. Arsenic is tolerated at moderately high levels by aquatic species.

Copper and zinc are essential micronutrients. However, copper becomes acutely toxic to aquatic organisms, particularly in marine environments, at concentrations of 8 to 10 $\mu\text{g L}^{-1}$. Copper toxicity, associated with the presence of the cupric ion, is most detrimental to the early life stages of marine invertebrates and can effect the reproduction (particularly migration) of salmonids in fresh water at levels exceeding 5.0 ppb. Salmonids are known to avoid copper concentrations in excess of 4.4 ppb.

With the exception of Washington State's chronic copper standard, it appears that regulatory standards are sufficient to protect aquatic life. Out-migrating salmonid smolts and returning adults should not be subjected to copper levels exceeding 5.0 ppb - irregardless of the water hardness. Specific activities, such as the hatchery production of salmonids and shellfish may require 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, copper and zinc are added to aquatic environments by treated wood." This question will be addressed in the following chapters.

Resulting From the use of Environments

Anticipated Environmental Impacts ACZA Treated Wood In Aquatic

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.

Leaching of arsenic, copper and zinc from ACZA treated wood. Best and Coleman (1981) examined the leaching of ACZA from small blocks of wood. Using the leach test protocols specified in AWWA Standard M11(1), and a retention of 19.4 kg ACZA m^{-3} they observed that 1.7% of the copper, <0.6% of the zinc and 0.4% of the arsenic were lost. This study also observed an exponential decrease in arsenic leaching with time. Little additional arsenic was leached from the treated wood after five days in de-ionized water at pH 6.5.

Ruddick and Ruddick (1992) reviewed an AWWA study that examined ACZA leaching. A sample containing 729 mg of copper, 183 mg of zinc and 545 mg of arsenic leached 3.3 mg of copper, <0.4 mg of zinc and 48 mg of arsenic. This formulation deviates from the 2:1:1 ratio of Cu:Zn:As currently used in ACZA. No information was provided on the sample size or leaching protocols. However, the losses of 0.45% copper and 0.22% zinc compare favorably with other studies. The 8.8% arsenic leached in this study

apparently results from the 4:1:3 ratio of Cu:Zn:As used in the treatment. The current 2:1:1 formulation has been found to optimally reduce the amount of arsenic lost.

Metal leaching rates from ACZA treated Douglas fir sapwood. Dahlgren (1975) suggests that from the wood treaters' point of view, the most important factors determining the leachability of waterborne 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 water salinity, and the chemical composition and anatomy of the wood. There are several other factors that cannot be controlled by the wood treater.

The following analysis is based on data presented by the J.H. Baxter Company to the Chemical Manufacturers' Association, Arsenic Acid Task Force, in support of the EPA re-registration of ACZA. The data was collected during a 60 day Aqueous Leaching Test for copper, arsenic and zinc associated with ACZA treated Douglas Fir sapwood in seawater, and in freshwater at pH 5, 7, and 9.

Three wood blocks treated to 2.5 pounds per cubic foot (40 kg m^{-3}) ACZA in the treated zone and were then leached in 30 ppt seawater at a pH of 8.0 ± 0.5 and $22 \text{ }^\circ\text{C}$. Each wood block, measuring $1.5'' \times 1.5'' \times 12''$ was leached for 60 days into separate 6.6 liter glass cylinders. Controls consisted of identical, untreated, wood blocks leached under the same conditions. All analyses were run in triplicate.

The fresh water leaching fluids were prepared using ASTM Type-1 water and adjusted to pH levels of 5, 7 and 9. Leaching tank pH was maintained using either carbon dioxide or sodium hydroxide. Each of the fluids was agitated with air throughout the test.

The leachate was examined on days 0, 1, 7, 14, 21, 30, 37, 45, 52 and 60 for arsenic, copper and zinc. Metal loss rates were expressed in micrograms lost per square centimeter of exposed wood for each period of exposure. Loss rates were determined only for fresh water and 30 ppt seawater. This did not allow for the development of a meaningful algorithm describing metal loss as a function of salinity. Therefore, two models will be presented, one for freshwater and a second for 30 ppt seawater. Correlation analysis and non-linear regression suggest the following:

Copper losses, resulting from the CMA/EPA study described above, are significantly a function only of time in both fresh water and marine environments. ACZA treated lumber does not appear to lose more copper at increasing salinity. The Pearson Correlation Coefficient relating copper losses with salinity was only 0.029. Copper loss algorithms, developed using non-linear regression techniques, are provided in Equations 1 and 2. Copper loss is marginally a function of pH in fresh water. The pH was included because it provides the highest Coefficient of Determination ($R_{2a} = 0.929$).

$$\text{Equation (1) Copper Fresh Water Loss Rate} = 1908.6 * \exp^{-0.429 * \text{Days}} * \exp^{-0.383 * \text{pH}}$$

$\mu\text{g cm}^{-2} \text{ day}^{-1}$
(N = 26, $R_{2a} = 0.929$)

$$\text{Equation (2) Copper Loss Rate at 30 ppt} = 32.5 * \exp^{-1.114 * \text{Days}} \mu\text{g cm}^{-2} \text{ day}^{-1}$$

(N = 10, $R_{2a} = 0.758$)

Arsenic losses were measured at pH 5.0 and pH 7.0 in fresh water. However, too few data points were provided to conduct meaningful regression analysis. Losses at all times, salinities and values of pH were low. The mean loss for all of the data was $0.099 \mu\text{g cm}^{-2} \text{ day}^{-1}$ with a minimum of 0.0, a maximum of 1.375, and a standard error of the mean equal to 0.066. Therefore, this analysis will assume a constant arsenic loss of $0.099 \mu\text{g cm}^{-2} \text{ day}^{-1}$.

Equation (3) Arsenic Loss Rate Under all Conditions $0.099 \mu\text{g cm}^{-2} \text{ day}^{-1}$

Zinc losses are influenced by both time (Pearson Correlation Coefficient = -0.458) and pH (Pearson Correlation Coefficient = -0.578). Zinc loss rates decrease with increasing pH and time. Non-linear regression analysis provides loss rates described in Equations (4) and (5).

Equation (4) Zinc Fresh Water Loss Rate = $166.6 * \exp(-1.02 * \text{Days} - 1.054 * \text{pH}) \mu\text{g cm}^{-2} \text{ day}^{-1}$

(N = 26, $R_{2a} = 0.85$)

Equation (5) Zinc Loss Rate at 30 ppt = $31.074 * \exp(-2.667 * \text{Days}) \mu\text{g cm}^{-2} \text{ day}^{-1}$
(N = 10, $R_{2a} = 0.999$)

Time. Initial copper losses predicted by the model decline quickly as seen in Figure 1. The adjusted coefficient of determination indicates that 92.9% of the variation in fresh water copper loss rates are explained by the non-linear regression used in this model. This is an excellent fit. Fresh water data are presented for a pH of 7.0. Copper losses are negligible within 4 days in marine environments and within 10 days in fresh water. Similar, temporal declines were observed for zinc, regardless of pH or salinity. Arsenic loss rates were very low ($< 1.3754 \mu\text{g cm}^{-2} \text{ day}^{-1}$) at all times, pH values and salinities.

