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

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December 5, 2001

Table of Contents

Page

Introduction 1

Background levels and sources of DDAC and copper in aquatic environments. 1

Cycling and fate of DDAC and copper in aquatic environments. 3

Bioaccumulation of DDAC and copper in aquatic environments. 6

Toxicity of DDAC and copper dissolved in the water column to aquatic fauna and flora. 8

Regulatory levels defining water quality criteria 14

Toxicity to aquatic organisms associated with sedimented copper 15

Regulatory standards for copper with respect to marine and freshwater sediments. 23

Toxicity to aquatic fauna and flora associated with didecyldimethylammonium chloride (DDAC) dissolved in the water column 27

Recommended water column benchmarks for DDAC 30

Toxicity to aquatic fauna and flora associated with sedimented DDAC 31

Recommended sediment benchmark for DDAC 32

Summary statement regarding recommended benchmarks for dissolved and sedimented Copper and DDAC for use in this risk assessment. 32

Anticipated environmental impacts resulting from the use of 0.4 pcf ACQ treated wood in aquatic environments. 34

Leaching of DDAC and copper from ACQ treated wood. 34

Factors affecting ACQ-B copper leaching rates 35

Environmental factor affecting the loss of DDAC from ACQ-B preserved wood 39

Preservative loss from overhead structures. 42

Table of contents - continued

Risk Assessment Part I. Anticipated environmental levels of copper and DDAC Resulting from the use of 0.4 pcf ACQ-B treated wood in freshwater environments Dominated by steady state currents (streams and rivers) 43

Water column concentrations of DDAC and copper lost from piling in fresh or Brackish water dominated by steady state currents. 44

Deposition rates of copper and DDAC to sediments in freshwater streams and rivers 44

Accumulation of copper in freshwater sediments 46

Accumulation of DDAC in sediments 47

Predictive computer model for 0.4 pcf ACQ-B preserved wood used in Freshwater environments with steady state current speeds. 47

ACQ-B projects proposed for small, closed, bodies of water such as ponds 52

Summary for the use of 0.4 pcf ACQ-B preserved southern yellow pine in Freshwater and evaluation of generalized risks. 53

Risk Assessment Part II. Anticipated environmental levels of copper resulting from the use of 0.4 pcf ACQ-B treated piling used in constructing large surface area projects, such as bulkheads (ACQbrisk.xls) 56

Water column concentrations of copper associated with large surface area projects such as bulkheads treated with ACQ preservative. 58

Sediment concentration of copper associated with the use of 0.4 pcf ACQ-B Treated lumber in bulkheads. 59

Predicted concentration of copper in the water column and sediments associated with the use of 0.4 pcf ACQ-B treated lumber used to construct bulkheads and other large surface area structures in freshwater environments including those influenced by tidal currents 60

Generalized risks associated with the use of ACQ-B treated wood used in the construction of freshwater bulkheads 61

Table of contents - continued

Risk Assessment Part III. Environmental risks associated with the use of 0.4 pcf ACQ-B preserved piling in environments influenced by tidal currents (ACQprisk.xls) 63

Sedimentation of adsorbed metals 63

Risk assessment model for piling used in freshwater areas influenced by tidal currents. 66

Model output. Water column copper concentrations associated with ACQ-B Treated piling installed in areas influenced by tidal currents. 69

Abrasion of ACQ-B treated wood piling 74

Treatment of complex structures 74

General recommendations for the use of 0.4 pcf ACQ-B preserved southern yellow Pine or hem-fir piling used in freshwater environments influenced by tidal Currents. 75

Summary and Conclusions 76

References 78

List of Tables

Table ***Page***

1. Summary of environmental fate properties of DDAC. 5

2. Metal concentration factors (dimensionless) for submerged aquatic plants. From Rai *et al*. (1995). 7

3. Mean number of total macroinvertebrates per sample (M), mean percentage contribution of selected major taxa to the total macroinvertebrate fauna (P), and number of species (S) observed by Gower *et al*. (1994) as a function of water column levels of copper expressed as proportional increases in the U.S. EPA freshwater copper criteria at the observed level of hardness. 10

4. Water chemistry at sample stations 1 (upstream), 3 (in roast pits) and 4 (immediately downstream from roast pits) in the study of Rutherford and Mellow (1994). 11

5. Selected macro-invertebrate taxa with significant sensitivity or tolerance to high copper levels at sample stations 1 (upstream), 3 (in roast pits) and 4 (immediately downstream from roast pits) in the study of Rutherford and Mellow (1994). Taxa exhibiting moderate to strong copper tolerance are bolded. Dissolved

copper concentrations are provided in parentheses after each station number (μg/L) 12

6. Total Copper Toxicity Measured in Controlled Bioassays. Values are EC_{50} or LC_{50} in ppb 14

7. Summary of copper concentrations in the water column and sediments of reference Loken Lake (LOK) and impacted Manitouwadge Lake (MAN). Significant macro-invertebrate data are included to indicated faunal response. All values are in mg/kg. Data are taken from Munkittrick *et al*. (1991). 18

8. Comparison of metal levels and infauna at four lakes downstream from the Con Mine in the Canadian subarctic. All metal concentrations are in mg/kg (dry sediment weight). 19

9. Heavy metal contents of sediments and of larvae of *Baetis rhodani* collected from six rivers in the German Federal Republic. Sediment Bioconcentration Factors are calculated for each river. All values are in mg Cu/kg dry sediment. 20

List of Tables – continued

10. Summary of sediment types, test conditions and results of copper spiked sediment bioassays reported by Cairns *et al*. (1984). 21

11. Background freshwater sediment copper levels reviewed in this assessment. All values are presented in mg Cu/g dry sediment. 21

12. Summary of the tolerance of various freshwater taxa to sedimented copper 22

13. Summary of jurisdictional screening level benchmarks for screening hazardous waste sites for contaminants of concern 25

14. Recommended benchmarks for assessing the environmental risks associated with sedimented copper lost from pressure treated wood. 26

15. Summary of conventional benchmarks for copper in freshwater (μg/L). The data are from Suter and Tsao (1996). The Environmental Protection Agency National Water Quality Criteria for copper was computed at a hardness of 100 mg ($CaCO_3$) /L. 27

16. Summary of DDAC LC_{50} data for aquatic species from Brooks *et al*. (1996). All values are in μg active ingredient/L 28

17. Summary of no-observed effect levels (NOEL) measured for DDAC 29

18. The effect of DOC on toxicity of the antisapstain chemical, DDAC, to fathead minnows in a 96 hr. static renewal acute toxicity test (from Brooks *et al*., 1996) 30

19. Water and sediment copper and DDAC benchmarks against which to assess the environmental suitability of ACQ-B preserved wood used in aquatic environments 33

20. Minimum current speeds required to meet the U.S. EPA chronic copper standard at hardness = 75 mg/kg ($CaCO_3$), water pH = 7.0 and with a background copper level of 1.5 μg/L as a function of the number of piling placed immediately adjacent to each other in a line parallel to the currents 54

List of Tables – continued

21. Minimum current speeds (cm/sec) required to maintain receiving water copper concentrations below the U.S. EPA freshwater chronic copper criteria. This table assumes neutral pH (7.0) and a background copper concentration of 2.0 μg Cu/L. The table is for a bulkhead of any length – assuming that the receiving water volume is large in comparison with the leaching surface area. 62

22. Recommended input parameters during preliminary evaluations or when specific information is unavailable 69

23. Minimum required values of the model velocity required at a range of hardness values (mg $CaCO_3$/L) to maintain copper concentrations less than the U.S. EPA chronic freshwater copper criterion. These values are appropriate for a single piling, placed in water with pH = 7.0 and a background copper concentration of 1.0 μg/L 75

List of Figures

Page

1. U.S. EPA chronic and acute copper criteria for freshwater. The copper standard is presented in μg/L and hardness values in mg ($CaCO_3$)/L. 15

2. Effect of Dissolved Organic Carbon (DOC) on the No Observed Effect Level of DDAC to fathead minnows in a 96 hour static renewal acute toxicity test (data from Springborn Laboratories). DOC and NOEL data are in mg/L 31

3. Copper loss as a function of time (μg/cm^2/day) from southern yellow pine poles, treated to 0.4 pcf with ACQ-B preservative and leached into 10 to 12 liters of distilled water amended to a pH of 5.0, 6.5 or 8.0 and in saltwater (30 ppm) at pH 8.0. Data from Jin (1997). 36

4. Copper loss as a function of pH (μg/cm^2/day) from southern yellow pine poles, treated to 0.4 pcf with ACQ-B preservative, and leached into 10 to 12 liters of fresh, distilled water amended to a pH of 5.0, 6.5 or 8.0 and in saltwater (30 ppm) at pH 8.0. Data from Jin (1997). 37

5. Copper loss (μg/cm^2/day) from southern yellow pine poles, treated to 0.4 pcf with ACQ-B preservative and leached into either freshwater (salinity = 0.0) or seawater (salinity = 30 g/L). Data from Jin (1997) 37

6. Copper loss (μg/cm^2/day) as a function of time and pH from southern yellow pine poles, treated to 0.4 pcf with ACQ-B preservative and leached into freshwater at pH values of 5.0, 6.5 and 8.0. Data from Jin (1997) 38

7. DDAC losses from 0.4 pcf ACQ-B treated southern yellow pine as a function of time at pH = 5.0, 6.5 and 8.0 and at salinities of 0.0 and 30.00 ppt. Data from Jin (1997) 39

8. DDAC losses from 0.4 pcf ACQ-B treated southern yellow pine as a function of pH at values of 5.0, 6.5 and 8.0 for all times and salinities reported in Jin (1997) 40

9. DDAC losses from 0.4 pcf ACQ-B treated southern yellow pine as a function of salinity at a pH value of 8.0 for all times reported in Jin (1997). 41

10. Summary of predicted copper and DDAC losses in μg/cm^2/day from 0.4 pcf, ACQ-B treated southern yellow pine in receiving water with a pH of 7.0 42

List of Figures - continued

11. Dilution zone geometry used to predict copper and preservative concentrations in sediments associated with the use of 0.4 pcf ACQ-B, preserved southern yellow pine 45

12. Copper and DDAC Accumulation in Water and Sediments Associated with the use of ACQ Treated Piling 51

13. ACQbrisk.xls Copper Losses from 0.4 pcf ACQ-B Treated Bulkheads 62

14. Tabular input and output from the Microsoft EXCEL ™ spreadsheet A:\ACQPrisk 73

15. Use of half-inch thick strips of high density polyethylene to reduce abrasion on wooden piling. The strips are nailed every six to eight inches using galvanized nails driven slightly below the surface of the bumper 74

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

Introduction. Ammoniacal copper quat (ACQ-B) is a wood preservative, developed and patented in Canada (Findlay and Richardson, 1983; 1990), containing between 62 and 71 percent copper oxide (CuO) and between 29 and 38 percent quat as didecyldimethylammonium chloride (DDAC). These active ingredients are dissolved in a water carrier to which is added ammonia (NH_3), equal in weight to the copper oxide in the preservative and carbonate equal to 0.65 times the amount of copper oxide.

The quaternary ammonium compound in ACQ-B promotes fixation in wood through ion exchange with anionic active sites and through other adsorption mechanisms at higher quat concentrations (Archer *et al.* 1992). Quat is fixed predominantly onto lignin, although interaction with holocellulose also occurs. Copper is fixed in wood through ion exchange reactions between cupriammonium ions and acidic functional groups such as the carboxylic acid groups of lignin and hemicellulose. Copper complexes with cellulose through hydrogen bonding with hydroxyl or amine nitrogen groups, or through replacement of an ammonia group from the cupriammonium ion with the hydroxyl ion of cellulose. Copper also forms insoluble copper carbonate salts resulting from the loss of ammonia during drying (Chen, 1994).

Copper does not generally constitute a human health risk. Neither copper, nor DDAC are expected to have carcinogenic, teratogenic or mutagenic effects. However, low concentrations of both copper in certain ionic forms and DDAC can be toxic to aquatic fauna and flora.

Several reviews assessing the environmental risks associated with treated wood have been compiled by Hartford (1976), Konasewich and Henning (1988), Stranks (1976), Ruddick and Ruddick (1992) and the U.S. Department of Agriculture (1980). The conclusion reached in these papers is that the use of treated wood causes no significant hazard to the environment. However, none of these reviews considered ACQ and all suffer from lack of quantitative analysis, leaving some doubt about the risks associated with using treated wood in aquatic environments. Brooks (1995, 1996, 1997a, 1997b, 1997c) has previously published a series of risk assessment guides for CCA-C, ACZA and creosote treated wood used in freshwater and marine environments. This risk assessment is for wood treated with ACQ-B to a retention of 0.40 pounds per cubic foot (6.2 kg-m^{-3}) in the treated zone. This retention is prescribed by AWPA (1996) for treatment of southern pine, coastal Douglas-fir, sitka spruce, western hemlock and hem-fir used in ground and/or fresh water contact. This risk assessment is not intended for
marine applications where salinity exceeds two parts per thousand for extended periods of time.

Background Levels and Sources of Copper and DDAC in Aquatic Environments.

Water column levels of copper. Copper is a naturally occurring element found in all aquatic systems. At low levels it is considered a micronutrient essential to the proper functioning of plants and animals. 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). Background levels of one to three µg Cu/L were observed by USGS between 1995 and 1997 in Columbia River water with a mean of 2.00 µg Cu/L. The lower Columbia River carries approximately 650 kilograms of copper past any point every day at a concentration of 2.0 µg/L.

Sediment levels of copper. Background levels of copper in lower Columbia River sediments ranged between 18 and 66 mg/kg (Siipola, 1991). Similarly, Tetra Tech (1994) observed sediment copper concentrations ranging from 19.3 to 49.9 with a median concentration of 27.6 mg/kg in the Columbia River. Munkittrick *et al.* (1991) reported reference area sediment copper concentrations of four to 23 mg/kg in northern Ontario. Cairns *et al.* (1984) reported copper levels of 59 mg/kg in control sediments from the Tualatin River, Oregon and 210 mg/kg in control sediments from Soap Creek Pond at Oregon State University.

Crocket and Kabir (1981) observed widespread increases in copper concentrations in the upper five centimeters of sediments from the Sudbury-Temagami area in Ontario to ca. 50 to 75 mgCu/kg dry sediment weight. They associated these increases to atmospheric deposition from the nearby Sudbury industrial complex. Hupp *et al.* (1993) observed sedimented copper concentrations of three to 24 mg/kg along the Chickahominy River in Virginia. Highest levels of sedimented copper were associated with the most urban-industrial part of the river basin. Their data indicated that 17,170,000 kilograms of sediment was deposited in wetlands along this river each year and that the annual deposition of copper to these sediments was 176 kilograms.Larsen (1983) estimated a mean annual atmospheric copper deposition rate of 1.81 to 2.77 mg/m^2 at four Danish lakes. Larsen (1983) cites Hovmand's (1979) finding that ten to 60 percent of the heavy metal loading to the Baltic Sea is from atmospheric deposition and measured copper concentrations in rainwater that varied between 1.79 and 2.49 µg/L.

These data suggest that background levels of sedimented copper can vary significantly at sites unaffected by identifiable sources of pollution. Background levels appear to vary from less than ten to perhaps 70 to 200 µg Cu/kg dry sediment weight. It also appears reasonable to conclude that atmospheric deposition is a significant source of copper over large areas.

Didecyldimethylammonium chloride (DDAC) is a member of the quaternary ammonium compounds (QAC). QACs were first synthesized in the late 1800's and their bactericidal properties were reported about two decades later. These compounds are well known for their germicidal, fungicidal, and algicidal properties when the alkyl fractions contain fewer than eight to 14 carbon atoms. Formulations containing between 0.01 and 1.0% QACs are used extensively as antiseptics, bactericides, fungicides, sanitizers and deodorants. QACs are also popular disinfectants for utensils, containers, and other instruments used in restaurants dairies, food plants, laundries, and operating rooms (Gosselin *et al*., 1984).

Quatenary ammonia compounds (QACs) with carbon chain lengths exceeding 14 are used extensively as softener's in laundry applications. Huber (1984) reports that 39,000 tons of quaternary ammonium compounds were marketed in the USA in 1978 for this purpose. Therefore, there is considerable opportunity for this class of compounds to enter aquatic ecosystems. Huber (1984) reported 19 µg/L DSDMAC and 5 to 20 µg/L DSBAS in waters of the Main River, near Frankfurt, West Germany. The point is that this general class of compounds is used extensively in modern society and they are finding their way into aquatic ecosystems in detectable amounts. Therefore, their ecological effects are of interest and they require management to insure that adverse effects are not associated with their use.

Didecyldimethylammonium chloride (DDAC) is not known to occur naturally. Hence, all DDAC found in aquatic environments results from spills and wastewater or stormwater discharges from commercial facilities using the chemical (antisapstain compounds and wood preservatives applied to lumber, laundry and residential waste water, restaurants, hospitals, etc.). As will be shown, DDAC is highly water-soluble with an octanol/water partition coefficient reported near zero. Therefore it has little propensity to accumulate in sediments, to bioconcentrate in aquatic organisms, or to biomagnify in food chains. No information describing detectable levels of DDAC in aquatic environments (sediments or water) was obtained.

Cycling and Fate of Copper and DDAC in Aquatic Environments

Copper. Copper occurs in soft natural waters primarily as the divalent cupric ion. It may be found as a free ion or complexed with humic acids, carbonate, or other inorganic and organic molecules in water of increasing hardness. 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. In contrast, Kerrison *et al*. (1988) found that copper added to enclosures placed in a shallow fertile lake rapidly became associated with suspended particulate material in the water column. The environment in which these experiments were conducted suggests that the particulate matter consisted of particulate organic matter (POM) and/or particulate inorganic matter (PIM) which would most likely be in the form of clay particles. Little suspended silt would be anticipated in a shallow freshwater lake.

Clarke (1974) noted that iron sulfide will render copper insoluble in anaerobic sediments. This report suggests 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, thus these environments may serve as an important mechanism for the removal of excess copper from aquatic environments.