Environmental pH effects. Copper losses, particularly those observed in the first two weeks, were lowest in seawater and increased in fresh water with decreasing pH. Model predictions for fresh water copper losses, as a function of pH, are presented in Figure 2. The effects of pH are short lived and copper losses decline very quickly to negligible rates within 10 days.

Salinity effects. As seen in Figure 1, copper losses are significantly higher in fresh water than in salt water. This is true, even when the higher pH (8.0) of the salt water leaching bath is taken into account. At a pH of 8.0, we would anticipate an initial loss of $89 \mu\text{g Cu cm}^{-1} \text{ day}^{-1}$ from fresh water which is nearly three times the value of $32 \mu\text{g Cu cm}^{-1} \text{ day}^{-1}$ observed in salt water.

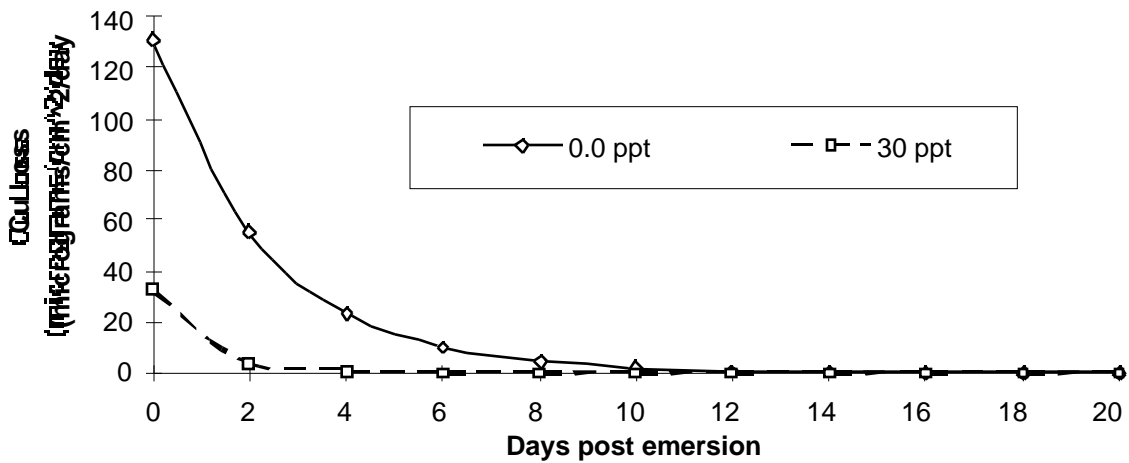


Figure 1. Temporal declines in copper loss rates, in fresh water (pH = 7) and salt water at 30 ppt (pH = 8.0). Fresh water data are for Douglas fir sapwood treated to 1.0 pounds per cubic foot (in the treated zone) with ACZA. Marine samples (30 ppt) are for Douglas fir sapwood treated to 2.5 pcf (in the treated zone) with ACZA.

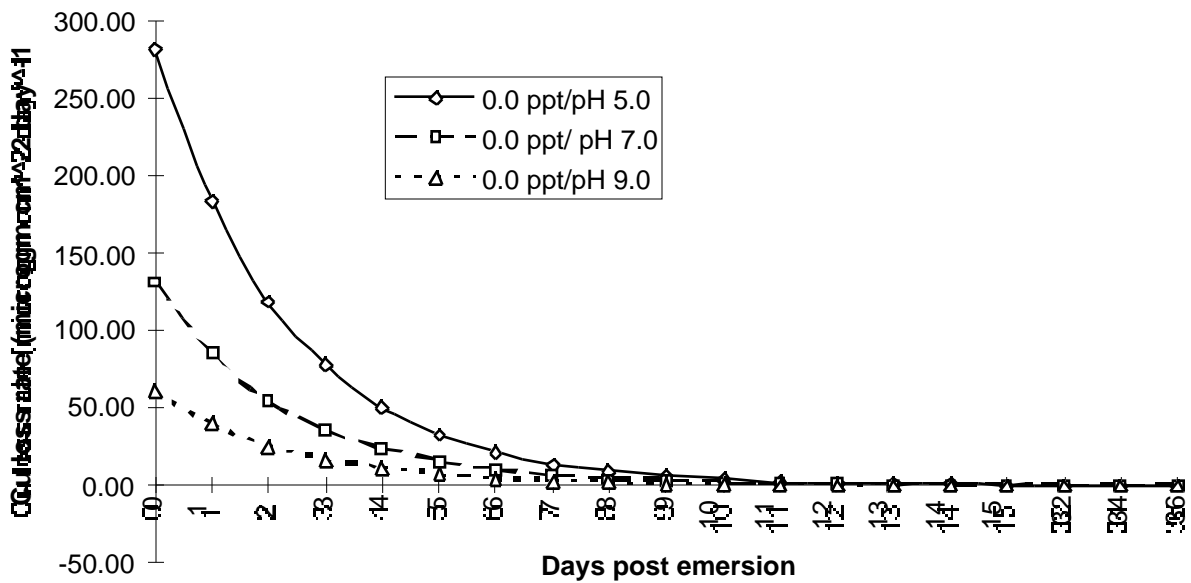


Figure 2. Effects of pH on copper losses from Douglas fir sapwood treated to 1.0 pcf (in the treated zone) and leached in fresh water at pH = 5.0, 7.0 or 9.0.

Summary. Equations 1 through 5 provide algorithms adequately describing the loss of arsenic, zinc and copper from ACZA treated wood intended for use in fresh water within a pH range of 5.0 to 9.0, or in salt water at 30 ppt and a pH of 8.0. Metal losses from ACZA treated Douglas fir sapwood decline very rapidly and reach negligible levels with ten days following immersion in fresh water or four days following immersion in sea water.

Anticipated Environmental Levels of Copper Resulting From the Use of ACZA Treated Wood In Aquatic Environments.

The leaching rates predicted by Equations 1 through 5 provide a means of estimating the final environmental concentrations of metal contaminants associated with the use of ACZA 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 ACZA treated piling and the second predicts water column and sediment levels of copper associated with large surface area ACZA 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. By large we mean that the receiving body should be at least 250 times the submerged area of ACZA treated wood.

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 be 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 copper 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 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 (6).

Equation (6) Stokes law for the settling velocities of small particles:

$$w = \frac{g D^2 (\rho_s - \rho_w)}{18 \mu}$$

Where: g = gravitational constant
 D = particle diameter
 ρ_s = particle density
 ρ_w = density of water
 μ = 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°C) of 2×10^{-1} to 10^{-3} cm/sec. An intermediate value of 5×10^{-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 speed can be modeled by the harmonic:

$$V_t = V_{\text{maximum}} \sin(\pi t/12)$$

Integrating this equation from $t = 0$ to $t = 6$ gives: Distance = $V_{\text{max}} \int_0^6 \sin(\pi t/12) dt$, or:

Equation (7) Distance = 3.82 (hours) x V_{maximum} = 1.3752 x 10⁴ (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 $0.64 V_{\text{maximum}}$

the $r =$ radius (measured from the periphery of pile) where copper is deposited.

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

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

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

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

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

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

Substituting for M, the relationship becomes:

$$(6) D = m^2 R_p dh/2 [h(V_{\text{model}}/V_{\text{vert}}) + R_p](V_{\text{model}}/V_{\text{vert}}) dh$$

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

$$\text{Equation 10. } D = mR_p/[r + R_p](V_{\text{model}}/V_{\text{vert}})]$$

Where $D =$ deposition rate (excluding degradation factors) measured in $\mu\text{g cm}^{-2}\text{-day}^{-1}$
 $m =$ metal migration rate, measured in $\mu\text{g cm}^{-2}\text{-day}^{-1}$ (see Equations 1 - 5.)
 $R_p =$ average piling radius measured in cm
 $V_{\text{vert}} =$ average vertical velocity of adsorption particles (silt = 0.05 cm-sec^{-1})
 $V_{\text{model}} =$ Model water velocity = $V_{\text{ss}} + 0.64V_{\text{maximum}}$
 $r =$ the distance from the periphery of the treated wood at which 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 11. 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 11. Surface Area Leaching Ratio = $1.84 \exp^{-0.01346 \times \text{Board Width (cm)}}$

Water column contamination associated with ACZA treated lumber used in Bulkheads. Significant quantities of ACZA 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 ACZA treated wood will be modeled as before. The model will assume that water is moving slowly along a bulkhead of length l 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) = 1.5×10^{-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 12.

Equation 12. Mixing Width = $2.5 \times 10^{-3} \times (\text{Velocity}_{\text{model}})^2 \times \text{Transit Time (sec)}$
Transit Time in this equation can be replaced with an equivalent expression:

Transit time = Bulkhead Length/Velocity_{model}
Substituting this into Equation 12 and simplifying gives Equation

13.

Equation 13. Mixing Width = $2.5 \times 10^{-3} \times \text{Bulkhead Length} \times \text{Velocity}_{\text{model}} \text{ (cm)}$

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 associated with water 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:

Copper Concentration = Copper Migration Rate x exposure time x Leaching Surface Ratio/Mixing Width

where exposure time = bulkhead length/V_{model}

Freshwater Copper Conc_(cu-bulkhead) = $1908 \times \exp^{-0.429 \times \text{Days} - 0.383 \times \text{pH}} \times 1.84 \exp^{-0.01346 \times \text{Board Width (cm)}}$
 $/ (86,400) \times (2.5 \times 10^{-3} \times (\text{V}_{\text{ss}} + 0.64(\text{V}_{\text{maximum}} - \text{V}_{\text{ss}}))^2$

or, after converting this to parts per trillion, we obtain Equation 14.

Equation 14.

$$\text{Freshwater Cu Conc}_{(\text{cu-bulkhead})} = 29,906.13 \times \exp^{-0.429 \times \text{Days} - 0.383 \times \text{pH} - 0.01346 \times \text{Board Width (cm)}} / (\text{V}_{\text{ss}} + 0.64(\text{V}_{\text{maximum}} - \text{V}_{\text{ss}}))^2$$

Note that this expression assumes that the water depth out to the edge of the Mixing Width is constant. Metal losses associated with bulkheads located on relatively steep shorelines would be further diluted by vertical mixing. 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.

Saltwater Copper Concentrations are developed in a similar manner, except that the algorithm for copper losses from ACZA treated wood in 30 ppt sea water are substituted into Equation 14. The result is presented in Equation 15.

Equation 15.

$$\text{Saltwater Cu Conc}_{(\text{cu-bulkhead})} = 509.41 \times \exp^{-1.114 \times \text{Days} - 0.01346 \times \text{Board Width (cm)}} / (\text{V}_{\text{ss}} + 0.64(\text{V}_{\text{maximum}} - \text{V}_{\text{ss}}))^2$$

Sediment concentrations of copper associated with the use of ACZA 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 predictions are considered conservative from a sediment 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 $\text{Velocity}_{\text{model}} + \text{Velocity}_{\text{mixing}}$ where we assume that the two vectors are orthogonal. $\text{Velocity}_{\text{mixing}}$ is determined from Equation 12 and equals:

$$\text{Equation 16. } \text{Velocity}_{\text{mixing}} = 2.5 \times 10^{-3} \times (\text{Velocity}_{\text{model}})^2$$

and therefore the vector sum of $\text{Velocity}_{\text{model}} + \text{Velocity}_{\text{mixing}}$ is:

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

An additional correction must be 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.

$$\text{Equation 18. } \text{Aspect Ratio Correction Factor (ARCF)} =$$

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

If we assume that the settling copper is distributed over an area equal, to $\text{ARCF} \times \text{Velocity}_{\text{vertical}}/\text{Velocity}_{\text{horizontal}}$ then we can model copper deposition to the sediments using Equation 19.

Equation 19. Deposition_{copper} = Copper Loss Rate (µgm-sec-1) x exposure time (sec)

$$\times \text{Velocity}_{\text{verticle}} / (\text{Velocity}_{\text{horizontal}} \times \text{ARCF}) \quad \text{or}$$

Deposition_{Cu} = Copper Loss Rate (µgm-sec-1) x (bulkhead length/Velocity_{model}) x Velocity_{verticle}

$$/ (|\text{Velocity}_{\text{mixing}} + (\text{Velocity}_{\text{model}}| \times \text{ARCF}) \quad \text{or}$$

In Fresh Water, copper accumulation in sediments associated with ACZA treated bulkheads equals:

$$(1,908/86,400) \times \exp^{-0.429 \times \text{Days} - 0.383 \times \text{pH}} \times 1.84 \exp^{-0.01346 \times \text{Board Width (cm)}} \times \text{bulkhead length} \times \text{Velocity}_{\text{verticle}} / \{6.25 \times 10^{-6} \times (\text{Velocity}_{\text{model}})^4 + (\text{Velocity}_{\text{model}})^2\}^{1/2} \times \text{Velocity}_{\text{model}} \times \{\sin(\tan^{-1}(\text{Velocity}_{\text{mixing}}/\text{Velocity}_{\text{model}}))\}$$

Assuming that $6.25 \times 10^{-6} \times \text{Velocity}_{\text{model}}^2$ is $\ll 1$, converting to parts per billion, and simplifying Equation 19, we obtain the final form of the sediment deposition model appropriate for fresh water predictions:

Equation 20.