Schmidt (1978) reported that average copper levels in open ocean water was ca. 1.15 μg/L with a rather broad range of 0.06 to 6.7 μg/L. Copper levels in coastal and nearshore water were higher with a mean of 2.0 μg/L. In nearshore water, more copper was found bound to particulate material (50.7%) than is found complexed in a dissolved form (49.3%). In open-sea samples, copper was partitioned between particulate (34.8%) and dissolved (65.2%) compartments. Schmidt (1978) reported that much of the copper in nearshore and offshore waters was associated with particulate material and that approximately 10% was adsorbed to clay. The average concentration of copper in suspended particulate material in the ocean was 109 μg/g with a range of 52 to 202. Schmidt (1978) noted that these levels were higher than those found in most nearshore sediments. He suggested that fine suspended particulates, rich in copper, are probably an important media for transporting continentally derived copper from the near shore to pelagic areas where the final repository for copper is likely in deep ocean sediments.

Cycling of copper from sediments as a function of the REDOX potential. Lu and Chen (1977) examined the release of copper from sediments as a function of sediment grain size and oxygen availability. Sediment grain size was not a factor in the amount of copper released to the overlying water column. Three oxidizing conditions were examined (oxidizing, 5 to 8 ppm dissolved oxygen; slightly oxidizing, $\leq$ 1 ppm dissolved oxygen; and reducing, $S(-II)_T$ = 15 to 30 ppm). Small amounts of bound copper were released from sediments into the overlying water in 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 (biologically healthy) environments. There are two ways to look at these results:

First, in coarse grained, highly oxygenated sediments, bound copper is more easily lost to the water column and dispersed over greater distances. Eventually, most of the copper deposited in areas with anaerobic sediments, where it is buried and incorporated into the lithosphere. These anaerobic sediments support reduced infaunal and epifaunal communities of organisms. As a result, we might expect reduced environmental impacts from copper incorporated into these sediments.

Alternatively, 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 cycle between sediments and interstitial and surficial waters 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 in this scenario. However, the biological effects associated with copper in this environmental would certainly be more significant than that associated with depauperate, anaerobic sediments.

The work of Lu and Chen (1977) suggests that caution is appropriate when dealing with copper material 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. 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 physicochemical conditions and copper 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. These factors may be important when estimating the relative risks associated with different sediment environments.

DDAC is a nonvolatile, photolytically stable salt which is highly soluble in water (Henderson, 1992). Its octanol/water partition coefficient is near zero (Huber, 1984; Henderson, 1982). Brooks *et al.* (1996) reviewed the available literature and reported the properties given in Table (1) for DDAC. There appears to be little degradation of DDAC associated with either photolysis or hydrolysis (Henderson, 1992)

Table 1. Summary of environmental fate properties of DDAC.

Photolysis	Solubility in Water	Hydrolysis	Sediment half-life (complexed with clay)	Half-life in aerobic sediments	Bioconcentration in Biota	Soil Sorption
No	High	No	45.6 days	11.2 days	Low	Strong

.

Based on these properties, the environmental fate of QACs, including DDAC, is likely adsorption to suspended inorganic material, most likely clay and subsequent sedimentation (Fernandez *et al*., 1991; Huber 1984). Daly (1989) examined the adsorption/desorption of DDAC at 25 ^{o}C in the dark in sand, sandy loam, silty clay loam, and silt loam at 0.25, 0.90, 2.05 and 2.1% organic carbon respectively. The study was conducted at a 1:200 soil to water ratio using four nominal concentrations of 0.70, 3.50, 5.25 and 7.00 ppm DDAC. The study concluded that DDAC is essentially immobile in soil. Adsorption/desorption mechanics and the effects of pH, interstitial water hardness, salinity, etc. were not addressed. While DDAC appears stable under the test conditions, it is not possible to determine from this paper, the potential for desorption and recycling back into the water column. The high water solubility and low K_{ow} associated with DDAC suggest that this may occur under some physico-chemical conditions. However, Huber (1984) describes the ionic binding of cationic QACs (including DDAC) as irreversible and it appears reasonable to conclude that DDAC is not easily recycled back into the water column in a dissolved form following adsorption to clay and sedimentation.

The literature describing the degradation of QAC's and DDAC in particular is equivocal. It should be remembered that QAC's with relatively short carbon chains (<14) are commonly used as bactericides. Above threshold concentrations toxic to bacteria, these compounds may adversely effect aquatic microflora that are important factors in their degradation.

Biodegradation is expected to be the main route of dissipation of DDAC in the environment (Agriculture Canada *et al*., 1988). Gawel and Huddleston (1972) reported complete degradation of DDAC within 48 hours at concentrations of 10 ppm by mixed bacterial cultures obtained from soil and sewage. Gerike and Gode (1990) found significant degradation at 5 mg/kg DDAC but poor ultimate degradation at 15 mg/kg DDAC. In contrast, Cranor (1991) observed little degradation of ^{14}C dosed DDAC at 10 mg/kg added to aerobic soils and monitored for one year. At the end of 365 days, 72.9% of the dosed radioactivity remained as parent compound and the estimated

anaerobic half-life of 1,048 days. Similar studies reported by Cranor (1991) estimated an aerobic aquatic half-life of 8,365 days and an anaerobic aquatic (microbially active water and sediment dosed with 10 mg/kg DDAC) half-life of 6,218 days. The refractory nature of QACs in anaerobic conditions is further supported by Huber (1984).

New data, not reported in Brooks *et al.* (1996), was developed by the manufacturer using natural sediment obtained from three sites on the Saint Clair River in Canada (Wildlife International, 1996). This new study suggested that the half-life for DDAC in aerobic sediments is 11.2 days. When DDAC was complexed with clay, the half-life increased to 45.6 days. Taken altogether, this review suggests that the sedimented half-life of DDAC varies with the availability of oxygen as well as the resident microbial community. No information was obtained as to whether or not DDAC provides a suitable sole carbon source for some species of bacteria, or if it is catabolized only in the presence of other organic compounds. Some refractory compounds, like high molecular weight PAH, cannot be metabolized in the absence of more labile and complex carbon substrates. If this is true, then the half-life of DDAC would vary with the amount of sedimented TOC. However, the Wildlife International (1996) study used unamended, natural sediments, and the observed half-life of between 11.2 and 45.6 days is likely more appropriate.

DDAC's strong affinity for soils suggests that losses from ACQ-B preserved wood will adsorb to clay particles and be sedimented. Based on this discussion, it appears that DDAC is stable in sediments at concentrations exceeding (10 ppm), but is degraded with a half-life of 1.1 to 45.6 days at lower concentrations. Additionally, it appears that DDAC degradation is dependent on oxygen tension in sediments and longer half-lives can be expected in anaerobic conditions or where microflora are compromised.

Bioaccumulation of Copper and DDAC In Aquatic Environments.

Copper is an essential micronutrient for plants and animals. Its uptake and metabolism is a normal biological process. DDAC is an anthropogenic compound. This chapter discusses the potential for the bioaccumulation of copper and DDAC by aquatic plants and animals.

Copper bioconcentration. 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. Marine mollusks concentrate copper by a factor of 5,000 in muscle and soft parts. Anderson (1977) reported metal bioconcentration factors in six species of freshwater clams from the Fox River in Illinois and Wisconsin. He found that soft tissues contained levels of copper equivalent to those found in sediments, which were significantly higher than water column levels. Anderson (1977) reported water column concentrations of copper at 0.001 – 0.006 μg/L or one to six parts per trillion. This appears to be low by a factor of 1000 and these data appear suspect. Assuming that these reported water column concentrations are in error by a factor of 1,000, a comparison of the mean copper soft tissue burden (12.24 μg/g dry tissue weight) with the mean water column copper concentration (0.0035 mg/L) implies a BCF of 3,497. This value is consistent with the NAS (1971) copper bioconcentration factor for bivalve mollusks. Hendriks (1995) observed that dry weight corrected concentrations of copper in freshwater plants and invertebrates from the Rhine Delta were 0.2 to 0.3 times the concentrations observed in suspended sediments – suggesting that copper adsorbed to suspended sediments is not readily bioconcentrated.

Marquenie and Simmers (1987) examined metal and polycyclic aromatic hydrocarbon levels in sediments and earthworms (*Eisenia foetida*) at an artificial wetland site created on a confined dredged material disposal facility that became a prolific wildlife habitat. At the six sites reported, they found an average copper concentration of 192.5 $\pm$ 107.6 μg Cu/g (dry weight) in soils. At the end of ca. 49 days, *Eisenia foetida* contained an average of 36.3 $\pm$ 14.9 μg Cu/g (ash-free tissue weight) suggesting that much of the sedimented copper was not biologically available (BCF = 0.19). Control earthworms, collected outside the dredge disposal site, where soil copper

levels averaged 16.5 µg/g, contained an average of 10.1 µg Cu/g giving a BCF of 0.61 (three times higher). It is possible that 49 days was an insufficient period of time for annelid tissue to come into equilibrium with the high environmental levels of copper. Alternately, it is also possible that *Eisenia foetida* is able to regulate copper uptake.

Rai *et al.* (1995) examined metal uptake from pond water amended with 1.338 µM (84 ppm) copper in eight species of submerged macrophytes. No acute effects were observed – although several of the plant species did not increase biomass. At the end of 15 days, the plants had removed significant quantities of metal from the pond water and the bioconcentration factors given in Table (2) calculated.

Table 2. Metal concentration factors (dimensionless) for submerged aquatic plants. From Rai *et al.* (1995).

	Metal					
Plant	Cu	Cr	Fe	Mn	Cd	Pb
Hydrodictyon reticulatum	2481	11394	37666	8712	6250	5000
Spirodela polyrrhiza	36500	7920	3878	3107	5750	2521
Chara carallina	1103	2081	3029	2030	2125	2133
Ceratophyllum demersum	53333	15332	37809	21600	3333	8064
Vallisneria spiralis	2009	1993	1344	333	2375	1777
Bacopa moonieri	18750	2016	2041	2487	29000	366
Alternanthera sessilis	1051	722	1156	6395	23000	555
Hygrorrhiza aristata	211	652	1138	1955	4600	7174

Copper uptake from the water column varied considerably from the concentration factors ranging from 211 in *H. aristata* to 53,333 in *C. demersum.* This study demonstrates high, but variable copper bioconcentration factors in most plant species and demonstrates the potential for plants to remove copper from stormwater in retention ponds or biofiltration swales. However, it is difficult to extrapolate from this study to natural environments where elevated copper levels would likely be less than 15 to 20 µg/L rather than 84,000 µg/L.

Copper biomagnification. Little information was reviewed on the biomagnification of copper by aquatic organisms. Van Eeden and Schoonbee (1993) examined copper levels in sediments, fennel-leaved pondweed ant various organs of the red-knobbed coot associated with a metal contaminated wetland in South Africa. They found that the pondweed contained less than half the copper levels found in the sediments. Copper levels in the various organs of the coot were similar to those in the pondweed – except that very little copper was transferred to eggs (shell or contents) of this bird. For the purposes of this paper, it will be assumed that copper accumulation in aquatic organisms is primarily a function of metal concentration in the ambient water. While many organisms may bioconcentrate copper, the available information suggests that copper is not biomagnified through food webs. The two processes (bioconcentration and biomagnification) are not necessarily directly related. Many materials are bioconcentrated, particularly by bivalves. However, many of those bioconcentrated substances are not biomagnified because they are either rapidly excreted or metabolized.

DDAC bioconcentration. Henderson (1992) and Huber (1984) conclude that DDAC (or other QACs) are not significantly bioconcentrated. Huber (1984) cites several studies indicating bioconcentration factors (BCFs) ranging from 5 to 32 for related QACs. Henderson (1992) reviewed this issue and reported a whole body bioconcentration factor of 81 for DDAC in the bluegill sunfish (*Lepomis macrochirus*).

Henderson (1992) assessed the pharmacokinetics of DDAC and concluded that because DDAC is highly ionic it is not expected to adsorb well across the gastrointestinal epithelium. The results of excretion studies in rats support this conclusion. Following oral dosing with ^{14}C-DDAC,

89 to 99 percent of the radioactivity was found in the feces and less than 2.5% in the urine. This finding was considered consistent with the predicted low absorption of DDAC. Absorbed DDAC was metabolized. The metabolic process was found to involve oxidation of the decyl side chain to a variety of oxidative products. Evidence seemed to favor initial hydroxylation of the carbon next to the terminal carbon, followed by formation of a hydroxyketone. The four major metabolites found in their study were more polar and presumed to be less toxic than the parent compound, although the specific chemical structures were not determined.

Depuration experiments reported by Henderson (1992) indicated that 67% of the DDAC accumulated in whole fish tissues was depurated within 14 days. The available literature suggests that QACs, including DDAC do not significantly bioconcentrate in aquatic organisms.

DDAC biomagnification. No direct evidence examining this question was reviewed. However, based on the low observed bioconcentration factors, rapid depuration and observed metabolism, biomagnification through the food chain is very unlikely and will not be considered an issue in this risk assessment.

Summary for the potential of Copper and DDAC to bioaccumulate. Copper is bioconcentrated at moderately high levels from the water column. It is not significantly bioconcentrated from sediments. No evidence of copper biomagnification was obtained. The available evidence suggests that DDAC does not bioconcentrate in aquatic organisms and the pharmokinetics of DDAC suggests that it does not significantly biomagnify through food-webs.

Toxicity of Copper and DDAC to Aquatic Fauna and Flora. In order to assess the potential impacts of ACQ-B treated wood used in aquatic environments, it is necessary to determine the minimum levels of DDAC and copper causing acute or chronic stress in fauna and flora.

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

Copper in freshwater. EPA's (1984) Ambient Water Quality Criteria reports that copper toxicity in aquatic environments is related to the concentration of cupric (Cu^{2+}) ions and perhaps copper hydroxides ($CuOH^{n}$). 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). Harrison *et al.* (1987) reported that copper discharged from the San Onofre power plant cooling system was found 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 they expected little or no impact from the discharges. Likewise, Nuria *et al.* (1995) and Kerrison *et al.* (1988) have observed that copper in freshwater lakes is generally associated with particulate organic and inorganic material rather than with dissolved organic matter (DOM). These authors conclude that natural water significantly reduces copper toxicity to aquatic organisms when compared with laboratory systems manipulated using synthetic chelators like EDTA.

Sundra (1987) has proposed a basic mechanism explaining 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 copper across the membrane would require that it interact with specific metal transport proteins in the membrane. Because the free ion activity is a measure of the potential reactivity of a metal, it reflects the ability of that metal to interact with these transport proteins. The many chemical forms of copper in aquatic environments are maintained in a dynamic

state of equilibrium that depends on salinity, temperature, pH, alkalinity, dissolved oxygen, sediment characteristics and the presence of other inorganic and organic molecules.

Clements *et al.* (1988) spiked freshwater mesocosms with 12 to 20 µg Cu/L and 15 to 27 µg Zn/L. They found significantly reduced numbers of taxa, numbers of individuals and abundance of most dominant taxa within four days. After ten days, control streams were dominated by Ephemeroptera and tanytarsid chironomids, whereas treated streams were dominated by Hydropsychidae and Orthocladiini. Responses of benthic communities to metals observed at the Clinch River (Russel County, Virginia), a system impacted by copper and zinc were similar to those in experimental streams. Copper levels on the Clinch River varied from not detectable at upstream controls to 105 µg/L at the point of discharge. Ephemeroptera and Tanytarsini, which comprised 48 to 46% of the macroinvertebrate community at upstream reference stations, were significantly reduced at all effluent sites. In this natural system, impacted stations were dominated by Hydropsychidae and Orthocladiini. Interestingly, significant decreases in the number of all taxa and the abundance of individual species was observed at station (6), where 9 ± 7 (one standard deviation) µg/L Cu was observed. They found that Tricoptera and Orthoclad chironomids were tolerant of high levels of copper. The hardness at these Clinch River (Virginia) stations averaged 169 ppm ($CaCO_3$) and the alkalinity averaged 148 µg/L. At this hardness, the EPA chronic criteria is 17.8 µg/L. However, it should be noted that this station was directly downstream from the discharge stations that had much higher levels (47 to 105 µg/L). Copper levels this high would likely have significant effects on the drift community. This is seen in a follow-up study (Clements, *et al. 1992*) in which data from 1986 through 1989 were examined upstream and downstream from the power plant following a decrease in the copper content of the plant's effluent from 480 µg/L in 1987 to 260 µg/L in 1989. Copper concentrations were reduced at downstream Station (8) from 127 µg/L in 1987 to 52.2 µg/L in 1989. The number of taxa increased from ca. ten in 1987 to 20 in 1989. Only small decreases in both the number of taxa and the number of individuals per sample were observed in 1989 suggesting only minor effects at the observed copper concentration of 52.2 µg/L.

Gower *et al.* (1994) examined the relationship between invertebrate communities and a variety of metals in southwest England. Their work suggested that copper followed by aluminum, zinc, and cadmium, was the metal most responsible for influencing the observed changes in the invertebrate community. Clements *et al.* (1982, 1992) found that Ephemeroptera and *Tanytarsini* were very intolerant of copper in the Clinch River whereas, Hydropsychidae and Orthocladid chironomids dominated impacted stations. The results of Gower *et al.* (1994) are summarized in Table (3). In this table, observed copper concentrations and hardness values are combined by dividing the observed copper concentration by the U.S. EPA chronic copper criteria at the documented level of hardness. These values should be interpreted as the numeric factors by which observed copper exceeded the U.S. EPA chronic freshwater standard. Community information is displayed by sample for each taxonomic group. The number of individuals in each taxonomic group is followed by the mean number of species, per sample, in parentheses.

Table 3. Mean number of total macroinvertebrates per sample (M), mean percentage contribution of selected major taxa to the total macroinvertebrate fauna (P), and number of species (S) observed by Gower *et al.* (1994) as a function of water column levels of copper expressed as proportional increases in the U.S. EPA freshwater copper criteria at the observed level of hardness.

Ratio of dissolved copper to the U.S. EPA chronic freshwater criteria

Taxonomic group	2.0 x		5.3 x		31.6 x		244.7 x	
	(M)	(S)	(M)	(S)	(M)	(S)	(M)	(S)
Macroinvertebrates	4598	39	989	21.3	2219	12.2	2378	9.2

	(P)	(S)	(P)	(S)	(P)	(S)	(P)	(S)
Tricladida (flatworm)	7.7	1.3	3.4	1.0	15.0	1.1	30.2	0.8
Oligochaeta	16.2	4.8	6.8	2.4	20.9	1.3	0.7	0.3
Ephemeroptera	17.4	3.1	38.1	2.0	16.7	0.6	0.0	0.0
Plecoptera	19.3	4.9	8.5	2.3	7.2	1.3	1.1	0.3
Coleoptera	4.0	2.4	0.6	0.8	0.7	0.4	0.6	0.6
Trichoptera (cased)	4.8	3.0	12.4	1.8	0.1	0.2	0.1	0.1
Trichoptera (caseless)	4.8	3.4	14.7	3.0	5.4	1.8	4.8	1.3
Total EPT[1]	46.3	14.4	73.7	9.1	29.4	3.9	6.0	1.7
Chironomidae	16.9	8.0	11.3	4.4	31.1	3.8	60.3	3.8
Orthocladiinae	9.1	4.7	4.8	1.8	18.4	2.1	54.5	2.4

[1] EPT refers to the aggregate numbers of insects in the orders Ephemeroptera, Plecoptera and Trichoptera.