Fresh Water Sediment Deposition_{copper} = 40.6 x exp^{-0.429 x Days - 0.383 x pH - 0.01346(Board Width)}

$$\times \text{bulkhead length} \times \text{Velocity}_{\text{verticle}} / (\text{Velocity}_{\text{model}})^2 \times \{\sin(\tan^{-1}(2.5 \times 10^{-3} \times \text{Velocity}_{\text{model}}))\}$$

3Velocity_{model})}

In Salt Water, copper accumulation in sediments associated with ACZA bulkheads equals:

$$(32.5/86,400) \times \exp^{-1.114 \times \text{Days} - 0.01346 \times \text{Board Width (cm)}} \times 1.84 \exp^{-0.01346 \times \text{Board Width (cm)}} \times \text{bulkhead length} \times \text{Velocity}_{\text{verticle}} / \{6.25 \times 10^{-6} \times (\text{Velocity}_{\text{model}})^4 + (\text{Velocity}_{\text{model}})^2\}^{1/2} \times \text{Velocity}_{\text{model}} \times \{\sin(\tan^{-1}(\text{Velocity}_{\text{mixing}}/\text{Velocity}_{\text{model}}))\}$$

Again, assuming that $6.25 \times 10^{-6} \times \text{Velocity}_{\text{model}}^2$ is $\ll 1$, converting to parts per billion, substituting the salt water copper loss rate from ACZA and simplifying Equation 19, we obtain the final form of the sediment deposition model appropriate for marine applications:

Equation 21. Salt Water Sediment Deposition_{copper} = 0.692 exp^{-1.114 x Days -0.01346 x Board Width (cm)}

$$\times \text{bulkhead length} \times \text{Velocity}_{\text{verticle}} / (\text{Velocity}_{\text{model}})^2 \times \{\sin(\tan^{-1}(2.5 \times 10^{-3} \times \text{Velocity}_{\text{model}}))\}$$

3Velocity_{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 an ACZA treated structure will remain in the top two centimeters of the sediment. Total accumulations were determined by summing the daily contributions. These sums become asymptotic at the following values. These values represent the total copper accumulation in adjacent sediments, expressed as a multiple of the first days contribution.

Salt water copper accumulation in sediments = 1.49 x first day's accumulation

Fresh water copper accumulation in sediments = 2.86 x first day's accumulation

Correction for deep water deposition. Where average water depths in the Mixing Width are greater than $0.025 \times \text{Bulkhead Length} / \text{Velocity}_{\text{model}}$, 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 m in length next to water flowing with $\text{Velocity}_{\text{model}} = 2.5 \text{ cm/sec}$, 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 an if-then statement that corrects sediment copper accumulation for this phenomena. Combining these factors with Equations 20 and 21, we obtain the final form of the copper bulkhead accumulation model in fresh water and marine sediments (Equations 22 and 23).

Equation 22.

Fresh Water Sediment Accumulation_{Cu} = 116.12 x exp^{-0.429 x Days - 0.383 x pH - 0.01346(Board Width)}
x bulkhead length x Velocity_{verticle}
/(Velocity_{model})² x {sin(tan⁻¹(2.5 x 10⁻³Velocity_{model}))}

Equation 23.

Marine (30 ppt) Sediment Accumulation_{Cu} = 1.031 exp^{-1.114 x Days - 0.01346 x Board Width (cm)}
x bulkhead length x Velocity_{verticle}
/(Velocity_{model})² x {sin(tan⁻¹(2.5 x 10⁻³Velocity_{model}))}
x 1.0 if Average Water Depth ≤ 0.025 x Bulkhead Length/ Velocity_{model} or
x 0.5 if Average Water Depth > 0.025 x Bulkhead Length/ Velocity_{model}

Predicted concentrations of copper in the water column and sediments associated with the use of ACZA 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:\ACZAprsk (for piling calculations) and A:\ACZAbrsk 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); 16.0 (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 $\exp(0.8545 * |\ln(\text{hardness})| - 1.465)$
11. Water Hardness (ppm CaCO₃)
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)
17. Freshwater pH

Notes:

1. Treated wood retention in kilograms-m⁻³. AWWA defines minimum ACZA 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. AWWA Standards (1992) require retention's of 40 kg-m⁻³ for piling and lumber submerged in marine environments and 15.6 kg-m⁻³ for 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:

$$\text{Circumference} = 2\pi r \text{ or } R_p = \text{circumference}/2 \quad . \quad (\text{one inch} = 2.54 \text{ cm})$$

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. Insufficient data is available to determine metal loss from ACZA treated wood in estuarine salinities (10 to 20 ppt). It is recommended that the following values be used

Salinity = 0.0 ppt to 15.0 ppt
Salinity = 15.1 ppt to 34 ppt

Use Fresh Water Model
Use the Saltwater

Model

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 environmentally conservative 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 (CaCO₃). The standard is determined using Equation 23. In areas, and at times, when adult salmon are migrating upstream or smolts are out-migrating, a value of 5.0 ppb copper should be considered the maximum allowable value in fresh water.

Equation 23. Fresh Water Copper Quality Standard = $\exp(0.8545 \cdot |\ln(\text{hardness})| - 1.465)$

or 5.0 ppb copper during times of active salmonid migration

11. Water Hardness. Water hardness is measured as the calcium and magnesium salts present in a sample of water. It is expressed as ppm CaCO₃.

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 effecting water column concentrations of copper in this model. However, bulkheads that are submerged less than 30 cm along steep shores (>10% slope) will result in 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).

Recommended input parameters for common situations are provided in Table 11. More specific information is available from the National Oceanographic and Atmospheric Agency (NOAA), local colleges and Sea Grant offices. Parameters have been selected which are easily measured in the field.

Table 11. Recommended input parameters during preliminary evaluations or when specific information is unavailable.

User Entry Estuarine	Fresh Water	Marine	
1. Treated wood retention in kg-m ⁻³	15.6	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) or 30.0	0.0	30.0	0.0
5. Settling Velocity (0.05 for silt; 0.0005 for clay) 0.05	0.05	0.05	
6. Average maximum Tidal Velocity (north)	0.00	10.0 (north)	10.0
(south)		5.0 (south)	5.0
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		2.9	
13. Sediment Density (grams/cubic centimeter) 2.2	2.2	2.2	

14. Bulkhead Length	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		
17. Freshwater pH	7.25	

Model Output

Water column copper concentrations associated with ACZA treated piling in fresh water. 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 $0.06451 \times V_{\text{maximum}}$. Combining this factor with copper leaching rates (Equation 1) for fresh water, we obtain:

$$\text{Concentration}_{\text{fresh water}} (C_{\text{FW}}) = \frac{1908.6 \times \exp^{-0.429 \times \text{Days} - 0.383 \times \text{pH}} \times 2\pi R_p}{24\pi[(1800 \times 0.0651 \times V_{\text{max}} + 1800V_{\text{ss}} + R_p)^2 - R_p^2]}$$

or, after simplifying this expression we obtain Equation 24.

Equation 24. Copper Concentration (C_{FW}) = $159.0 \times \exp^{-0.429 \times \text{Days} - 0.383 \times \text{pH}} \times R_p$

$$\frac{R_p^2}{[(234.36 \times V_{\text{max}} + 3600V_{\text{ss}} + R_p)^2 - R_p^2]}$$

and in saltwater, the appropriate algorithm predicting copper concentrations in the water column associated with ACZA treated piling is:

Equation 25. Copper Concentration (C_{sw}) = $2.71 \times \exp^{-1.114 \times \text{Days}} \times R_p$

$$\frac{R_p^2}{[(234.36 \times V_{\text{max}} + 3600V_{\text{ss}} + R_p)^2 - R_p^2]}$$

Where:

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

Model output for a poorly flushed marine environment. 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 poorly flush marine environment is summarized in Table 12.

Table 12. Predicted metal concentrations resulting from the use of ACZA piling in a very poorly flushed marine environment with no steady state currents and

maximum tidal flows of 2.5 cm sec⁻¹. Details of the input and output are included in Appendix 1.

	Marine Water Copper	Fresh Water Arsenic	Zinc	Copper	Arsenic	Zinc
Water Conc. (ng L ⁻¹)	437.4	0.3	300.9			
Marine Water Standard (ng L ⁻¹)			2900.0	36000.0	76600.0	

Fresh Water Standard (ng L⁻¹)

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 lose (on the first day) 32.55 µg cm⁻² Cu day⁻¹ or 1.36 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 437.4 ppt 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 15% of the marine standard (2.9 ppb), giving a safety factor of 6.6. Metal losses from ACZA treated wood decrease very quickly and within three days, copper losses will be 3.5% of the initial value or 15.5 parts per trillion - giving a safety factor of 187. In addition, at poorly flushed sites, 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).

Note that arsenic and zinc losses from ACZA treated wood are very small at all times. On the first day of emersion in this very poorly flushed marine environment, water column concentrations of arsenic and zinc are 8.3 x 10⁻⁶ and 3.9 x 10⁻³ of the respective Washington State water quality standards.

Model output for a poorly circulated fresh water environment. Currents at specific sites in lakes and rivers should be measured with either a drogoue or a current meter. These currents may be wind driven on a diurnal basis, or they may be relatively steady state as such as would be found in an unrestricted river. On impounded rivers, such as the Columbia River, observed currents will be the result of significant river flow, coupled with wind driven currents, particularly in the summer. The model can accommodate all of these situations because measured currents can be modeled and inputted in any user defined combination of steady state and harmonic components. In Table 13, the results of an analysis in which ACZA treated piling is used in a poorly circulated area of the Columbia River is presented.

Table 13. Predicted metal concentrations resulting from the use of ACZA piling in a slow flowing lentic environment with steady state currents of 1.0 cm sec⁻¹. Input parameters were set at a pH of 7.25 and 50 ppm (CaCO₃) hardness. Details of the input and output are included in Appendix 1.

	Marine Water Copper	Fresh Water Arsenic	Zinc	Copper	Arsenic	Zinc
Water Conc. (ng L ⁻¹)				45	0.038	0.030
Marine Water Standard (ng L ⁻¹)						
Fresh Water Standard (ng L ⁻¹)					6539	190000
						52493

Note that the predicted copper concentration of 45 parts per trillion is 6.9 x 10⁻³ times the fresh water standard. Arsenic and zinc losses are very small being 2.0 x 10⁻⁷ and 5.72 x 10⁻⁷ of the Washington State fresh water chronic standards.

Predictions made by this model must be added to background levels in order to evaluate environmental risks. Johnson and Hopkins (1991) measured whole (unfiltered) copper levels in the Columbia at the USGS stations at Warrendale, Oregon (river mile 141.0) and at Bradwood, Oregon (river mile 38.9). They found copper levels of $1,800 \pm 200$ ppt at Warrendale and $2,200 \pm 200$ ppt at Bradwood. The addition of ACZA treated piling at Warrendale would increase the copper loading by 2.5% to 1845 ppt. At Bradwood, the increase would be 2.0% resulting in a concentration of 2245 ppt.

In either case, these levels are significantly lower than the 5,000 parts per trillion level at which incipient effects are observed in the migratory behavior of salmon. These effects were observed only after long term (165 days) exposure to 5,000 parts per trillion copper. Within four days, water column concentrations at a similar site on the Columbia river would be 8.1 parts per trillion which is 1.6×10^{-3} times the level at which effects in migratory behavior are observed. Further analysis suggests that deleterious effects on the migratory behavior of salmon would not be encountered during the first day following installation unless average observed currents at the site were less than $0.125 \text{ cm sec}^{-1}$. Wind driven currents, waves and mechanical disturbances associated with boats, etc. will, in most cases, exceed this value. Therefore, with existing copper levels in the Columbia River, it is very unlikely that copper lost from ACZA treated wood piling would increase background levels to those associated with any known impact on salmonid, or other, resources.

Sediment contamination associated with ACZA 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 ACZA treated wood projects. Assumptions made in defining this model are:

1. Copper loss rates from ACZA treated wood are a function of salinity, time after treatment and retention rates. The following copper loss algorithms are used in this model. The output is in $\mu\text{g cm}^{-2} \text{ day}^{-1}$.

$$\text{Saltwater Copper Losses} = 32.5 \times \exp^{-1.114 \times \text{Days}}$$

$$\text{Fresh Water Copper Losses} = 1908.6 \times \exp^{-0.429 \times \text{Days} - 0.383 \times \text{pH}}$$

2. Copper Adsorbed Particle Settling Velocities are measured in cm sec^{-1} and referred to in this model as 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 $0.001 \text{ cm sec}^{-1}$. For purposes of this model we will assume an intermediate velocity of 0.05 cm sec^{-1} .

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

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 26) 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 26. 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 27 is used to predict copper deposition.

Equation 27. Deposition (D) = MR_p/[r(V_{model}/V_{vert}) + R_p]

- 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 Equations 28 (saltwater) and 29 (fresh water).

Equation 28.

Sediment Cu Accumulation_{marine} = 0.90 x (1 + V_{model}/10) x R_p x 32.5 x exp-1.114 x Days
/[(r + R_p) x (V_{model}/V_{vert})]

Equation 29. Sediment Cu Accumulation_{fresh} = (1 + V_{model}/10) x R_p
x 1908.6 x exp-0.429 x Days -
0.383 x pH
/[(r + R_p) x (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 ACZA 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 14. In addition to the tabular output, A:\ACZAprsk presents the results in graphical form. A copy of the graphical output accompanying Table 14 is provided in Figure 3. 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 14 and Figure 3.

Notes for A:\ACZAprsk output. The project described in Table 14 is a piling project in which 30 cm (1 foot) diameter piling, treated to a retention of 15.6 kg m⁻³ (freshwater) or 40.6 kg m⁻³ (saltwater) is newly installed in a fresh or salt water. The area has poor flushing and steady current speed of 1.0 cm sec⁻¹ was observed. The freshwater pH was measured at 7.25 and the observed hardness was 50 ppm (CaCO₃).

Recall that we integrated copper losses from $t = 0$ to and found that total copper accumulations in adjacent sediments will be 2.86 (freshwater) or 1.49 (saltwater) 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). The predicted water column concentrations of copper (45 pptrillion), arsenic (0.038 pptrillion) and zinc (0.03 pptrillion) anticipated from this structure are provided for both marine environments (30 ppt) and fresh water (0 ppt). Obviously, it is the copper concentration that should be monitored. Arsenic and zinc losses are simply too low to be of concern. Also note that this case is for day zero, and therefore represents the maximum predicted water column concentrations of these metals. 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).