These data are presented in some detail because they clearly demonstrate the insensitivity of at least one flatworm species (Tricladida) some caddis flies (Trichoptera) and chironomids, particularly Orthocladiinae at very high water column concentrations of copper (245 x EPA standard). Oligochaetes, caseless caddis flies and stone flies (Plecoptera) are relatively insensitive at copper concentrations up to 32 times the EPA standard but the population was essentially extirpated at the highest levels of 245 times the EPA standard. It is certainly possible that caseless caddis flies and stone flies represent the drift community in this study and the period of exposure to elevated copper concentrations is unknown. This observation is supported by the reduced numbers of resident (cased) caddis flies observed in areas where the copper concentrations exceeded the EPA chronic copper standard by a factor of 5.3.

Interestingly, the Order Ephemeroptera, frequently described as very susceptible to copper intoxication, represented nearly 40% of the macroinvertebrate community at 5.3 x the EPA standard and at least one species was able to tolerate 31.6 x the EPA standard. In addition to describing general trends in copper susceptibility, these data suggest that some species in the sensitive orders Ephemeroptera, Plecoptera and Trichoptera are able to tolerate very high levels of copper - suggesting that increasing information is provided by identification of infauna to the level of genus or species. On the other hand, it should be noted that total species richness (number of species) declines monotonically and is perhaps the best indicator of increasing copper toxicity in this study. While the numbers of Ephemeroptera, Plecoptera and Trichoptera do not following this monotonically decreasing trend, if we consider these Orders in the aggregate, we find that species richness is inversely correlated with copper concentrations.

Kiffney and Clements (1994) examined the effects of heavy metals on a macroinvertebrate assemblage from a Rocky Mountain stream in experimental microcosms and found significant reductions in a number of taxa at their “1x” treatment of 12 µg Cu/L. The author’s stated that this value was approximately equal to the U.S. EPA freshwater chronic copper standard at the measured hardness of 38.3 mg/kg ($CaCO_3$). However, at that hardness, the EPA acute criteria is approximately half the tested concentration (6.9 µg/L versus 12 µg/L) and the chronic EPA criteria is only 38% of the test concentration. The results of this study followed that of others reported herein. Significant reductions were observed in the Order Ephemeroptera, particularly in the family Heptageniidae. A large variation was observed in chironomid response to copper with significant reductions in the Tanytarsini and Tanypodinae and a small reduction in the Orthocladiinae and Chironomini.

Rutherford and Mellow (1994) examined the effects of low pH and high dissolved metal (particularly copper) content on the fish and macroinvertebrates in beaver ponds located on an abandoned ore roast yard near Sudbury, Ontario, Canada. Table (4) summarizes the physico-chemical properties of the water at three of the sample stations. Hardness values were not provided in this study.

Table 4. Water chemistry at sample stations 1 (upstream), 3 (in roast pits) and 4 (immediately downstream from roast pits) in the study of Rutherford and Mellow (1994).

Station	pH	Temp(°C)	Dissolved Oxygen	Copper (μg/L)
1 (upstream)	6.7	22.2	8.0	18
3 (roast yard)	3.7	22.2	8.1	600
4 (downstream)	6.2	23.3	7.6	45

Dissolved copper at all of the tested stations exceeded background levels by factors of six at Station One to 200 at Station Three. Other metals were elevated, but not to the very high levels associated with copper and it appears reasonable to suggest that most of the effect seen in the macrobenthic community is associated with this metal.

Table (5) provides a summary of the numbers of individuals within the most copper sensitive and copper tolerant species observed in this study and suggests that the genus *Chironomus* is very tolerant to even extraordinary levels (600 μg/L) of copper. The Tanypodinae are tolerant of moderate (45 μg/L) copper levels as are several species of dragonflies (Order Odonata). In contrast, all of the mollusks in this study were intolerant of copper at 45 μg/L but survived concentrations six times that of the background of ca. 3 μg/L. Macroinvertebrates were sampled with a D-frame net (1 mm mesh) in near-shore vegetation, the detritus and muck at the bottom of the pools and in open water. The net was maneuvered for ca. 15 seconds in each of these habitats. Based on Brook's (unpublished data) experience, the number of taxa at stations one and four can be representative of beaver dam habitats. However, the low abundance of all taxa suggests that these areas were not very productive. The intolerance of mollusks, arthropods and some oligochaetes (Naididae) to copper is noteworthy. These data, like that of many other studies reviewed herein, suggest that copper tolerance varies widely among genera – even within the same family. These data also suggest that diverse (albeit suppressed) communities of macroinvertebrates can tolerate dissolved copper concentrations of at least 45 μg/L.

Table 5. Selected macro-invertebrate taxa with significant sensitivity or tolerance to high copper levels at sample stations 1 (upstream), 3 (in roast pits) and 4 (immediately downstream from roast pits) in the study of Rutherford and Mellow (1994). Taxa exhibiting moderate to strong copper tolerance are bolded. Dissolved copper concentrations are provided in parentheses after each station number (μg/L)

		Sample Station		
Taxon		**1 (18 μg/L)**	**3 (600 μg/L)**	**4 (45 μg/L)**
Total Number Species		40	1	25
Total Number Macroinvertebrates		228	105	145
Chironomidae: Tanypodinae		**10**	**0**	**14**
	Chironomus	**13**	**105**	**23**
	Cladopelma	**12**	**0**	**2**
	Microtendipes	3	0	0
	Polypedilum	**9**	**0**	**8**
Diptera:	***Chaoborus***	**28**	**0**	**2**
Himiptera:	***Corisella***	**7**	**0**	**3**
Odonata:	**Corduliidae**	**13**	**0**	**4**
	Leucorrhinia	**1**	**0**	**23**
	Coenagrionidae	**0**	**0**	**44**

Trichoptera: *Oecetis*	**0**	**0**	**2**
Banksiola	**0**	**0**	**3**
Amphipoda: *Hyallela azteca*	3	0	0
Naididae:	37	0	0
Mollusca: *Physa*	8	0	0
Helisoma	29	0	0
Sphaerium	15	0	1
Hirudinea:	5	0	0

In summary, these studies demonstrate trends in the relative sensitivity of freshwater macroinvertebrates to copper intoxication. However, Gower *et al.* (1994) also points out that at least some species within the sensitive EPT can tolerate very high levels of copper intoxication. Lastly, these data suggest that species richness for all fauna, or for the aggregated Orders EPT, is better correlated with the degree of copper intoxication than is an analysis at some lower levels of taxonomic structure. Ammann *et al.* (1997) provided an excellent review of the idea of *Taxonomic Sufficiency* for measures of impact in aquatic systems. They conclude that in at least one series of studies, identification and evaluation of infauna to the level of phylum was sufficient to document effects.

Copper in marine water. Roesijadi (1980) reported that copper is normally present at relatively high levels in the tissues of marine animals (> 1,000 ppb). Roesijadi (1980), Harrison, *et al.* (1987) and Harrison and Lam (1985) review both the environmental detoxification of copper and the physiological detoxification of copper by *Mytilus edulis, Protothaca staminea, Patella vulgata, Ostrea edulis* and *Littorina littorea*. Copper detoxification and metabolic regulation was associated with copper binding by low and high molecular weight metallothionein-like proteins in the digestive gland and the 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 the bioconcentration of copper. At high concentrations of the cupric ion, copper bioconcentration increases in an unregulated manner and larval growth was inhibited.

Harrison *et al.* (1987) conducted copper bioassays on a number of aquatic invertebrate and vertebrate species. They found that *Crassostrea gigas* embryos were most sensitive (48-hour LC_{50} =10 ppb) and larval herring the least sensitive. The range of 48-hour LC_{50} values for copper was 10-2,000 ppb. Dinnel, *et al.* (1983) published the results of copper toxicity bioassays on various life stages of a number of marine organisms. They report a very low LC_{50} (1.9 ppb) for the sperm of the red sea urchin (*Strongylocentrotus franciscana*). This value seems suspect because it falls within the range normally expected in unpolluted seawater. Reported values from the Dinnel, *et al.*(1983) study are presented in Table (6).

Gametes and 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 that 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 might result in only a small fraction being present in the toxic form. The majority of the copper would likely be detoxified by adsorption to sediments 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.

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

Table 6. Total Copper Toxicity Measured in Controlled Bioassays. Values are EC_{50} or LC_{50} in ppb.

	Taxa	**EC_{50} or LC_{50}**
Sperm		
	Purple Sea Urchins	34.0
	Oysters	12.1
	Salmon	44.2
Embryo		
	Purple Sea Urchins	6.3
	Oysters	6.1
	Mussels	21.0 - 35.0
Larvae		
	Crab Zoea	95.7
	Squid	309.0
	Cabezon	95.3
Adults		
	Sand Shrimp	898.5
	Shiner Perch	417.7
	Coho Salmon Smolt	601.0

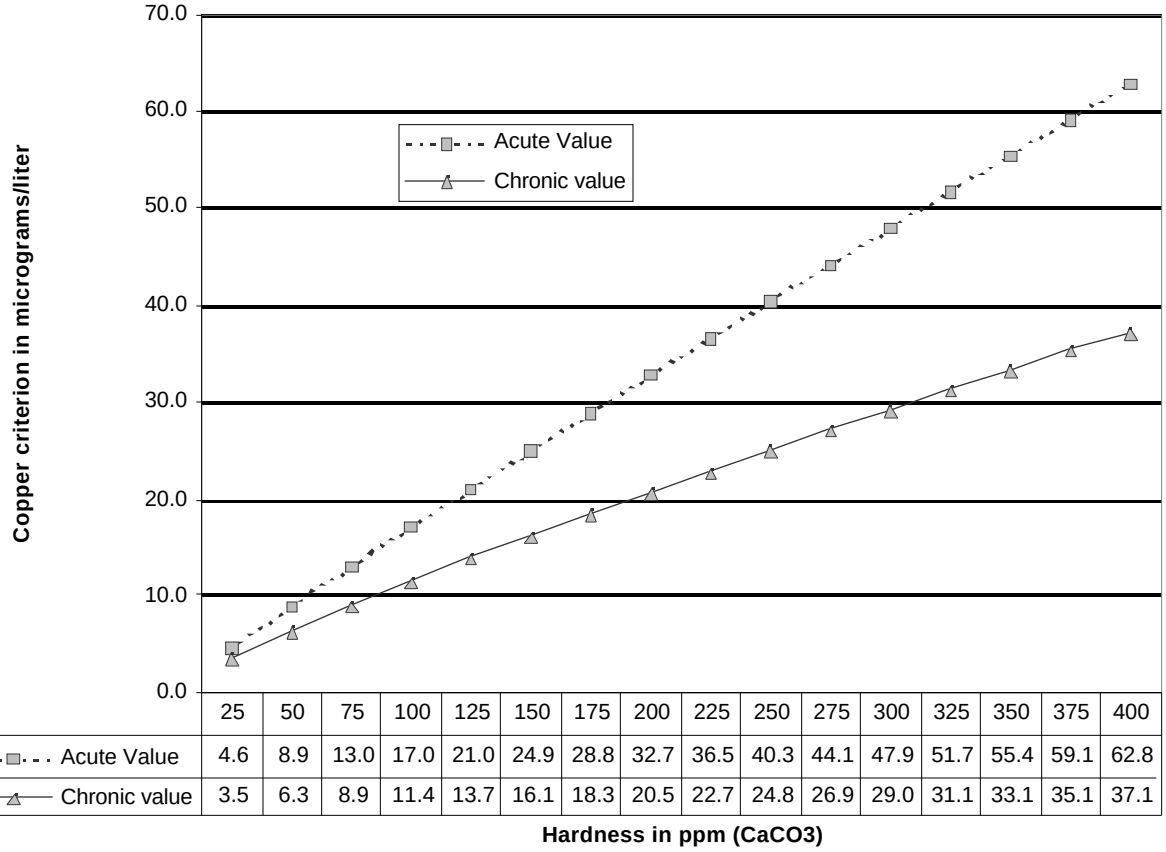
Regulatory levels defining water quality criteria. This risk assessment will rely on the U.S. Environmental Protection Agency (U.S. EPA, 1995) acute and chronic freshwater copper criteria as a standard against which to measure the suitability of specific ACQ-B treated wood products in specific receiving waters. The extensive review of available toxicity data in preparation of this risk assessment did not find evidence suggesting that the EPA criteria is not fully protective of aquatic organisms. The EPA acute criteria and chronic criteria are dependent on water hardness and are given in Equations (1) and (2) and summarized in Figure (1).

Equation (1) U.S.EPA acute copper criterion $\leq 0.960 * \exp^{0.9422[\ln(\text{hardness})] - 1.464}$

Note: The acute copper criterion is a one hour average that is not to be exceeded more than once every three years on the average.

Equation (2) U.S. EPA chronic copper criterion $\leq 0.960 * \exp^{0.8545[\ln(hardness)] - 1.465}$

Note: The chronic criterion is a four-day average concentration not to be exceeded more than once every three years on the average.



	25	50	75	100	125	150	175	200	225	250	275	300	325	350	375	400
Acute Value	4.6	8.9	13.0	17.0	21.0	24.9	28.8	32.7	36.5	40.3	44.1	47.9	51.7	55.4	59.1	62.8
Chronic value	3.5	6.3	8.9	11.4	13.7	16.1	18.3	20.5	22.7	24.8	26.9	29.0	31.1	33.1	35.1	37.1

Figure 1. U.S. EPA chronic and acute copper criteria for freshwater. The copper standard is presented in μg/L and hardness values in mg ($CaCO_3$)/L.

Toxicity to aquatic organisms associated with sedimented copper. Cain *et. al.* (1992) compared copper concentrations in the insect orders Trichoptera and Plecoptera with concentrations in mine waste contaminated sediments on the Clark Fork River in Montana. They observed sediment concentrations of 779 μg/kg in river reach 0 – 60; 408 μg/g in river reach 107 – 164 and 129 μg/g in reach 192 – 381. These levels were significantly elevated above the 18 μg/g observed at unaffected reference sites. They found significant variability in uptake between various taxonomic and functional groups. Detritivores held higher levels of copper than either omnivores or predators. This was especially true in the most contaminated reach (0 – 60 km). No appropriate analysis of the community structure was presented.

Diks and Allen (1983) examined the bioavailability of different forms of copper associated with sediments. In their study, the distribution of copper was determined by assessing different levels of sedimented copper (0.0, 2.5, 5.0, 7.5 and 10.0 mg Cu/kg) in five geochemical fractions of chemically extracted sediments, and in tubificid worms. They used five chemical extraction

protocols with a range of aggressiveness in liberating copper from the five geochemical compartments being considered. The least aggressive was 1.0 M $MgCl_2$, pH 7, with extraction at room temperature for one hour. This procedure was considered appropriate for extracting only the absorbed/exchanged copper. The most aggressive procedure was 1.0 M NH_2O_2.HCl in 25% HOAc, with extraction at 96°C for six hours. This procedure was considered sufficient to extract all copper including moderately reducible forms incorporated into the crystalline structure of iron oxides.

Diks and Allen (1983) found that free ionic metals, as well as most metals ion exchanged onto fine-grained solids were biologically available. Less available forms included metals contained in solid organic materials or precipitated and coprecipitated metal oxide coatings. Metals incorporated into crystalline structures were not biologically available. Regression analysis was used to evaluate the effects of the extraction technique and metal levels in each of the geochemical compartments on copper uptake by the tubificid worms. They found that only the copper extracted from the manganese oxide/easily reducible phase was significantly correlated ($\alpha = 0.05$) with copper uptake. They suggested that the redox potential and pH in the gut of the worm was such that manganese oxide coatings were dissolved during digestion making the copper available for uptake. This study suggests that the 0.1 M $NH_2OH.HCl$ + 0.01 M HNO_3, pH = 2 extraction, conducted at room temperature for 30 minutes (See Chao, 1972) is most appropriate for determining biologically available copper in sediments. This is important because in the four sediments tested at 10 mg Cu/L (Des Plaines, Calumet, Flatfoot and Wabash), the proportion of copper biologically available in the amended sediments averaged 72%. The remaining 28% was found in geochemical phases that appeared to not be biologically available. Even more striking was the distribution of copper in the natural (unamended) sediments. In these natural sediments, only 35% of the total copper burden appeared to be biologically available while 65% was incorporated in biologically unavailable geochemical phases.

The purpose of this discussion is to suggest that extraction techniques and the biological availability of copper in sediments are important parameters to the determination of sediment standards against which to assess biological risks. For purposes of this assessment, a mildly aggressive extraction technique such as that (Chao, 1972) is recommended. More aggressive extraction techniques used for assessing background copper may result in assuming a higher than appropriate existing level of biologically available copper, leading to an overly conservative assessment, whereas less aggressive extraction techniques may result in assessments that are insufficiently protective of biological resources.

Flemming and Trevors (1988) dosed a calcareous, southern Ontario stream sediment with up to 10,000 µg Cu(II)sulfate/g dry sediment and examined its uptake of copper and microbial response. They found that sediment uptake of copper was nearly 100% to 2,800 µg Cu/g. At higher levels of copper, the sediment uptake capacity was diminished and at 10,000 µg Cu/g sediment, only ca. 60% of the copper was removed from the water column. Aerobic heterotrophic bacteria were unaffected at the end of two months in sediments amended with as much as 1,000 µg Cu/g sediment. Bacterial colony counts actually increased at higher copper levels. The authors attributed this to the development of a population of copper tolerant microorganisms. The bacterial community from the high copper amended sediments displayed a 500-fold increase in copper tolerance over bacteria from control sediments when plated on nutrient agar amended with excess copper. The authors suggested that 87.5% of the copper added in these studies was transformed from the toxic Cu^+ form to carbonate complexes (87.5%); 12% was complexed with dissolved organic matter and that only 0.5% was available as potentially toxic copper hydroxide complexes or as the toxic Cu^{+2} free ion. The point in this discussion is that calcareous sediments can significantly reduce the toxicity of very high concentrations of cupric ions. At least that statement appears true for the microbial community.

Munkittrick *et al.* (1989) examined the response of aquatic invertebrates to a gradient of copper and zinc contamination associated with mining activities along the Manitouwadge chain of lakes in northern Ontario. Their data are summarized in Table (7). The 22.7 $\pm$ 6.4 mg Cu/kg

sediment at Station (3) on unaffected Loken Lake (LOK) is not significantly different from the level of 25 ± 8 mg Cu/kg sediment at Station (3) on impacted Manitouwadge Lake (MAN). However, the water column copper concentration at unaffected LOK was only 1.7 µg/L compared with 9.8 µg/L at significantly impacted MAN. Station (1) at Lake Manitouwadge (MAN) has the highest level of sediment copper (160 mg/kg) of the three stations in that lake. This station also has the highest abundance (12,838 invertebrates/m^2), the highest diversity (21 species/sample) and the highest number of typically sensitive cladocerans when compared with the other two stations in this lake, each of which has lower levels of sedimented copper. Munkittrick *et al.* (1989) also presented detailed enumeration of the Chironomid species in each lake. Interestingly, for nearly all genera of Chironomids, the sample station with the highest levels of sedimented copper in lake MAN also have the highest number of Chironomid species. It is interesting to note that the copper intolerant chironomid genera *Polypedilium, Cladotanytarsus* and *Tanytarsus*, are abundant in the control lake LOK and present only at Station (3) (the station with the highest sediment concentration of copper) in affected Manitouwadge Lake.

In contrast, under conditions of the reported low water column copper concentrations in Loken Lake, there is an apparent decrease in the number of sensitive amphipods, gastropods and oligochaetes at the station with the highest sedimented copper concentration (Station 3 @ 22.7 mg Cu/kg sediment). This pattern was also observed in the more detailed chironomid taxonomy where Station (3) typically held as many or more chironomids of all genera than did the other stations with lower levels of sedimented copper. I say generally true because *Polypedilium simulans* was observed in much lower abundance at Station (3) than at the other reference stations.

These observations suggest that the primary invertebrate response in these lakes was associated with elevated water column concentrations of copper and not to the sedimented levels which spanned a large range of values. This is likely because the sedimented copper is not biologically available. The point is that the elevated water column concentrations of copper in affected Lake Manitouwadge appear to be masking any effect associated with sedimented copper up to the observed level of 160 µg Cu/kg dry sediment weight.

Miller *et al.* (1992) further examined the Manitouwadge chain of lakes. They reported average water column concentrations of 15 µg/L in Manitouwadge Lake at a hardness of 110 ppm $CaCO_3$. This exceeds the U.S. EPA copper criterion for freshwater (12.31). Sedimented copper in Manitouwadge Lake averaged 93 mg Cu/kg sediment. No significant difference was observed in the standard length, weight, age or condition factor of white suckers between Manitouwadge Lake and Loken Lake. Copper levels in invertebrates (tissue levels) were significantly correlated (Spearman's correlation at $p \leq 0.01$) with water column concentrations of copper, but not with sediment copper concentrations over a wide range of values.

Table 7. Summary of copper concentrations in the water column and sediments of reference Loken Lake (LOK) and impacted Manitouwadge Lake (MAN). Significant macro-invertebrate data are included to indicated faunal response. All values are in mg/kg. Data are taken from Munkittrick *et al.* (1991).

End Point	LOK (1)	LOK (2)	LOK (3)	MAN (1)	MAN (2)	MAN (3)
Sediment Copper	7.5	4.0	22.7	160.0	123.0	25.0
Water Copper	0.0032	0.0013	0.0017	0.0098	0.0095	0.0098
Cladocera	1484	1746	5326	437	175	87
Copepoda	172023	1383	4366	1834	1048	262
Chironomids (Total)	11701	20585	13598	9868	5502	4017
Procladius	1659	1878	4803	1834	2358	873
Cryptotendipes	262	74	0	1048	0	87

Pagastiella	175	144	87	4629	3057	1310
Polypedilium	5852	4544	1572	0	0	0
Cladotanytarsus	873	6113	1921	1397	0	175
Tanytarsus	1659	5458	2620	262	0	175
Total Abundance	47069	36083	25737	12838	8035	5240
Diversity	36	35	28	21	8	17

Kraft and Sypniewski (1981) examined the effects of high sedimented copper on the macroinvertebrate community of the Keweenaw Waterway. They found high concentrations of copper (<589> mg Cu/kg dry sediment) in areas where the sediment consisted of ca. 66% silt and clay and much lower copper levels (<33> mg Cu/kg dry sediment) in areas where the silt-clay content averaged 27% if the sediment grain size matrix. They observed significant differences in community structure with *Hexagenia, Tanytarsus, Peloscolex, Sphaerium* (mollusk) and *Pontoporeia* (arthropod) virtually excluded from the area with the high copper content. In contrast the area with high sedimented copper held more individuals in the genera *Chironomus, Atribelos, Limnodrilus, Ceratopogonidae* and *Dicrotendipes.*

Moore *et al.* (1979) compared sediment concentrations of arsenic, mercury, copper, lead and zinc with infauna in a series of lakes downstream from the Con Mine in the Canadian subarctic. In general, all of the metals were significantly elevated in the upstream water column and sediments, complicating the analysis. Observed metal and infauna data is summarized in Table (8).

The sediments and water column in Meg Lake are significantly impaired by each of the metals investigated. The most common species was the bivalve, *Pisidium casertanum*, which is apparently very tolerant to metal intoxication. Seven chironomid and six mollusk species were observed in Keg Lake under the influence of very high metals content in sediments and the water column. Cironomids represented up to a maximum of 60% by numbers in the benthos with *Procladius culiciformis* and *Psectrocladius barbimanus* dominating. Unlike Meg Lake, *Pisidium casertanum* was rare in Keg Lake with *Physa jennessi, Valvata sincera* and *Lymnaea elodes* dominating at various times of the year. Metal levels between Meg and Keg Lakes were similar and it must be assumed that other environmental parameters were responsible for the shift in the mollusk community. Metal levels dropped significantly in Peg Lake where a total of 14 species were found (8 chironomids, 5 mollusks and one amphipod). Infaunal abundance increased significantly to 5,500/m^2 in Peg Lake – likely in response to the reduced metal concentrations. Further reductions were observed in Great Slave Lake. Sedimented copper levels were only ca. 15% and arsenic was only 3%of the maximum found in Keg Lake. Baseline infauna and metals were not evaluated at a remote (control) site in Great Slave and it is not possible to determine whether or not conditions reported in this paper are representative of background. However, 44 species were observed in these samples with a mean abundance of ca. 3100 infauna/m^2. Considering the high latitude at which this study was conducted, these numbers are similar to those observed at un-impacted reference areas by the author (Brooks, unpublished data). These data suggest that reasonably abundant and diverse infauna can be associated with copper levels as high as 82 µg Cu/g (dry sediment).

Table 8. Comparison of metal levels and infauna at four lakes downstream from the Con Mine in the Canadian subarctic. All metal concentrations are in mg/kg (dry sediment weight).

Endpoint	Meg Lake		Keg Lake		Peg Lake		Great Slave Lake	
	Sediment	Water	Sediment	Water	Sediment	Water	Sediment	Water
Arsenic	539	2.000	349	1.900	76	0.700	12	0.020
Mercury	132		47		80		53	

Copper	477	0.200	544	0.050	106	<0.020	82	<0.020
Lead	11	0.100	8	0.100	8	<0.020	14	0.008
Total Number Species	9		13		14		44	
Number of Insect Species	5		7		8		25	
Number Mollusk Species	4		6		5		10	
Total Infaunal Abundance	800		1300		5500		3100	

Puckett *et al*. (1993) have shown that metals, including copper, are associated with the silt-clay fraction of sediments and that wetlands appear to be important repositories for metals adsorbed to these fine grained sediments. This finding supports the conclusion that copper adsorbs to silt and clay rather than the more coarse fractions of the sediment.

Rehfeldt and Sochtig (1996) observed high metal tolerance in *Baetis rhodani.* The larvae of this species are scrapers, picking up diatoms from the surface of stones. Depending upon the developmental stage and the availability of food, *B. rhodani* can also feed on detritus. It is a polyvoltine species, occurring in different larval stages in rivers at all times of the year. Sediments in rivers studied by Rehfeldt and Sochtig (1996) contained between 30.7 and 2917.4 mg Cu/kg dry sediment. *Baetis rhodani* contained between 64.0 and 226.2 mg Cu/kg dry tissue weight. Copper content in the larvae were highly correlated with sediment copper concentrations (Spearman rank correlation coefficient = 0.94, $P < 0.01$). Table (9) describes the sediment bioconcentration factor for this species. The data are from Rehfeldt and Sochtig (1996)

Table 9. Heavy metal contents of sediments and of larvae of *Baetis rhodani* collected from six rivers in the German Federal Republic. Sediment Bioconcentration Factors are calculated for each river. All values are in mg Cu/kg dry sediment.

River	Cu in Sediment	Cu in *B. rhodani*	*Bioconcentration Factor*
Oker (Probsteib)	2917.4	169.2	0.06
Oker (Schladen 1985)	438.8	226.2	0.52
Ecker	30.7	64.0	2.08
Grane	365.7	168.2	0.46
Laute	155.5	126.5	0.81
Tolle	90.7	110.2	1.21

Water in these rivers was described as "soft" with neutral pH (7.1 to 8.5). The sediments were dried, ground to a powder, sieved to a particle size of < 2 mm. Metals were extracted by boiling in 100 ml of nitrohydrochloric acid for an unspecified period of time. This rather aggressive extractive technique may have liberated copper from other than biologically available geochemical partitions as previously discussed. This would help explain the wide variability in sediment BCF (0.06 to 2.08) documented in Table (9) for a single species. Alternatively, there may be some copper regulation occurring because the copper concentration in *B. rhodani* is fairly constant, varying only by a factor of 3.5, with the lowest tissue burdens associated with the lowest sediment burdens. It is also interesting to note that dissolved copper concentrations in the River Oker were very high at 132.9 ± 53 μu/L (mean and 95% confidence interval) further suggesting that *B. rhodani* can regulate copper uptake.

Significant differences were observed in the macrobenthic communities associated with polluted and unpolluted rivers by Rehfeldt and Sochtig (1996). They found that gammarid amphipods were particularly intolerant of copper and that mayflies of the genus Baetus were highly tolerant to copper. Other species in the EPT group were found in both polluted and unpolluted streams but at generally reduced numbers in polluted areas. Chironomids were found in reduced numbers in polluted streams. This suggests that tolerant chironomid species are probably not present in these watersheds.

Cairns *et al.* (1984) spiked control sediments from the Tualatin River and Soap Creek Pond with varying levels of copper to achieve sedimented copper levels varying between 59 mg/kg and 10,600 mg/kg. Overlying water in these experiments was continually renewed until the sediments and water came into equilibrium. They then conducted sediment bioassays using sensitive species of arthropods (*Chironomus tetans, Daphnia magna, Gammarus lacustris* and *Hyalella azteca.* A summary of the test conditions and results are provided in Table (10).

There was little or no difference between control survival and survival of any species in copper spiked sediments at concentrations 488 to 618 mg Cu/kg dry sediment in Soap Creek Pond. Nine of the ten *Chironomus tetans* survived for ten days in sediment copper concentrations of 1080 mg/kg. Four survived at concentrations to 3,950 mg/kg. Control and treatment survival of *D. magna* was equal (9/10) at sediment concentrations to 400 mg Cu/kg dry sediment. This experiment suggests that copper is not bioavailable in sediment rich in organic carbon and a high percentage of fines (silt and clay). This study also suggests that copper levels less than perhaps 600 mg/kg have little biological consequence in these "robust" sediments.

Table 10. Summary of sediment types, test conditions and results of copper spiked sediment bioassays reported by Cairns *et al.* (1984).

			Sediment 10-day LC_{50}			
Sediment	% TOC	% Silt-clay	*C. Tetans*	*D. magna*[1]	*G. lacustris*	*H. azteca*
Tualatin River	1.8	59.3	2296	937	-	-
Soap Creek Pond	3.0	84.8	857	681	964	1078

[1]All bioassays were based on a ten day exposure except that for *Daphnia magna* which is a 48-hr LC_{50}.

Toxicity summary for sedimented copper. The bioavailability of sedimented copper appears dependent on sediment physicochemical characteristics including the proportion fines (silt and clay), overlying and interstitial water pH, hardness and dissolved oxygen, and the presence of sedimented organic carbon. Background levels of copper reviewed in the assessment varied as shown in Table (11).

Table 11. Background freshwater sediment copper levels reviewed in this assessment. All values are presented in mg Cu/g dry sediment.

Source	**Geographic Location**	**Reported**
Background		
Siipola (1991)	Lower Columbia River	18.0 to 66.0
Tetra Tech (1994)	Lower Columbia River	19.3 to 49.9
Munkittrick *et al.* (1989)	Loken Lake, northern Ontario	22.7 $\pm$ 6.4 (ie. < 35.2)
Munkittrick *et al.* (1991)	northern Ontario	4.0 to 23.0
Cairns *et al.* (1984)	Tualatin River, Oregon	59.0
Cairns *et al.* (1984)	Soap Creek Pond, University of Oregon	210.0
Cain *et al.* (1992)	Clark Fork River in Montana	18.0
Moore *et al.* (1979)	Great Slave Lake	82.0
Schmidt (1978)	"unpolluted sediments from nearshore areas"	2.0 to 78.0

These data suggest that sedimented copper concentrations in unpolluted reference areas can vary from 2.0 to at least 80 mg Cu/kg dry sediment. Diks and Allen (1983) suggest that moderately aggressive copper extraction protocols, such as that of Chao (1972) are appropriate for

determining the bioavailable copper in sediments. More aggressive protocols using hot acid extraction techniques over extended periods of time will overestimate the amount of bioavailable copper by liberating copper from the lattice structure of other minerals.

Given that copper delivered to the sediments from the overlying water column and that water column and sediment concentrations are generally positively correlated, it appears that it is the copper concentration in the overlying water column that is most influential on aquatic fauna and flora. Copper does bioconcentrate and Cain *et. al* (1992) present data suggesting that infauna, particularly detritivores, can bioaccumulate copper from sediments, copper does not appear to biomagnify through food webs.

This review suggests that aquatic invertebrates vary significantly in their response to sedimented copper. For instance of the seven genera of midges described in these studies, five are tolerant of sedimented copper to levels exceeding 100 mg Cu/kg dry sediment. Only the genera *Tanytarsus* and *Polypedilium* appear intolerant at levels of 123 to 160 mg/kg. It should be noted that the concentration of water in the study of Munkittrick *et al*. (1991) was 9.5 to 9.8 µg Cu/L. Water hardness was not provided in the paper and it is not possible to assess whether the response of these species was to copper in the water or sediments. Based on this review, it appears that only *Tanytarsus, Polypedilium, Hexagenia, Sphaerium* and *Pontoporeia* potentially intolerant of sedimented copper. It was not possible from the papers presented to determine whether or not their susceptibility was to sedimented copper or copper carried in the water column. Confirmation of the susceptibility of these taxa to sedimented copper would require sediment bioassays, such as that performed by Cairns *et al.* (1984). This review indicates that many species are very tolerant to exceptionally high levels of sedimented copper (Table 12). Many of these tolerance levels are much higher than the background values presented in Table (11).

Table 12. Summary of the tolerance of various freshwater taxa to sedimented copper.

Taxon	Relative Tolerance	Source	Sediment Cu Concentration (mg Cu/kg dry sediment)
Cladocera			
Daphnia magna	Tolerant	5	681 to 937
Chironomids			
Chironomus	Tolerant	2,5	589 to 2296
Procladium culciformis	Tolerant	3	477 to 544
Psectrocladius barbimanus	Tolerant	3	477 to 544
Dicrotendipes	Tolerant	2	589
Pagastiella	Tolerant	1	123 to 160
Polypedilium	Intolerant	1	123 to 160
Tanytarsus	Intolerant	1, 2	123 to 589
Ephemeroptera			
Hexagenia	Intolerant	2	589
Baetis rhodani	Tolerant	4	< 2,917
Diptera			
Ceratopogonidae	Tolerant	2	589

Table (12) continued

Taxon	Relative Tolerance	Source	Sediment Cu Concentration (mg Cu/kg dry sediment)
Molluska			

Sphaerium	Intolerant	2	589
Pisidium casertanum	Tolerant	3	477 to 544
Physa jennessi	Tolerant	3	477 to 544
Valvata sincera	Tolerant	3	477 to 544
Lymnaea elodes	Tolerant	3	477 to 544
Amphipoda			
Pontoporeia	Intolerant	2	589
Gammarus lacustric	Tolerant	5	964
Hyalella azteca	Tolerant	5	1078
Oligochaeta			
Limnodrilus	Tolerant	2	589

1) Munkittrick *et al.* (1991)
2) Kraft and Sypniewski (1981)
3) Moore *et al.* (1979)
4) Rehfeldt and Sochtig (1996)
5) Cairns *et al.* (1984)

Regulatory standards for copper with respect to marine and freshwater sediments. Washington State has developed Marine 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 standard of 390 mg Cu/kg dry sediment weight will be used as a benchmark against which to judge the environmental acceptability of sediment accumulated copper in marine sediments.

Standards for freshwater sediments were not available from any jurisdiction. Jones *et al.* (1997) have summarized available toxicological benchmarks for screening contaminants of potential concern for effects on sediment-associated biota. The U.S. Department of Energy accomplished this work in an effort to identify benchmark levels of contaminants that warrant further assessment, or that are at a level that requires no further attention at hazardous waste sites. It should be emphasized that these benchmarks were not developed or intended as sediment quality criteria for surface waters. The authors note that, "Sediment benchmarks must not be used as the sole measure of sediment toxicity. Field studies and toxicity tests shall be the primary indicators of toxicity of sediments; benchmarks may be used to determine which chemicals present in the sediment are most likely causing the toxicity." The following approaches, and sediment concentrations for copper, were discussed:

Screening Level Concentration Approach (SLC). This approach estimates the highest concentration of a particular contaminant in sediment that can be tolerated by ~95% of benthic infauna. The SLC is derived from synoptic data on sediment chemical concentrations and benthic invertebrate distributions. First, the species screening level concentration (SSLC) is calculated by plotting the frequency distribution of the contaminant concentrations over all sites (at least 10) where the species is present. The 90th percentile of this distribution is taken as the SSLC for that species. Next, a large number of SSLCs are plotted as a frequency distribution to determine the contaminant concentration above which 95% of the SSLCs occur. This final concentration is the SLC.