Table 14. Tabular output from the Microsoft EXCEL™ spreadsheet

A:\ACZAPrsk.

Water column and sediment copper concentrations associated with ACZA treated piling.

Copper Accumulation in Water and Sediments Associated with the use of ACZA Treated Piling												
User Entries				Intermediate Output								
				Marine Water			Fresh Water					
				Copper	Arsenic	Zinc	Copper	Arsenic	Zinc			
1. Retention in kilograms per cubic meter			40.00	Migration (migr/cm2-day)	32.55	0.10	22.40	118.79	0.10	0.08		
2. Average piling radius (centimeters)			15.00	Age Factor	1.00	1.00	1.00	1.00	1.00	1.00		
3. Piling Age in Days			0.00	Retention Factor	0.99	0.99	0.99	0.99	0.99	0.99		
4. Salinity (parts per thousand, ppt)			0.00	Mixing Width (cm)	25.00	25.00	25.00	25.00	25.00	25.00		
5. Settling Velocity (0.05 for silt; 0.00005 for clay)			0.050	Model Velocity (cm/sec)	1.00	1.00	1.00	1.00	1.00	1.00		
6. Average Maximum Tidal Velocity			0.00	Geometry Factor	1.10	1.10	1.10	1.10	1.10	1.10		
7. Steady State Currents (measured at slack tide)			1.00									
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 ACZA Treated Piling								
10. Fresh Water, Chronic, Copper Standard			6.54									
11. Water hardness (ppm CaCO3)			50.00	Water Conc. (pptrillion)	12	0.038	8	45	0.038	0.030		
12. Marine Water Copper Standard			2.90	Marine Water Standard	2900	36000	76600					
13. Sediment Density (grams/cubic centimeter)			2.2	Fresh Water Standard				6539	190000	52493		
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									
17. Fresh Water pH.			7.25									
Predicted Sediment Copper Levels in micrograms/square cm sediment surface, or ppm												
Distance	Marine P1 Accum.	Marine P2 Accum.	Total Copper Acc.	Cu Conc. (PPM)	Sed. Std.	SIZ Maximum	Corr.	Dolphin	FW - P1	FW-P2	Total Cu.	Cu. Conc
400	1.35	2.60	3.95	0.90	390.00	390.00	1.57	2.12	4.92	9.49	14.41	3.28
375	1.43	2.94	4.38	1.00	390.00	390.00		2.25	5.23	10.74	15.98	3.63
350	1.53	3.39	4.92	1.12	390.00	390.00		2.41	5.59	12.37	17.97	4.08
325	1.65	4.00	5.64	1.28	390.00	390.00		2.58	6.00	14.58	20.59	4.68
300	1.78	4.86	6.64	1.51	390.00	390.00		2.79	6.48	17.75	24.23	5.51
275	1.93	6.21	8.14	1.85	390.00	390.00		3.03	7.04	22.68	29.72	6.75
250	2.11	8.61	10.72	2.44	390.00	390.00		3.31	7.70	31.41	39.11	8.89
225	2.33	13.98	16.31	3.71	390.00	390.00		3.66	8.51	51.04	59.54	13.53
200	2.60	27.97	30.57	6.95	390.00	390.00		4.08	9.49	102.07	111.57	25.36
175	2.94	13.98	16.93	3.85	390.00	390.00		4.62	10.74	51.04	61.78	14.04
150	3.39	8.61	12.00	2.73	390.00	390.00		5.32	12.37	31.41	43.78	9.95
125	4.00	6.21	10.21	2.32	390.00	390.00		6.27	14.58	22.68	37.26	8.47
100	4.86	4.86	9.73	2.21	390.00	390.00		7.64	17.75	17.75	35.50	8.07
75	6.21	4.00	10.21	2.32	390.00	390.00		9.76	22.68	14.58	37.26	8.47
50	8.61	3.39	12.00	2.73	390.00	390.00		13.51	31.41	12.37	43.78	9.95
25	13.98	2.94	16.93	3.85	390.00	390.00		21.95	51.04	10.74	61.78	14.04
5	27.97	2.60	30.57	6.95	390.00	390.00		43.91	102.07	9.49	111.57	25.36
25	13.98	2.33	16.31	3.71	390.00	390.00		21.95	51.04	8.51	59.54	13.53
50	8.61	2.11	10.72	2.44	390.00	390.00		13.51	31.41	7.70	39.11	8.89
75	6.21	1.93	8.14	1.85	390.00	390.00		9.76	22.68	7.04	29.72	6.75
100	4.86	1.78	6.64	1.51	390.00	390.00		7.64	17.75	6.48	24.23	5.51
125	4.00	1.65	5.64	1.28	390.00	390.00		6.27	14.58	6.00	20.59	4.68
150	3.39	1.53	4.92	1.12	390.00	390.00		5.32	12.37	5.59	17.97	4.08
175	2.94	1.43	4.38	1.00	390.00	390.00		4.62	10.74	5.23	15.98	3.63
200	2.60	1.35	3.95	0.90	390.00	390.00		4.08	9.49	4.92	14.41	3.28
225	2.33	1.27	3.60	0.82	390.00	390.00		3.66	8.51	4.64	13.15	2.99
250	2.11	1.20	3.31	0.75	390.00	390.00		3.31	7.70	4.39	12.09	2.75
275	1.93	1.14	3.07	0.70	390.00	390.00		3.03	7.04	4.17	11.21	2.55
300	1.78	1.09	2.86	0.65	390.00	390.00		2.79	6.48	3.96	10.44	2.37
325	1.65	1.04	2.68	0.61	390.00	390.00		2.58	6.00	3.78	9.78	2.22
350	1.53	0.99	2.52	0.57	390.00	390.00		2.41	5.59	3.61	9.21	2.09
375	1.43	0.95	2.38	0.54	390.00	390.00		2.25	5.23	3.46	8.69	1.98
400	1.35	0.91	2.26	0.51	390.00	390.00		2.12	4.92	3.32	8.24	1.87
425	1.27	0.87	2.15	0.49	390.00	390.00		2.00	4.64	3.19	7.83	1.78
450	1.20	0.84	2.04	0.46	390.00	390.00		1.89	4.39	3.07	7.46	1.70
475	1.14	0.81	1.95	0.44	390.00	390.00		1.79	4.17	2.96	7.12	1.62
500	1.09	0.78	1.87	0.42	390.00	390.00		1.71	3.96	2.86	6.82	1.55
525	1.04	0.76	1.79	0.41	390.00	390.00		1.63	3.78	2.76	6.54	1.49
550	0.99	0.73	1.72	0.39	390.00	390.00		1.55	3.61	2.67	6.28	1.43
575	0.95	0.71	1.66	0.38	390.00	390.00		1.49	3.46	2.58	6.04	1.37
600	0.91	0.69	1.60	0.36	390.00	390.00		1.43	3.32	2.50	5.82	1.32
625	0.87	0.67	1.54	0.35	390.00	390.00		1.37	3.19	2.43	5.62	1.28
650	0.84	0.65	1.49	0.34	390.00	390.00		1.32	3.07	2.36	5.43	1.23
675	0.81				390.00	390.00		1.27	2.96			
700	0.78				390.00	390.00		1.23	2.86			