Dr. Connie Gaudat, Acting Head Soil and Sediment Section, Evaluation and Interpretation Branch, Guidelines Division of Environment Canada noted that the Ontario guidelines were developed without reference to water or sediment pH, total organic carbon, sediment grain size or any other environmental parameter effecting the fate, transport, deposition and bioavailability of the compounds under consideration (Gaudat, 1995; personal communication). In discussing copper for instance, she stated that documentation of worst cases involving metals may have occurred with very low pH values or coarse sediments. This may be especially true in Ontario, where the

guidelines were developed, because it lies on the continental shield characterized by low soil buffering capacity and low pH. She noted that many pristine areas in Canada have background levels which exceed the Ontario guidelines. She stated that Environment Canada is developing sediment standards, but until those standards are developed, they (and the Ontario Ministry of Environment) use site specific risk assessments to determine appropriate sediment quality criteria. She said that the site-specific standards are always greater than Ontario's guidelines because they seldom, if ever, encounter the worst case conditions associated with the guidelines. It should be noted that Jones *et al.* (1997) do not recommend the SLC method even for developing benchmarks against which to assess the potential biological effects of contaminants at hazardous waste sites.

Apparent Effects Threshold Approach. The AET approach uses data from matched sediment chemistry and biological effects measures. Biological effects could be assessed by either benthic community survey or sediment toxicity tests. An AET concentration is the sediment concentration of a selected chemical, above which statistically significant biological effects always occur. Jones *et al.* (1997) defended the use of estuarine benchmarks for evaluation of freshwater sites when freshwater benchmarks are not available. The Washington State Apparent Effects Threshold for copper in marine environments is 390 µg Cu/g dry sediment.

National Oceanic and Atmospheric Administration (NOAA) Approach. NOAA annually collects and chemically analyzes sediment samples from sites located in coastal marine and estuarine environments throughout the United States. These data were used to evaluate three basic approaches to the establishment of effects-based criteria: the equilibrium partitioning approach (applicable to nonionic organic compounds), the spiked-sediment toxicity test approach, and various methods of evaluating synoptically collected biological and chemical data in field surveys (Long and Morgan, 1991). Chemical concentrations observed or predicted by these methods to be associated with biological effects were ranked, and the lower 10th percentile [Effects Range-Low (ER-L)] and median [Effects Range-Median (ER-M)] concentrations identified. The ER-L and ER-M values were recalculated by Long *et al.* (1995) after omitting the few freshwater data included in the Long and Morgan (1991) calculation and after adding additional, more recent data.

Jones *et al.* (1997) note that the NOAA values may be used to help identify sites with the potential to cause adverse biological effects. They caution that these are not NOAA criteria or standards and are not intended for use in regulatory decisions or any other similar applications. The NOAA ER-L for copper is 34 mg Cu/kg dry sediment and the ER-M is 270 mg Cu/kg dry sediment.

Florida Department of Environmental Protection Approach. The Florida Department of Environmental Protection (FDEP) methodology is similar to the NOAA approach. The updated and revised data set used by Long *et al.* (1995) was also used by MacDonald (1994) to calculate Threshold Effects Levels (TELs) and Probable Effects Levels (PELs). Unlike the ER-Ls and ER-Ms, the TELs and PELs also incorporate chemical concentrations observed or predicted to be associated with no adverse biological effects (no-effects data). The TEL is the geometric mean of the 15th percentile in the effects data set and the 50th percentile in the no effects data set. The PEL is the geometric mean of the 50th percentile in the effects data set and the 85th percentile in the no effects data set. The TEL represents the upper limit of the range of sediment contaminant concentrations dominated by no effects data. The PEL represents the lower limit of the range of contaminant concentrations that are usually or always associated with adverse biological effects (MacDonald, 1994). The FDEP TEL is 18.7 µg Cu/g dry sediment weight and the PEL is 108 µg Cu/g dry sediment weight.

Recommended interim marine and freshwater sediment benchmarks for copper and DDAC. Jones *et al.* 1996 recommend that a suite of benchmarks be used in evaluating the potential adverse effects associated with a chemical on a site specific basis. However elegant that

approach may be, the usual permitting of projects using treated wood, particularly personal use piers and floats, ferry terminals, etc. does not warrant development of a project specific sediment quality standard. Recognizing that both the U.S. EPA and Environment Canada have cautioned that the use of the following screening benchmarks are not appropriate as sediment quality standards. The values are provided in Table (13) as background.

Table 13. Summary of jurisdictional screening level benchmarks for screening hazardous waste sites for contaminants of concern.

Jurisdiction	Criteria in μg/g	
Washington State Marine Sediment Quality Criteria	390	
National Oceanographic and Atmospheric Administration	ER-L = 34	ER-M 270
Florida Department of Environmental Protection	TEL = 18.7	PEL = 110
Ontario Ministry of the Environment Screening Levels	SLC Low = 16	SLC Severe = 110

The preceding discussion describing the bioavailability and toxicity of copper suggests that sedimented total organic carbon, percent fines (silt and clay), pH, dissolved oxygen, water hardness and alkalinity can all effect the bioavailability and toxicity of sedimented copper. The author would greatly prefer to rely on well thought-out freshwater sediment quality standards. Unfortunately, those standards have not been developed. The only regulatory level is Washington State's Apparent Effects Threshold for copper in marine sediments at 390 μg/g. The previous review suggests that this level is too high to protect freshwater benthic organisms.

Until appropriate freshwater sediment quality standards are developed, the benchmarks given in Table (14) are proposed for evaluating the benthic effects associated with copper lost from preserved wood. These levels are consistent with the range at which threshold effects are reported by Jones *et al.* (1997) and at which sediment effects were reported in the reviewed literature. In addition, they appear consistent with background levels of copper found in many parts of North America and should avoid the curious penchant of some jurisdictions to invoke metal concentration criteria that are well below apparently unpolluted ambient levels. Loehr (1997) notes that several states have surface water quality arsenic standards in the range of 1.4 to 0.002 ppb. He notes that the average concentration of arsenic in five brands of bottled water was 4.2 ppb or 2,100 times the lowest of these standards. He further notes that surface water in Washington State contains 0.1 to 1 ppb and that ocean water holds ca. 1.7 ppb. USDA (1980) reports that Washington well water contains between 5.0 and 6.0 ppb and Oregon well water contains as much as 1,700 ppb arsenic. Mr. Loehr comments that it is illegal to dump any of the tested bottled drinking water into any surface water.

Table 14. Recommended benchmarks for assessing the environmental risks associated with sedimented copper lost from pressure treated wood.

Sediment and Water Column Characteristics	Acceptable levels of Sedimented Copper.
1. Coarse grained sediment (silt & clay <10%) Total Organic Carbon < 0.5% Moderate to low pH (5.5 to 6.5) Low hardness and alkalinity (25 to 35 ppm $CaCO_3$)	30 μg Cu/g dry sediment
2. Intermediate sediments (silt & clay between 10% and 25%) Total Organic Carbon between 0.5% and 1.5%	65 μg Cu/g dry sediment

Neutral pH (6.5 to 7.5)
Moderate hardness and alkalinity (35 to 100 ppm $CaCO_3$)

3. Low energy, well buffered streams and lakes (fines > 25%) 100 µg Cu/g dry sediment
Total Organic Carbon >1.25%
Greater than neutral pH (pH > 7.5)
High hardness and alkalinity (> 100 ppm $CaCO_3$)

These values are higher than the NOEL and/or TELs described in Table (13). It should be emphasized that all of the values in Table (13) are based on worst cases and do not take into consideration environmental factors that mediate environmental toxicity. For instance, the Ontario screening criteria for sedimented copper (16 µg/L) is based on the worst cases in the Ontario database, an area lying on the continental shield in which worst cases likely involve very low pH, low alkalinity and hardness and coarse (rocky) substrates. As previously discussed, Environment Canada does not recognize these values as standards and cautions that background levels in other parts of Canada consistently exceed this screening value with no evidence of toxic effects. The benchmarks provided in Table (14) are consistent with the range (28.5 – 96 µg Cu/g dry sediment) of threshold effects levels presented by Jones *et al.* (1997).

Some insight regarding the appropriateness of adopting the copper screening values in Table (14) as regulatory standards can be obtained by comparing similar data for the water column with the U.S. Environmental Protection Agency freshwater regulatory standard for copper, adopted by many jurisdictions throughout the world. Suter and Tsao (1996) present conventional benchmarks for priority contaminants in freshwater. In Table (1) of their document they compare the EPA chronic value for copper (12 µg/L at 100 mg/L hardness) with the lowest chronic values in the literature (similar to the NOELs or TELs presented in Table (13) of this document for sedimented copper). The results are presented in Table (15).

Table 15. Summary of conventional benchmarks for copper in freshwater (µg/L). The data are from Suter and Tsao (1996). The Environmental Protection Agency National Water Quality Criteria for copper was computed at a hardness of 100 mg ($CaCO_3$) /L.

Metal	National Water Quality Criteria		Lowest Chronic Values for:				
	Acute	Chronic	Fish	Daphnids	Non Daphnid Invertebrates	Aquatic Plants	All Organicms
Copper	18	12	3.8	0.23	6.066	1.0	0.23

All of the lowest chronic values are lower than the EPA chronic copper criteria at 100 mg/L hardness. The literature clearly indicates that these lowest chronic values were likely obtained under conditions of low alkalinity, low total hardness, low levels of organic carbon (dissolved and particulate), low levels of particulate inorganic carbon and low pH. These conditions are unrepresentative of most natural bodies of water; and therefore, adoption of the lowest chronic values as a standard would be unnecessarily restrictive. The lowest daphnid value (0.23 µg Cu/L) is less than ambient copper levels in most natural bodies of water.

It is unfortunate that regulatory standards have not been developed for sedimented copper in freshwater. Eventual development of appropriate standards by the Environmental Protection Agency will take into account the environmental factors that affect sedimented copper toxicity and will provide reasonable estimates of sedimented copper that will not adversely affect biological resources.

Toxicity to aquatic fauna and flora associated with didecyldimethylammonium choride (DDAC). Brooks *et al.* (1996) conducted an extensive quality assurance review of the toxicological database for DDAC and suggested that the LC_{50} values summarized in Table (16) represented the best estimates of true values. Brooks *et al.* (1996) reported that the toxicity of formulated products, using DDAC as the active ingredient, was lower than toxicity associated with the technical grade.

Table 16. Summary of DDAC LC_{50} data for aquatic species from Brooks *et al.* (1996). All values are in μg active ingredient/L.

Species	96 hr. LC_{50}
Sturgeon larvae (*Acipenser transmontanus*)[1]	0.001 to 0.010
Sturgeon larvae (*Acipenser transmontanus*)[5]	0.415
Zebra Fish[1]	0.172
Fathead minnow (80% DDAC)[1]	0.195 (0.122 – 0.224)
Bluegill sunfish (*Lepomis* macrochirus)[4]	0.320
Bluegill sunfish (*Lepomis* macrochirus)[4]	0.295
Bluegill sunfish (*Lepomis* macrochirus)[4]	0.270
Rainbow trout (*Oncorhynchus mykiss*)[1]	0.466 ± 0.1
Rainbow trout (*Oncorhynchus mykiss*)[4]	1.24 (range = 0.52 to 2.81)
Rainbow trout (*Oncorhynchus mykiss*)[3]	1.700 (1.4 –2.0)
Coho salmon (*Oncorhynchus kisutch*)[4]	0.840 (range from 0.67 to 1.00)
Catfish[1]	0.590
Chinook salmon (*Oncorhynchus tshawytscha*)[1]	0.705 ± 0.015
Chinook salmon (*Oncorhynchus tshawytscha*)[4]	0.360
Guppies[4]	0.600
Sheepshead minnow (80% DDAC)[1]	0.940 (0.770 – 1.200)
Flounder[1]	2.050
Catfish (96 hr LC_{50})[4]	1.300
Daphnia magna[1]	0.052
Daphnia magna (48 hr EC_{50})[2]	0.060 (0.051 – 0.072)
Mysid shrimp	0.069

Notes: [1] Farrel cited in Brooks *et al.* (1996)
[2] Handley *et al.* (1994c)
[3] Handley *et al.* (1994b)
[4] Henderson (1992)
[5] Schoenig (1998)

It should be noted that the sturgeon bioassay conducted by Farrell used yolk-sac and 30 to 40 day old larvae. Anecdotal evidence provided by Dr. Gerald Schoenig (personal communication) suggested that Dr. Farrel's sturgeon larvae were the survivors of two highly stressful events occurring just prior to the DDAC bioassays. These stresses were created during shipping in which half the larvae were lost and by the inadvertent introduction of lethal quantities of chlorine into the holding tank the day prior to the DDAC bioassays resulting in the loss of an additional 50% of the larvae. Subsequent laboratory bioassays (*AQUA-Science*, 1997a) on 78 day old sturgeon larvae indicate a 96-hr LC_{50} of 416 μg DDAC/L which is consistent with other fish bioassays. Test conditions were: temperature = 16 to 17 °C; dissolved oxygen = 5.4 to 9.8 mg/L; pH = 7.05 to 7.79; hardness = 94 to 135 mg/L and alkalinity = 77 to 130 mg/L. This study also reported a 96-hr LC_{25} of 225 μg/L and a 96-hr NOEC of 100 μg/L.

A second larval sturgeon bioassay was conducted with the addition of ca. 1/16" of sediment from the Fraser River in British Columbia to the bottom of the test chambers (*AQUA-Science*, 1997b). This bioassay was conducted under similar physicochemical conditions but at reduced

alkalinity (57 to 89 mg/L) and hardness (43 to 110 mg/L). Higher toxicity thresholds were determined in the presence of sediment:

Endpoint	µg DDAC/L
96-hr NOEC	2,409
96-hr LOEC	8,030
96-hr LC_{25}	3,814
96-hr LC_{50}	5,220

For purposes of this report, the sturgeon bioassay data reported by *Aqua-Science* (1997a) will be used (96-hr LC_{50} = 416 µg DDAC/L). These data suggest that sturgeon larvae (*Acipenser transmontanus*) are not particularly sensitive to DDAC.

Only limited data were available describing the chronic effects of DDAC on aquatic species. Twenty-four hour exposures of rainbow trout to DDAC concentrations of 0.400 mg/L have been shown to affect blood plasma glucose levels, plasma corticosteroid hormones and lactate levels and reduced swimming performance in rainbow trout was observed by Wood *et al.*,(in preparation, cited in Brooks *et al. 1996*) at 0.200 mg DDAC/L. Table (17) summarizes the available No Observed Effects Levels for DDAC.

Table 17. Summary of no-observed effect levels (NOEL) measured for DDAC.

Species	NOEL (mg/L)
Rainbow trout[2]	1.000
Bluegill sunfish (*Lepomis macrochirus*)	0.100
Coho salmon	0.590
Scenedesmus subspicatus (algae)[1]	1.000
Daphnia magna[3]	0.032
Daphnia magna[4]	0.074
Mysid shrimp	0.052

Notes: [1] Handley *et al.* (1994a)
[2] Handley *et al.* (1994b)
[3] Handley *et al.* (1994c)
[4] Henderson (1992)

Effects of Dissolved Organic Carbon. Wood leachate contains high levels of organic extractives in addition to preservative. Taylor *et al.* (1996) reported high biological oxygen demand (BOD) of 1,660 to > 2,600 mg/L in wood leachate. DDAC has the potential to bind to dissolved organic matter in water. In general, sorption of compounds to dissolved organic matter reduces their bioavailability and thus their toxicity to aquatic organisms (Mills, 1993). Springborn Laboratories (1994) indicated lower acute toxicity of DDAC to fathead minnows associated with increasing levels of DOC. The results of this study are summarized in Table (18). These data suggest that DDAC behaves like other organic molecules (PAH, etc.) in that toxicity is mediated by the availability of organic material in the water column and in the sediments. Ultimately, the availability of environmental levels of organic material (DOC, POC, sedimented TOC, etc.) should be taken into account in developing either water quality or sediment standards for this material.

Table 18. The effect of DOC on toxicity of the antisapstain chemical, DDAC, to fathead minnows in a 96 hr. static renewal acute toxicity test (from Brooks *et al.*, 1996)

Amount of humic acid added to DDAC solution (mg/L)	96-hr LC_{50} (mg a.i./L) with 95% confidence limits	NOEC (mg a.i./L)
0.0	0.19 (0.16 – 0.27)	0.092
10.0	0.77 (0.65 – 1.0)	0.40
20.0	1.2 (0.94 – 1.6)	0.94

DDAC toxicity to aquatic plants. Handley *et al.* (1994) reported a no-observed effects level of 1.0 mg/l with a 96 hr. EC_{50} of 3.0 mg/L for *Scenedesmus subspicatus.* The end points examined in different tests were a 50% reduction in growth rate and a 50% reduction in biomass.

Henderson (1992) cited Walker and Evans (1978) in noting that QACs suppress growth in *Chlorella* and duckweek (*Spirodela oligorhiza*) at concentrations above 3.0 to 5.0 mg/L. In duckweed, sublethal levels of QACs caused a yellowing or browning of the frond margins and the production of smaller sized fronds. In *Chlorella,* the size, shape, and internal organization of the cells were affected; death appeared to be due to disruption of chloroplast structures.

Carcinogenic, mutagenic and teratogenic effects. Henderson (1992) reviewed several specific studies describing each of these issues and found no evidence for adverse effects. Specifically, Henderson's (1992) review suggests that DDAC does not have carcinogenic, mutagenic or teratogenic effects on mammals.

Recommended water column benchmarks for DDAC. Based on the available toxicological database described above, it appears that the geometric mean of the two values of the NOEL for *Daphnia magna* (0.049 mg DDAC/L) provide a conservative benchmark against which to judge environmental risk. This value is considered conservative because non-linear regression analysis of the NOEL versus DOC data in Table (18) suggests an increase in the NOEL of $\exp^{0.116 \times \text{DOC (mg/L)}}$ as DOC increases. This very simple (and preliminary) analysis suggests that the NOEL would be 12% higher at 1.0 mg/L DOC and 42% higher at 3.0% DOC; both of which are realistic levels. A summary of the DOC data and regression analysis is provided in Figure (2). The physicochemical interactions resulting in the observed decrease in toxicity are unknown. Based on the very low (near zero) octanol-water partition coefficient, it would not appear that DDAC would readily complex with DOC.