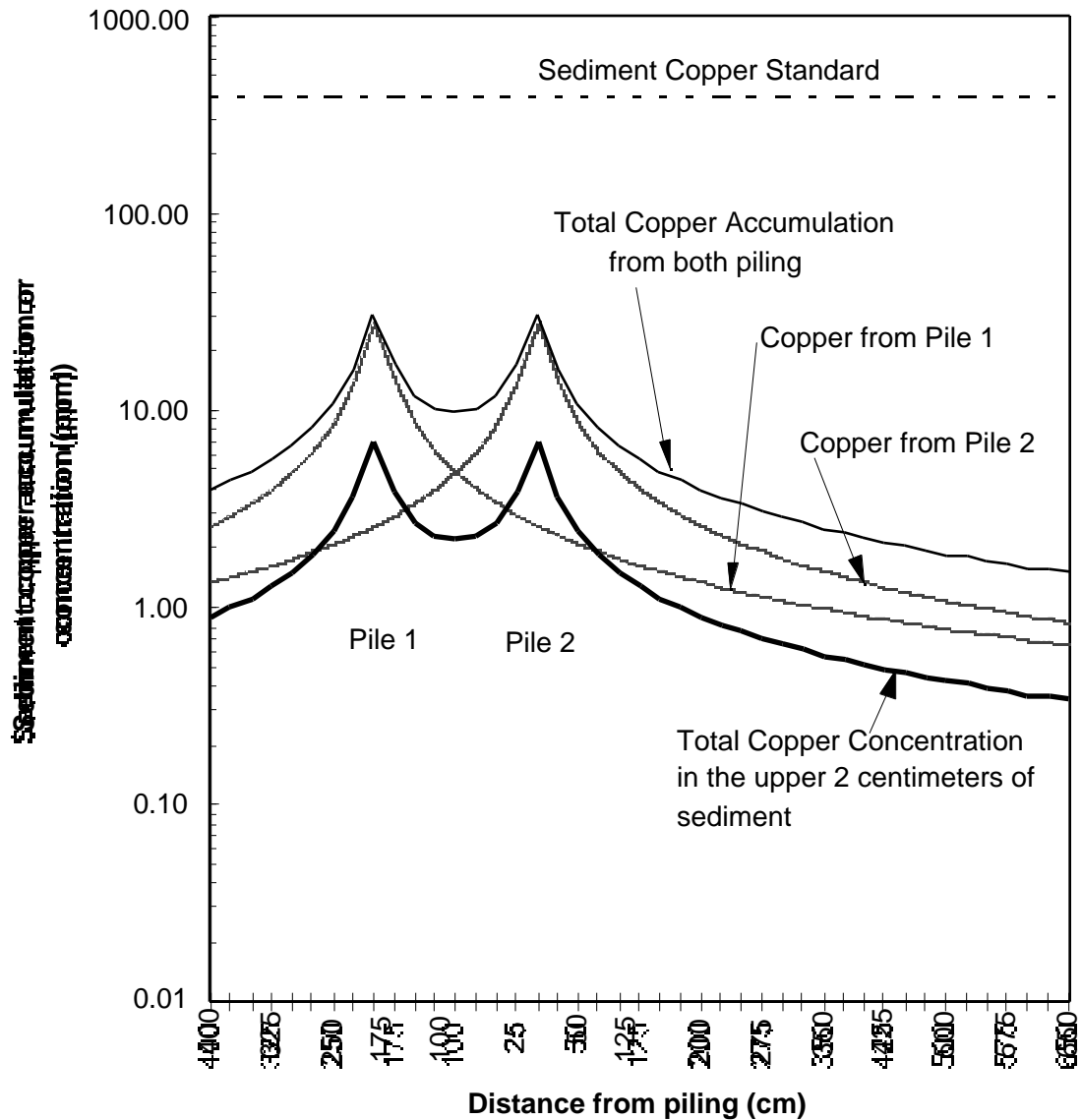


Figure 3. Graphical output from ACZAprsk.xls describing sediment accumulation and resulting concentrations of copper associated with ACZA treated piling. The Washington State sediment quality standard of 390.0 ppm copper is annotated on the graph.

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 50 ppm hardness, the Washington State fresh water standard is 6539 parts per trillion copper. Similarly, the Washington State standards for Arsenic (190,000 pptrillion) and Zinc (52,493 pptrillion) are provided.

Distance. This column contains the values (in centimeters) of (r) for which sediment 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 $\mu\text{g cm}^{-2}$.

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 the P2 column and moving the first entry 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 two weeks following emersion, observed copper concentrations will approach predicted values within two weeks 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 ACZA treated lumber may come into contact with water in bulkheading and sheet piling projects. The large leaching surface area associated with these projects suggests that this application may represent a worst case, 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:\ACZABrsk. Copper loss rates from ACZAA treated wood will be modeled as before, but converted to losses per second instead of losses per day. The copper concentrations predicted by Equations 14 and 15 are 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 14.

$$\text{Freshwater Conc}_{(\text{cu-bulkhead})} = \frac{29,906.13 \times \exp^{-0.429 \times \text{Days} - 0.383 \times \text{pH} - 0.01346 \times \text{Board Width (cm)}}}{(V_{ss} + 0.64(V_{\text{maximum}} - V_{ss}))^2}$$

Equation 15.

$$\text{Saltwater Conc}_{(\text{cu-bulkhead})} = \frac{509.41 \times \exp^{-1.114 \times \text{Days} - 0.01346 \times \text{Board Width (cm)}}}{(V_{ss} + 0.64(V_{\text{maximum}} - V_{ss}))^2}$$

Sediment accumulation of copper associated with large surface area structures treated with ACZA. The accumulation of copper in sediments associated with large surface area ACZA treated structures is predicted in Equations 22 and 23.

Equation 22.

$$\text{Fresh Water Sediment Accumulation}_{\text{Cu}} = 116.12 \times \exp^{-0.429 \times \text{Days} - 0.383 \times \text{pH} - 0.01346(\text{Board Width})}$$

$$\times \text{bulkhead length} \times \text{Velocity}_{\text{verticle}} / \{(\text{Velocity}_{\text{model}})^2 \times \sin(\tan^{-1}(2.5 \times 10^{-3} \text{Velocity}_{\text{model}}))\}$$

Equation 23.

$$\text{Marine (30 ppt) Sediment Accumulation}_{\text{Cu}} = 1.031 \times \exp^{-1.114 \times \text{Days} - 0.01346 \times \text{Board Width (cm)}}$$

$$\times \text{bulkhead length} \times \text{Velocity}_{\text{verticle}} / \{(\text{Velocity}_{\text{model}})^2 \times \sin(\tan^{-1}(2.5 \times 10^{-3} \text{Velocity}_{\text{model}}))\}$$

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

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

Output describing sediment accumulation of copper is provided in Table 15. The data is for an orthogonal transect midway along the bulkhead. These are the maximum anticipated accumulations. After approximately two weeks 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 15. Tabular output from the Microsoft EXCEL™ spreadsheet A:\ACZABrsk. Water column copper concentrations associated with bulkheads.