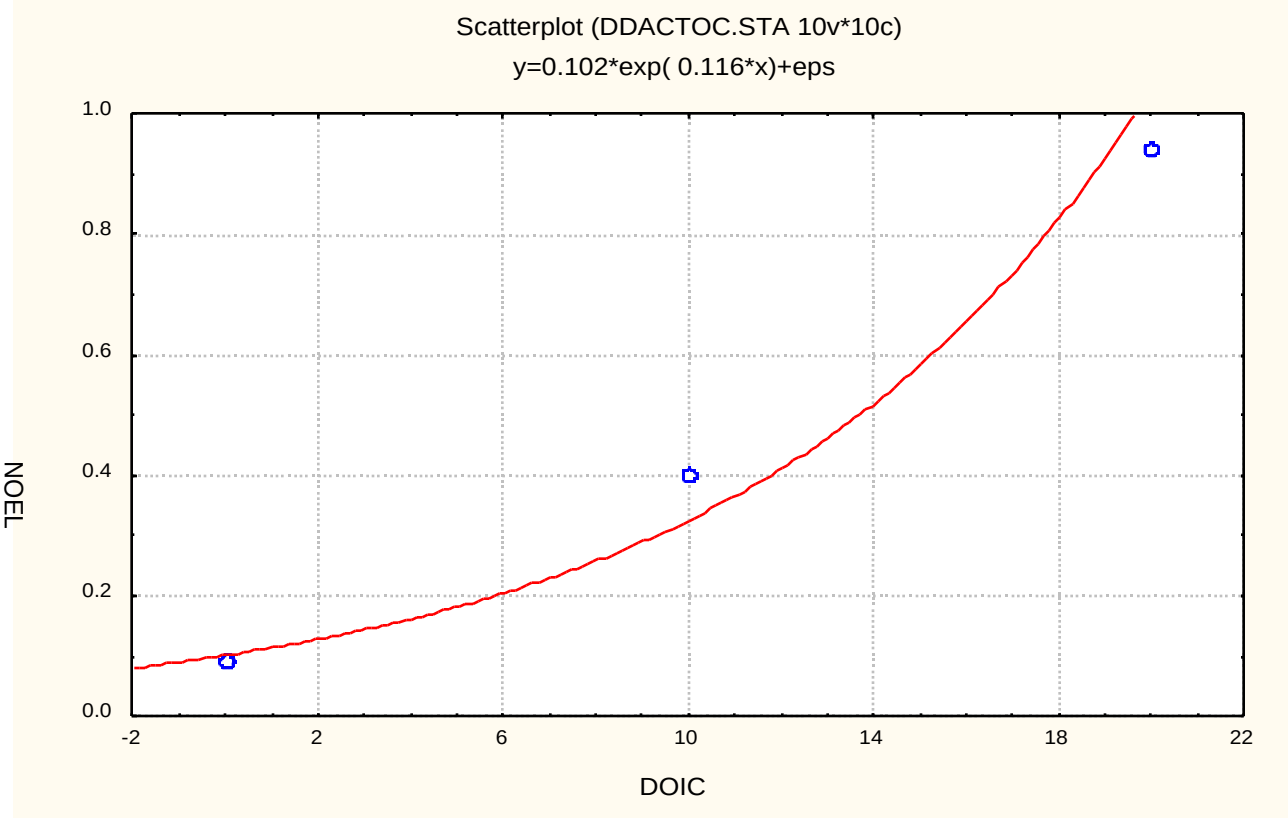


Figure 2. Effect of Dissolved Organic Carbon (DOC) on the No Observed Effect Level of DDAC to fathead minnows in a 96 hour static renewal acute toxicity test (data from Springborn Laboratories). DOC and NOEL data are in mg/L.

It was the conclusion of the Antisapstain Review Committee in British Columbia that insufficient evidence existed for lowering the stormwater discharge criteria from 700 µg DDAC/ to 395 µg DDAC/L. It should be noted that applying a safety factor of ten to the current discharge limit of 700 µg DDAC/L results in an allowable receiving water concentration of 70 µg DDAC/L, which is higher that the 49 g DDAC/L benchmark chosen for this assessment

Aquatic toxicity associated with sedimented DDAC. ABC Laboratories (1995) examined the toxicity of DDAC incorporated into sediments to the midge (*Chironomus tetans*). Test chambers were maintained in a temperature-controlled waterbath with temperatures ranging from 21 to 22 °C. Dissolved oxygen ranged from 3.3 to 8.1 mg/L throughout the test. Water pH ranged from 6.9 to 8.3. Measured endpoints included survival and growth at the end of 14 days as well as survival and emergence success at the end of 28 days exposure. The 14-day and 28-day LC_{50} values were calculated at >1,000 and 2085 mg/kg respectively. A 14-day EC_{50} value was calculated at 1,287 mg DDAC/kg based on total observed adverse effects (decreased size and mortality). The NOEC, based on larval weight and time to emergence was 530 mg DDAC/kg. The geometric mean maximum acceptable toxicant concentration (MATC) calculated from the above data was 728 mg/kg.

No empirical evidence describing the fate and transport of DDAC in open aquatic environments was available. The very high water solubility and low K_{OW} of DDAC suggests that it will likely bind ironically to finely divided inorganic particulate material, particularly clay, in the water column. The strong sorption to soils reported in Brooks *et al.* (1996) suggests little

propensity to desorb and re-enter the water column form sediments. No information was available describing the potential for infaunal detritivores to ingest DDAC sorbed to clay particles or for the movement of this material across the gut epithelia. However, Henderson (1992) observed poor absorption of DDAC across the gut of fish, very low bioconcentration factors and a small potential for biomagnification through food chains. He also reported that fish rapidly catabolize and/or excrete DDAC. Based on this evidence it appears unlikely that significant biological risks to eukaryotes will be associated with DDAC at sedimented values less than ca. 500 to 700 mg DDAC/kg. There is evidence that sediment concentrations above 10 mg DDAC/kg could effect microbial flora resulting in unknown changes in nutrient fluxes and decomposition of organic matter in sediments.

Recommended sediment benchmark for DDAC. For purposes of this report, the assumption will be made that DDAC, dissolved in the water column, adsorbs to clay particles that are deposited in sediments. Furthermore, this assessment concludes that risks associated with sedimented DDAC are acceptable at levels less than 10 ppm. It is acknowledged that this assessment is based on inadequate information. A better understanding of the potential for biological risk could be achieved with laboratory experiments designed to examine the transport of DDAC from the water column to sediments and to examine the effects of sedimented DDAC on infaunal communities of freshwater organisms. The data for larval sturgeon and midges discussed above suggests that this benchmark of 10 mg DDAC/kg dry sediment is very conservative when applied to eukaryotes.

Summary statement regarding recommended benchmarks for dissolved and sedimented copper and DDAC for use in this risk assessment. Copper is an essential micronutrient found at levels of one to ten µg/L in anthropogenically unaffected surface water. It is the cupric ion (Cu^{2+}) and perhaps some species of copper hydroxides ($CuOH^{n}$) that are toxic. The form of copper in surface water is dependent on pH, alkalinity, hardness and the availability of organic and inorganic binding sites (DOC, PIM, POM, etc.). The U.S. EPA has defined a freshwater copper standard that is dependent on hardness. The review conducted in support of this risk assessment did not find instances in which this standard was under-protective of aquatic fauna or flora. The EPA copper standard for marine water (3.11 µg/L) is independent of other environmental parameters and the value was also not found to be under-protective. These EPA criteria are used as benchmarks against which to assess the environmental suitability of 0.4 pcf, ACQ-B pressure treated wood used in aquatic environments.

Freshwater sediment standards for copper or DDAC were not available. Interim benchmarks for sedimented copper in freshwater were derived from Jones *et al.* (1997). The Washington State AET based marine copper sediment standard of 390 µg/g is adopted as a benchmark for this assessment.

DDAC is an ionic carbon molecule that is highly soluble in water and which strongly binds to clay. DDAC is toxic at low levels but does not appear to bioconcentrate or biomagnify. The No-Observed-Effect-Level (NOEL) for *Daphnia magna* (49 µg DDAC/L) is adopted as a benchmark in this risk assessment.

It appears that DDAC is not bioavailable in sediments. However, it exhibits anti-microbial activity at concentrations above 10 mg DDAC/kg dry sediment weight and this value has been chosen as a benchmark.

These benchmarks are summarized in Table (19). In healthy sediments, bioturbation is expected to homogenize the upper three to four centimeters of the sediment column. Consistent with the Puget Sound Estuary Protocols (1986), samples taken to determine background levels of contaminants or to evaluate contaminant levels after construction of a project should include the top two centimeters of the sediment column.

Table 19. Water and sediment copper and DDAC benchmarks against which to assess the environmental suitability of ACQ-B preserved wood used in aquatic environments.

Freshwater copper benchmark: EPA chronic criterion $\leq 0.960*\exp^{0.8545[\ln(\text{hardness})] - 1.465}$

Freshwater DDAC benchmark: 0.049 mg DDAC/L

Freshwater sedimented copper benchmark:

Sediment and Water Column Characteristics	Recommended Copper Benchmark
1. Coarse grained sediment (silt & clay <10%) Total Organic Carbon < 0.5% Moderate to low pH (5.5 to 6.5) Low hardness and alkalinity (25 to 35 ppm $CaCO_3$)	30 µg Cu/g dry sediment
2. Intermediate sediments (silt & clay between 10% and 25%) Total Organic Carbon between 0.5% and 1.5% Neutral pH (6.5 to 7.5) Moderate hardness and alkalinity (35 to 100 ppm $CaCO_3$)	65 µg Cu/g dry sediment
3. Low energy, well buffered streams and lakes (fines > 25%) Total Organic Carbon >1.25% Greater than neutral pH (pH > 7.5) High hardness and alkalinity (> 100 ppm $CaCO_3$)	100 µg Cu/g dry sediment

Saltwater copper benchmark: EPA saltwater criterion $\leq$ 3.11 µg Cu/L (dissolved copper)

Saltwater DDAC benchmark: 0.049 mg DDAC/L

Saltwater sediment copper benchmark: Washington States Standard of 390 mg Cu/kg

Saltwater sediment DDAC benchmark: 10 mg DDAC/kg dry sediment

Anticipated Environmental Impacts Resulting From the use of ACQ-B Treated Wood In Aquatic Environments. 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.

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

Leaching of copper and DDAC from ACQ-B treated wood. The copper and DDAC leaching data presented in this assessment was developed by Chemical Specialties Incorporated (Jin, 1997).

Materials and methods. Six southern yellow pine posts, averaging 17.2 cm in diameter were cut into five to 12 inch long sections. The cut ends were sealed and the sections kiln-dried to a moisture content of 20% or below prior to treating with ACQ-B to an average retention of 0.43 pounds per square foot (pcf) in the treated zone (range = 0.40 to 0.46 pcf). A retention of 0.40 pcf required by the American Wood Preservers Association (AWPA, 1996) for southern yellow pine in contact with fresh water. The treated sections were covered for three to five days and then kiln-dried to a moisture content less than 20% prior to introduction into the leaching system.

Four replicates of these 0.4 pcf treated sections were leached at each of four pH values (5.0, 6.5, 8.0 and 8.0 at a salinity of 30 parts per thousand (ppt)). Each acid rinsed leaching container contained 10 to 12 liters of distilled water amended with HCL and/or NaCl to achieve the desired test conditions. In addition, an untreated control from the same pole was leached at each of the four pH and salinity values. The average water volume to exposed wood surface area was 3.95 ml/cm^2.

Copper was analyzed in the leachate using Inductively Coupled Plasma (ICP) on Days 0.5, 1.5, 3.0, 5.5, 10.5, 21, 38.5, 54, 66 and 76.5. Copper loss rates (μg/cm^2/day) for each time interval were computed from the known surface area of the pole and the volume and cumulative copper content in the leachate.

DDAC content in the leachate was determined using HPLC with a two-phase titration method for those samples below the detection limit of the basic HPLC method on days 0.5, 1.5, 3.0, 5.5, 10.5 and 21. DDAC content in the leachate at that time had apparently stopped increasing. DDAC does not readily degrade in the water column (Brooks *et al*., 1996) and therefore it was concluded that measurable losses of DDAC were not occurring after day 21 and no further DDAC analyses were accomplished. DDAC loss rates (μg/cm^2/day) for each time interval were computed from the known surface area of the pole and the volume and cumulative DDAC content in the leachate.

Results. The copper and DDAC data provided by CSI were analyzed independently using nonlinear, multifactor regression analysis followed by analysis of variance. Because this is the only immersed leaching study for ACQ-B treated southern yellow pine, the analysis is discussed in detail in the following paragraphs.

actors affecting ACQ copper leaching rates. Dahlgren (1975) suggests that from the wood treaters' point of view, the most important factors determining the leachability of water borne wood preservatives are the retention and type of preservative, the drying and storage conditions, and the choice of wood species. Other important parameters are the ion-exchange fixation capacity of copper, the natural pH of the receiving water, and the chemical composition and anatomy of the wood. This risk assessment is specific for ACQ-B used to preserve southern yellow pine at a retention of 0.4 pcf. There are several other factors that cannot be controlled by the wood treater.

Fixation. The quaternary ammonium compound in ACQ fixes in wood through ion exchange with anionic active sites and through other adsorption mechanisms at higher quat concentrations (Archer *et al*., 1992). Quat is fixed predominantly onto lignin, although interaction with holocellulose also occurs. Copper is fixed in wood through ion exchange reactions between cupriammonium ions and acidic functional groups such as carboxylic acid groups associated with lignin and hemicellulose. Copper complexes with cellulose through hydrogen bonding with hydroxyl or amine nitrogen groups, or through replacement of an ammonia group from the cupriammonium ion with the hydroxyl ion of cellulose. In addition, copper also forms insoluble copper carbonate salts resulting from the loss of ammonia during drying (Chen, 1994). It is

assumed that the preservative was fixed in the wood by the covered storage followed by kiln drying reported by Jin (1997).

Time after installation in aquatic environments. Leaching is strongly time-dependent especially during the first three days following immersion. The scatterplot provided in Figure (3) clearly illustrates this. Note that there is significant variability in the Day (0.5) metal loss rates. This is in part due to short term differences associated with water pH (see Figures 4 and 10). However, the magnitude of the pH variability is not sufficient to account for the range of copper loss rates seen on Day 0.5 (18.4 to 61 µg/cm^2/ on day 0.5). In can be hypothesized that some of the variability is associated with varying amounts of preservative remaining on the surface of the wood. Surface deposits of ACQ-B would not have binding sites available and therefore would not be well fixed to the wood structure. Dissolution of this surface preservative could account for the initially high losses, with the pronounced break at ca. 3.0 days, followed by relatively lower copper loss. The exponential fit is provided to illustrate the difficulty in describing this data using a single non-linear relationship. This section discusses the way in which various environmental variables affect copper loss rates from ACQ-B treated wood. Piecemeal regression will eventually be used to model copper losses from ACQ-B treated wood.

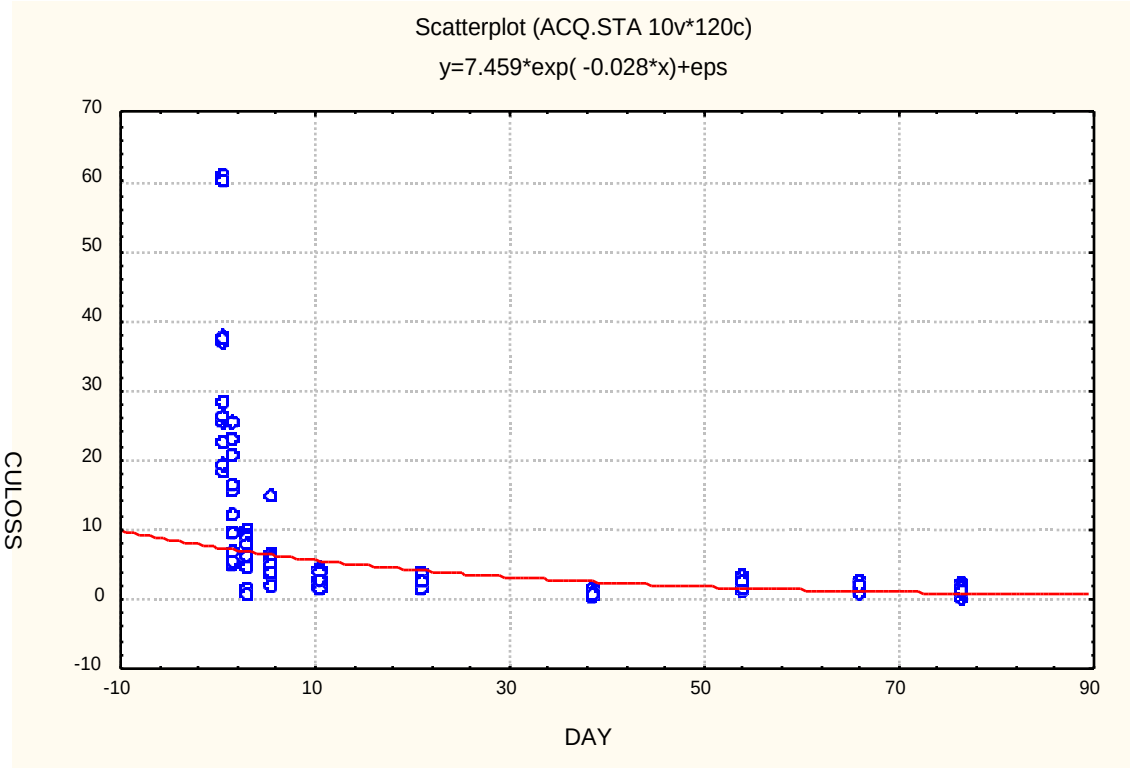


Figure 3. Copper loss as a function of time (µg/cm^2/day) from southern yellow pine poles, treated to 0.4 pcf with ACQ-B preservative and leached into 10 to 12 liters of distilled water amended to a pH of 5.0, 6.5 or 8.0 and in saltwater (30 ppm) at pH 8.0. Data from Jin (1997).

Environmental pH effects. In general, the loss of copper from other waterborne preservatives in dependent on pH effects. Brooks (1997a) provides an assessment of the effects of pH on copper loss from ACZA treated wood and Brooks (1997c) discusses this same issue for CCA-C treated wood. Figure (4) provides a scatterplot describing copper loss (in µg/cm^2/day) from southern yellow pine pressure treated with ACQ-B to a retention of 0.4 pcf and leached at pH values of 5.0, 6.5 and 8.0. There is an apparent decrease in variability with increasing pH. This

suggests either that either the surficial deposits described in the previous section are more easily dissolved at higher pH, or that small scale differences in wood characteristic create physicochemical conditions leading to variability in copper loss as a function of pH. The first alternative appears more likely because the sections were cut from the same poles and were large enough to average out at least small scale differences in wood characteristics. As will be seen, differences in copper loss associated with pH were significant at $\alpha = 0.05$.