Copper Accumulation in Water and Sediments Associated With Large Surface Area ACZATreated Projects						
User Entries			Intermediate Output			
					Freshwater	Saltwater
1. Retention in kilograms per cubic meter		16 FW/40 SW	Migration (migr/cm ² -day)		32.80	1.15
2. Freshwater pH		7.25	Age Factor		0.87	0.87
3. Age of structure (days)		3.00	Mixing Width (cm)		75.00	75.00
4. Salinity (parts per thousand, ppt)		0.0 FW/ 30 SW	Model Velocity (cm/sec)		20.00	20.00
5. Settling Velocity (0.05 for silt; 0.00005 for clay)		0.050	Geometry Factor		3.00	3.00
6. Average Maximum Tidal Velocity		0.00	Mixing Velocity (cm/sec)		0.05	0.05
7. Steady State Currents (measured at slack tide)		20.00				
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		6.54	Water Column Copper Conc.			
11. Water hardness (ppm CaCO ₃)		50.00	Associated with CCA Bulkheads			
12. Marine Water Copper Standard		2.90				
13. Sediment Density (grams/cubic centimeter)		50	Water Conc. (pptrillion)		4463.87	85.02
14. Bulkhead Length (cm)		1500	Marine Water Standard			2900.00
15. Board Width (cm) (2x6 = 14, 2x8 = 19, 2x12 = 29.2)		14	Fresh Water Standard		6539.34	
16. Average Water Depth in the Mixing Width (cm)		100.00				
Predicted Sediment Copper Levels in micrograms/square cm sediment surface					123.95	1.52
Predicted Sediment Copper Levels in parts per million (upper 2 cm of sediment surface)					1.24	0.02
Sediment Quality Standard					390.00	390.00

Notes for the output from a:ACZABrsk.xls in Table 23. The basis for the analysis in Table 15 is a newly installed, 15 meter long bulkhead installed in a reasonably well flushed (stead state current = 20.0 cm sec⁻¹) marine or fresh water environment.

Predicted water copper concentration. The model output predicts copper losses on the third day of 32.8 µg cm⁻² day⁻¹ in fresh water and 1.15 µg cm⁻² day⁻¹ in salt water. This copper is diluted in a mixing width of 75 cm during transit of the bulkhead. The resulting copper concentration is 2,426.7 parts per trillion in the fresh water column and 85.02 parts per trillion in saltwater. The fresh water value must be added to ambient copper concentrations to determine if the Washington State Water Quality Standard would be exceeded. In the Columbia River, copper concentrations average approximately 2,000 parts per trillion. If this site were in the Columbia River, then we would expect a total copper concentration of 4,426 parts per trillion on the third day following project completion. Copper concentrations within 75 cm of this bulkhead would likely exceed Water Quality criteria on the first day following completion. After that, copper losses from ACZA treated wood are reduced to the point where this project would contribute very little copper to the water. Copper levels would approach ambient levels within two weeks.

Reduced copper losses from ACZA treated wood in marine environments results in saltwater copper predictions that are well within the EPA water quality criteria at three days. This project would meet the marine standard at all times, even immediately following construction.

Predicted Sediment Copper Levels. Sediment concentrations of copper will increase over time. A total of 1.24 ppm copper will be added to the upper two centimeters of the fresh water sediment column by this bulkhead. This deposition is along the shore to a width equal to the mixing width (75 cm). As in the piling model, sediment concentration predictions are for $t =$. However, measured copper levels will approach predicted concentrations within 14 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.

Small Water Bodies. The concentration of copper in small bodies of water is difficult to model. Copper losses from ACZA 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 Material (POM) and clay with settling velocities on the order of 5×10^{-5} cm/sec. This assumption means that the residence time of copper in the water is long with respect to the temporal decline in copper loss rates from ACZA treated wood. The result is that nearly all of the copper lost from ACZA treated wood remains in the water compartment and is not sedimented until after copper loss rates reach negligible values. Total copper losses are determined by integrating the copper loss model over the residence time.

Dilution is based on the volume of the receiving water. Water depth is measured as the ratio of the average depth of the receiving water divided by the depth to which the ACZA structure is submerged. This parameter is called the Water Depth Ratio (WDR). Output is provided in terms of the ratio of the minimum required receiving water body surface area to the area of exposed ACZA treated wood.

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 $16,700/\text{WDR}$ times the area of submerged ACZA treated wood. For a 200' long bulkhead submerged in two feet of water, along the shore of a lake, whose average depth is 12 feet and a hardness of 50 ppm (CaCO_3), the minimum water body surface area would be 208 acres. Equations 22 and 23 provide maximum ratios of water body surface area to submerged ACZA 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 (one to two weeks).

Equation 22. Marine Water Area \geq ACZA Area \times 16,700/WDR

Equation 23. Fresh Water Area \geq ACZA Area \times 395,998/[WDR \times $\exp(0.8545 \times \ln(\text{hardness}) - 1.465)$]

where: \ln = natural logarithm

hardness = CaCO_3 expressed in milligrams/liter; ie. at 75 ppm CaCO_3 enter

75.

Treatment of complex structures. There is an endless variety of configurations for ACZA treated wood in actual structures. Output from the A:\ACZAPrsk.xls model will predict copper 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 piling radius (centimeters)). A larger (by a factor of $\sqrt{2}$) surface area will be exposed in this instance. This can be accounted for

by entering $\sqrt{2} = 1.57$ 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. Copper 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 22, copper accumulation at the center of this array would be $4 \times 0.49 = 0.196 \mu\text{g cm}^{-2}$ copper.

The contribution from any number of piling at any point on the bottom 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 is the predicted sediment level.

Testing the Model.

Environmental scale tests of ACZA 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. Metal loss rates for ACZA and CCA have different characteristics. However, with this exception the models are very similar. Data from these studies will be used to test the model reported here.

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 $\mu\text{g cm}^{-2} \text{ day}^{-1}$. These snail and alga experiments used a block of wood with a total surface area of 228 cm² 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 16 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 LC₅₀'s for shiner perch (417.7 ppb) and Coho salmon smolts (601 ppb). The results of Weis *et al.* (1991) suggest an LC₅₀ 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 16. Copper losses from 228 cm² 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) 265.0	600.0	312.5	125.0
Leaching time (days) 21.0	7.0	14.0	14.0
Observed Copper Losses (micrograms centimeters ⁻² day ⁻¹) 0.22	1.50	0.39	0.16
Predicted Copper Losses (micrograms centimeters ⁻² day ⁻¹) 0.21	1.61	0.97	0.26
EPA marine Cu water quality standard (parts per billion) 2.90	2.90	2.90	2.90
Environmental Levels (ppb) predicted by this model 0.13	0.92	0.58	0.30

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 24. 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 flushinated wood.

Generalized Risks Associated With ACZA Treated