Salinity effects. Copper loss rates were determined at salinity's of 0.0 and 30.0 parts per thousand in this study. A scatterplot describing the results for pH = 8.0 is provided in Figure (5). At a retention of 0.4 pcf, salinity was not a significant parameter in determining copper loss and was not included in the regression analysis. It should be noted that AWPA (1996) requires a retention of 2.5 pcf ACQ-B for southern yellow pine immersed in saltwater and therefore, this risk assessment is not intended for marine uses.

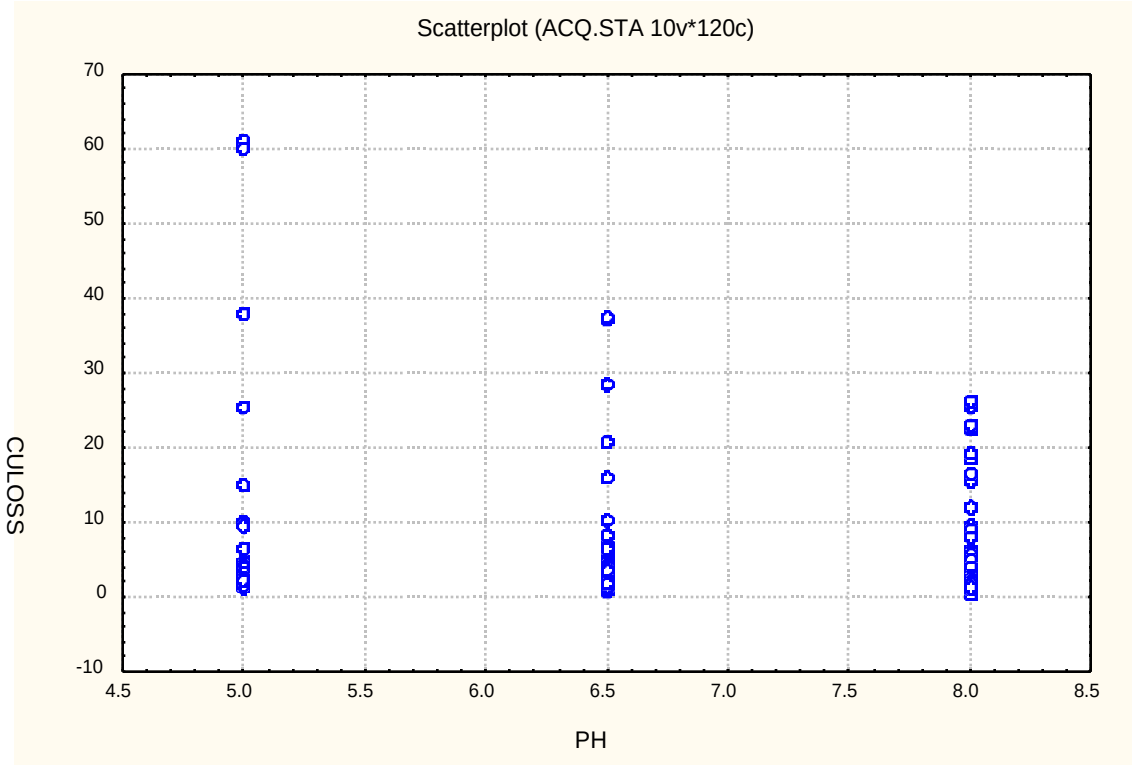


Figure 4. Copper loss as a function of pH ($\mu g/cm^2/day$) from southern yellow pine poles, treated to 0.4 pcf with ACQ-B preservative, and leached into 10 to 12 liters of fresh, distilled water amended to a pH of 5.0, 6.5 or 8.0 and in saltwater (30 ppm) at pH 8.0. Data from Jin (1997).

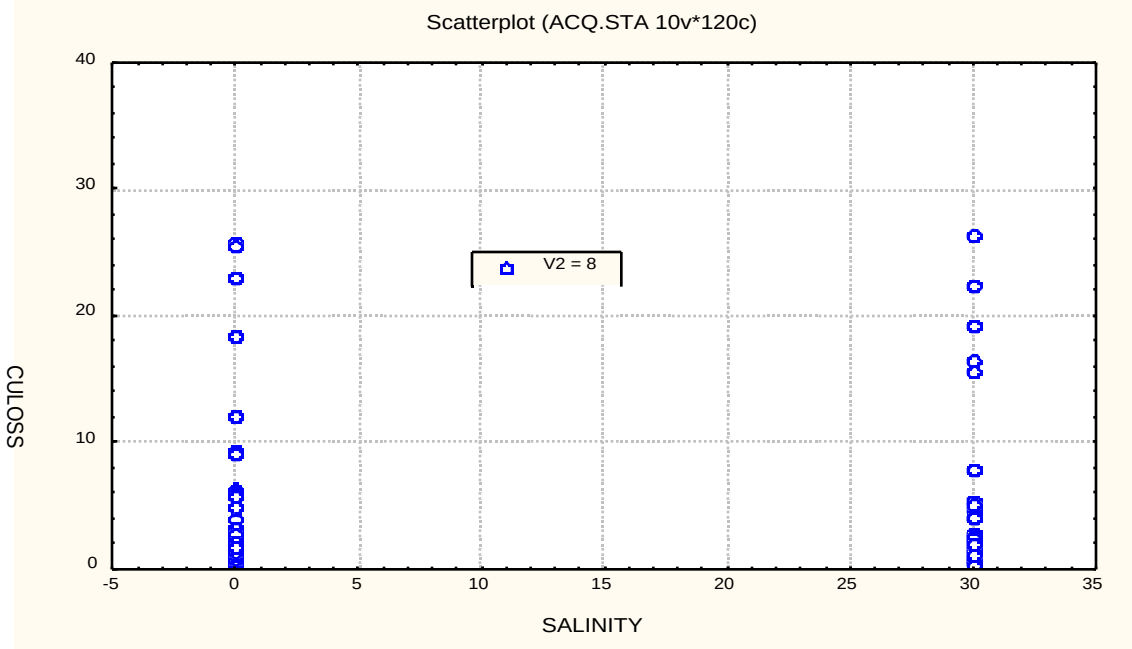


Figure 5. Copper loss (μg/cm^2/day) from southern yellow pine poles, treated to 0.4 pcf with ACQ-B preservative and leached into either freshwater (salinity = 0.0) or seawater (salinity = 30 g/L). Data from Jin (1997)

Combined temporal and pH effects. The data provided by Jin (1997) was subjected to non-linear regression analysis with of immersion and pH as independent factors. The resulting relationship is defined in Equation (3) and described in Figure (6).

Equation (3). Square root (Copper loss (μg/cm^2/day)) = 1.42 + 14.6 x exp$^{(-0.58x\ day\ -\ 0.14\ x\ pH)}$

The given regression explains 85% of the variation in the database and all of the coefficients are highly significant ($P < 0.0000$). A square root transformation of the dependent variable was necessary in order to meet the underlying assumptions for regression analysis (normally distributed residuals and homoscedasticity). This relationship is described in Figure (6).

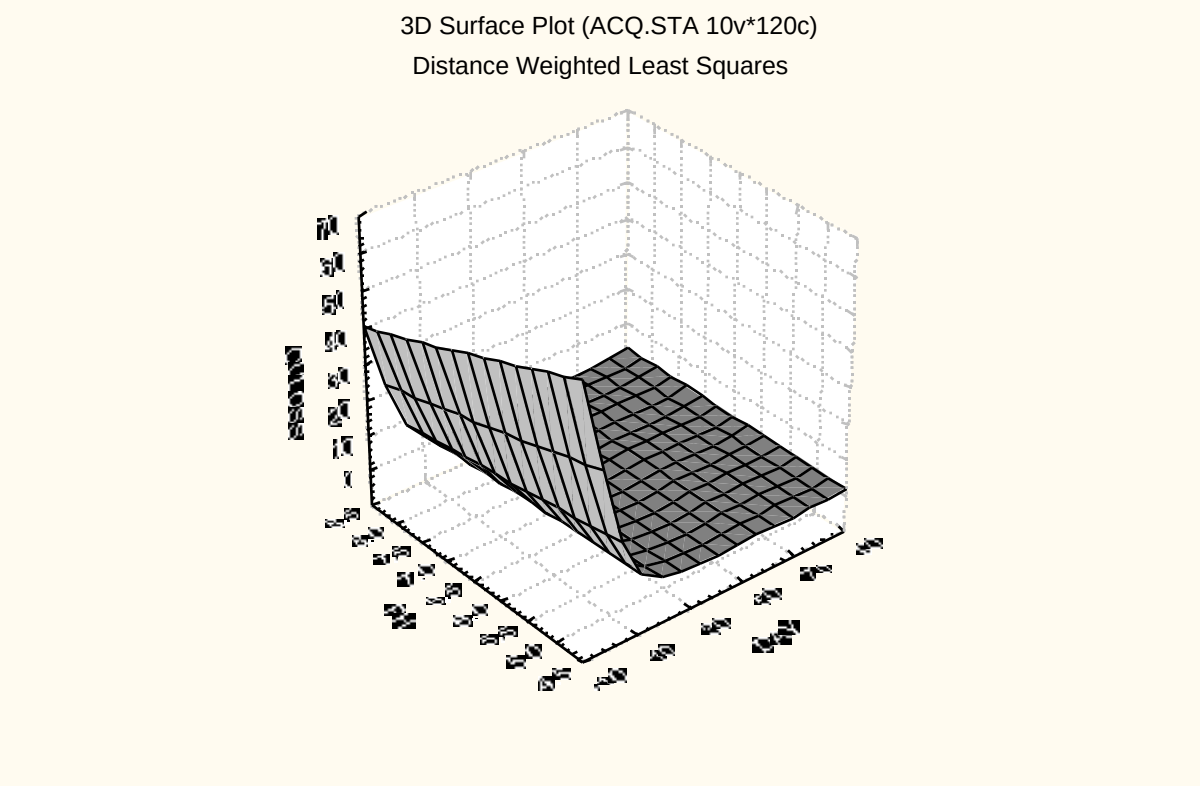


Figure 6. Copper loss (μg/cm²/day) as a function of time and pH from southern yellow pine poles, treated to 0.4 pcf with ACQ-B preservative and leached into freshwater at pH values of 5.0, 6.5 and 8.0. Data from Jin (1997)

It is apparent in the data and in Figure (6) that the influence of pH is confined primarily to the initial leaching period (first 5.5 days) and that pH effects are not apparent beyond 5.5 days. This is substantiated by regression on a database in which day was restricted to >5.5 and where the probability that the coefficient on pH was equal to zero, increased to $p = 0.258$ which is not significant.

Summary of environmental effects describing the loss of copper from ACQ-B preservative. At a retention of 0.4 pcf, salinity is not a significant factor affecting copper losses from ACQ-B preserved wood. These results indicate that near-term copper loss is a function of both time and pH. At immersion times greater than 5.5 days, pH is no longer a significant factor and copper losses are only a function of time.

Environmental factors affecting the loss of DDAC from ACQ-B treated wood. Figure (7) describes DDAC losses in $\mu g/cm^2/day$ as a function of time at all pH and salinity values tested. Initial losses decline very quickly and are near zero within three days. The fitted exponential relationship is that which was eventually used to model DDAC losses from ACQ-B treated wood at 0.4 pcf when used in freshwater.

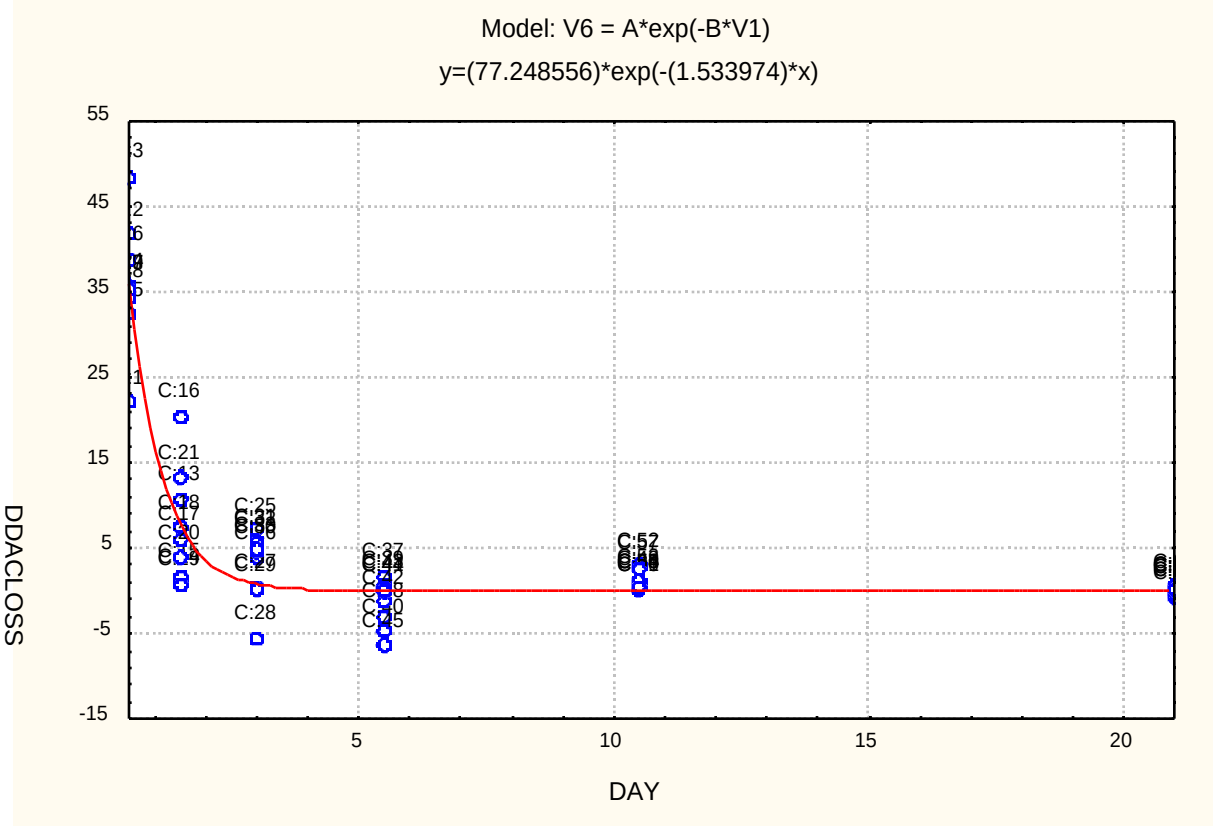


Figure 7. DDAC losses from 0.4 pcf ACQ-B treated southern yellow pine as a function of time at pH = 5.0, 6.5 and 8.0 and at salinities of 0.0 and 30.00 ppt. Data from Jin (1997).

DDAC loss as a function of pH. DDAC losses were not a function of pH (P = 0.996) at the environmentally realistic values tested by Jin (1997) and was not included as a parameter in developing the final DDAC loss algorithm. Losses, expressed as a function of pH for all values of time and salinity are provided in Figure (8).

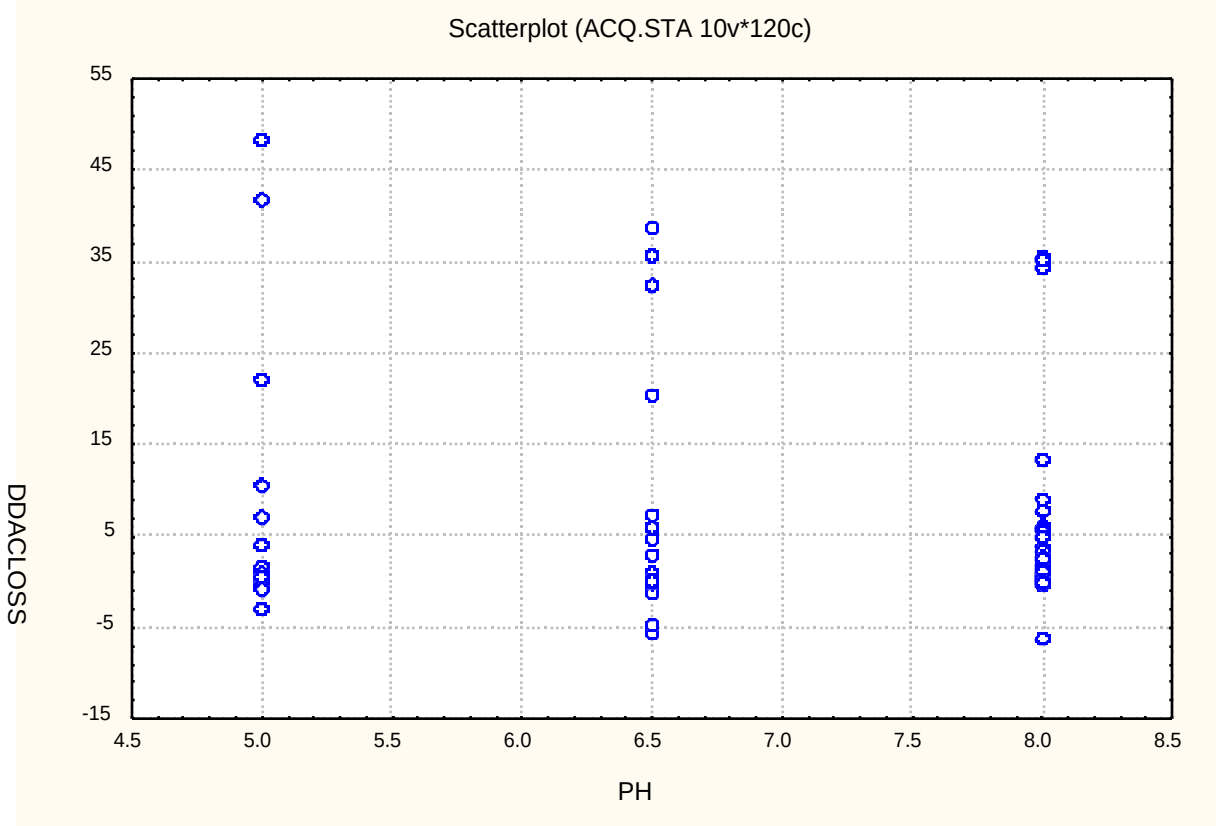


Figure 8. DDAC losses from 0.4 pcf ACQ-B treated southern yellow pine as a function of pH at values of 5.0, 6.5 and 8.0 for all times and salinities reported in Jin (1997).

DDAC loss as a function of salinity. DDAC was negatively correlated with salinity (decreasing DDAC loss with increasing salinity). However, the correlation was not significant and linear regression analysis (only two values for the independent variable) indicated a nonsignificant coefficient (P = 0.12). Salinity was not included in the final algorithm describing DDAC loss from ACQ-B treated wood. The results provided in Jin (1997) are described in Figure (9).

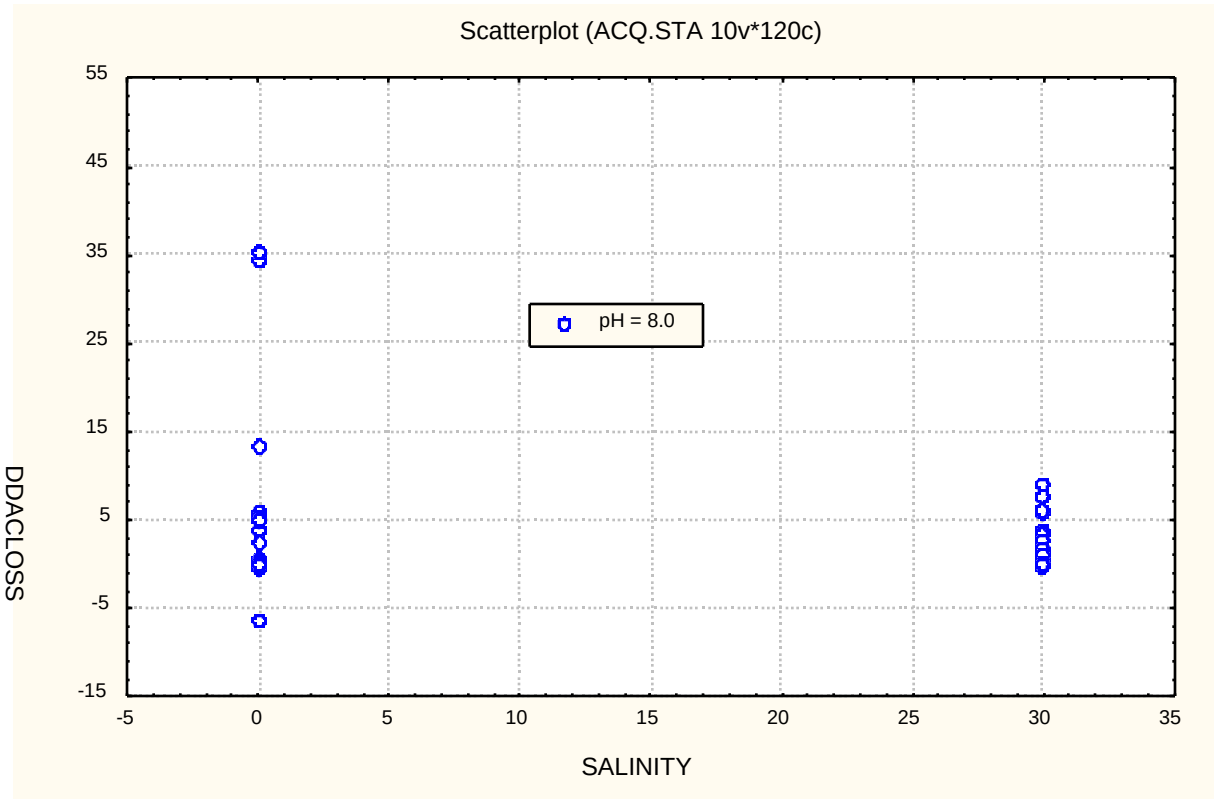


Figure 9. DDAC losses from 0.4 pcf ACQ-B treated southern yellow pine as a function of salinity at a pH value of 8.0 for all times reported in Jin (1997).

Leaching of copper and DDAC from 0.4 pcf, ACQ-B treated southern yellow pine used in fresh water. Because of the apparent discontinuity in the copper loss data described in Figure (3), the copper loss algorithm was developed using piecemeal regression. The break was at 4.5 days. Equation (4) defines the algorithm used in this risk assessment to describe copper losses during the first 4.5 days. This equation is valid for pH values between 5.0 and 8.0 and for times between 0.5 and 4.5 days. This relationship will be used to compare maximum copper concentrations in the water column within 2 cm of the treated wood on the first day of immersion with the EPA chronic criteria (Equation (2) to assess the environmental suitability associated with ACQ-B preservative use in a specific project.

Equation (4). Copper loss ($\mu g/cm^2/day$) for days < 4.5 = 265.14 x $exp^{(-0.924 \text{ x day} - 0.239 \text{ x pH})}$

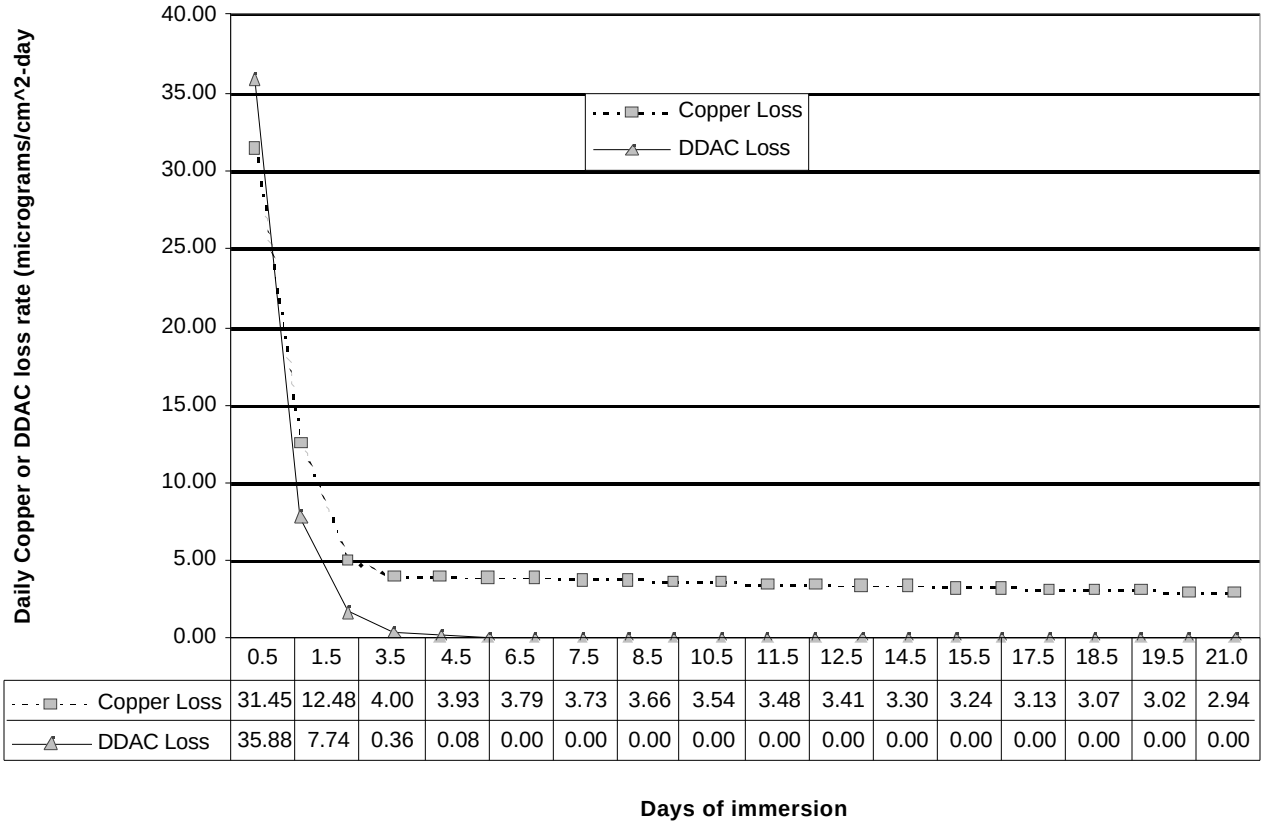
Copper losses at times greater than 4.5 days are described by the relationship given in Equation (5).

Equation (5). Copper loss ($\mu g/cm^2/day$) for days $\geq$ 4.5 = 4.25 x $exp^{-0.0175 \text{ x day}}$

DDAC losses are predicted by the single algorithm provided in Equation (6).

Equation (6). DDAC loss ($\mu g/cm^2/day$) = 77.24856 x $exp^{-1.534 \times day}$

Predicted copper and DDAC loss rates ($\mu g/cm^2/day$) from 0.4 pcf ACQ-B treated southern yellow pine are summarized in Figure (10). These algorithms will be used as a basis for this risk assessment.



	0.5	1.5	3.5	4.5	6.5	7.5	8.5	10.5	11.5	12.5	14.5	15.5	17.5	18.5	19.5	21.0
Copper Loss	31.45	12.48	4.00	3.93	3.79	3.73	3.66	3.54	3.48	3.41	3.30	3.24	3.13	3.07	3.02	2.94
DDAC Loss	35.88	7.74	0.36	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Figure 10. Summary of predicted copper and DDAC losses in $\mu g/cm^2/day$ from 0.4 pcf, ACQ-B treated southern yellow pine in receiving water with a pH of 7.0.

Preservative loss from overhead structures. Rainfall, leaching studies appropriate for assessing copper and DDAC losses from overhead structures, decks, etc., were not available. However, the loss rates described in Figure (10) can be used to estimate risks until appropriate data are available.

The leaching rates estimated by Equations (4) (5) and (6) provide a means of estimating the final environmental concentrations of copper and DDAC associated with the use of ACQ-B treated wood products. Three Microsoft EXCEL™ based spreadsheet models are presented in the following sections. The first describes anticipated levels of copper resulting from the use of ACQ-B treated piling installed in streams, rivers and lakes. The second predicts water column and sediment levels of copper and DDAC associated with large surface area wood structures such as bulkheads. The third is appropriate for assessing risks associated with ACQ-B preserved piling used in freshwater that is influenced by both steady state and tidal currents.

Risk Assessment Part I. Anticipated environmental levels of copper and DDAC resulting from the use of 0.4 pcf ACQ-B treated wood in freshwater environments dominated by steady state currents. This model can be used to assess the environmental risks associated with the use of ACQ-B treated wood used in freshwaters not influenced by tidal currents such as upland streams and lakes and rivers at elevations above those where water levels are influenced by the tides. The following assumptions have been made in constructing the model.

i. that the volume of the receiving water is large (> 400 square meters per piling) in comparison with the total amount of preservative being considered.

ii. that detoxification processes due to natural chelation, complexation and sedimentation are long compared with the speed of the current and uptake by aquatic organisms. This conclusion leads to an assumption that DDAC remains in its most toxic form. In fact, natural processes may very quickly detoxify the DDAC.

iii. that released copper and DDAC adsorbs to the heavy clay fraction of the suspended particulate load with a vertical settling velocity of 5×10^{-3} cm/sec.

iv. copper and DDAC concentrations in the water column are determined in the immediate vicinity of the piling or bulkhead. No allowances are made for turbulent mixing or diffusion.

v. that copper accumulates in sediments and remains there for an infinite period of time. This ignores bedload movements in streams and or burial by new sediments.

vi. that there is no additional sedimentation around the piling. The addition of new sediment would reduce the concentration of accumulated copper or DDAC.

vii. Bioturbation typically homogenizes the upper three to ten centimeters of the sediment column. This biological activity redistributes surface deposited contaminants throughout the bioturbed sediment column – reducing the concentration. The assumption will be made that copper and DDAC are distributed only within the upper 2.0 cm of the sediment column.

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 have been designed to provide a worst case analysis. Predicted preservative levels in the water column are the maxima observed within a centimeter of the piling. At all other distances, the copper or DDAC levels will be significantly reduced.

Water column concentrations of copper and DDAC lost from piling in fresh or brackish water environments dominated by steady state currents. A conservative model for copper or DDAC concentrations in lotic systems assumes that preservative lost from a piling are diluted in a column of water defined by the current speed and the diameter of the pile. The following equation defines such a dilution volume after converting velocities from centimeters per second to centimeters per day to correspond with the algorithm used to define preservative migration rates.

$$\text{Dilution volume} = 2R_p V_{ss} 86{,}400$$

Where: R_p = the radius of the piling (cm)
V_{ss} = the current speed (cm/sec)
86,400 = number of seconds in one day

The dilution zone is not a function of the depth of water because we assume that currents are equal at all depths. Therefore the preservative lost from an incremental piling height is diluted in an incrementally high volume of water defined by the piling diameter and steady state current speed. Combining this dilution volume with the predicted preservative migration rate developed in Equations (4), (5) and (6) gives a conservative prediction of the water column concentration of copper or DDAC associated with an ACQ-B treated piling. This risk assessment is for the maximum predicted copper concentrations, which occur during the first day (Day = 0.5) and therefore Equations (4) and (6) are appropriate.

$$DDAC_{Water\ Conc.} = (2BR_p \times 77.25 \times \exp^{-1.534 \times day})/2R_pV_{ss}86{,}400$$

$$Copper_{Water\ Column} = (2BR_p \times 265.14 \times \exp^{-0.924 \times day - 0.239 \times pH})/2R_pV_{ss}86{,}400$$

Simplifying these equations leads to the following expressions describing the concentration of DDAC and copper in the water column in the immediate vicinity of the piling (within one or two centimeters).

Equation (7) $\mathbf{DDAC_{Water\ Conc} = (0.002809 \times \exp^{-1.534 \times day})/ V_{ss}}$

Equation (8) $\mathbf{Copper_{Water\ Column} = (0.009641 \times \exp^{-0.924 \times day - 0.239 \times pH})/ V_{ss}}$

Deposition rates of copper and DDAC to sediments in freshwater streams and rivers. The models presented in Brooks (1995a, 1995b and 1995c) were optimized for poorly circulated marine environments where harmonically driven tidal currents interact with weak steady state currents. The dilution algorithms for these models are modified in the following paragraphs to provide more accurate predictions in lotic systems. This dilution model assumes that water is passing a piling with constant velocity. Turbulence associated with the piling creates the geometry described in Figure (11).

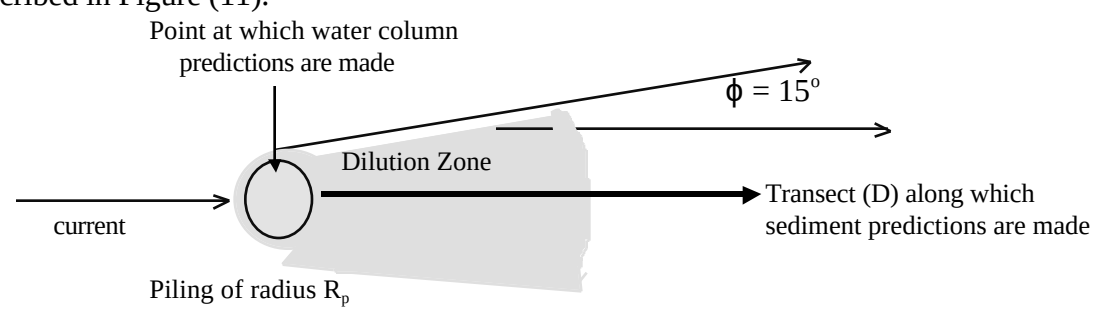


Figure 11. Dilution zone geometry used to predict copper and preservative concentrations in sediments associated with the use of 0.4 pcf ACQ-B, preserved southern yellow pine.

In this model we let $dA = 2R_p dD + 2D\phi dD$, where

dA = the incremental area
R_p = radius of the piling
dD = the incremental distance along transect D
ϕ = the angle representing turbulent mixing = 15° = 0.2618 radians

Simplifying, we obtain $dA = 2(R_p + 0.2618D)dD$. Note that $D = h(V_{ss}/V_v)$ and therefore $dD = (V_{ss}/V_v)dh$, where V_{ss} is the steady state current speed and V_v is the vertical velocity of clay to which the copper of DDAC is adsorbed. Both are expressed in cm/sec. The expression then becomes:

$$DA/dh = 2(R_p + 0.2618D)V_{ss}/V_v$$

This is combined with the appropriate expression describing the copper or DDAC loss per square centimeter per day (m), giving an expression for the sediment deposition of preservative components.

$$\text{Deposition} = M/dA = \pi R_p m/[(R_p + 0.2618D)(V_{ss}/V_v)dh]$$

This expression can be further simplified by substituting $h = DV_v/V_{ss}$ to obtain the final form of the algorithm describing sediment deposition of copper or DDAC in $\mu g\text{-}cm^{-2}day^{-1}$.

$$\text{Deposition } (\mu g\text{-}cm^{-2}day^{-1})/dh = \pi R_p m V_v/[(R_p + 0.2618D)V_{ss}]$$

The sediment deposition rate of copper or DDAC is predicted by substituting the dilution algorithm with the preservative loss rates (m) developed earlier.

$$\text{Copper deposition rate for days} < 4.5 = \pi R_p V_v \text{ x } 265.14 \text{ x } \exp^{(-0.924 \text{ x day} - 0.239 \text{ x pH})} /[(R_p + 0.2618D)V_{ss}]$$

$$\text{Copper deposition rate for days} \geq 4.5 = \pi R_p V_v \text{ x } 4.25 \text{ x } \exp^{(-0.0175 \text{ x day})} /[(R_p + 0.2618D)V_{ss}]$$

$$\text{DDAC deposition rate} = \pi R_p \text{ x } V_v \text{ x } 77.25 \text{ x } \exp^{(-1.53 \text{ x day})} /[(R_p + 0.2618D)V_{ss}]$$

It should be noted that the immersed length of the piling is not a parameter in this relationship. The reason is that we assume that the current speed (V_{ss}) and clay-copper complex settling velocity (V_{ss}) are constant. Furthermore, we assume there is no turbulent mixing and that the sediment surface is a flat plane. Therefore, a one-centimeter height of immersed piling contributes copper or DDAC to an area defined by the relationship

Equation ( ) $\text{Depositional distance} = V_{ss}dh/V_v$

V_{ss} is the steady state current speed;
dh is the incremental height on the piling;
V_v is the settling velocity of the clay particle = 0.005 cm/sec. See Part II of this risk assessment for a more complete discussion describing the determination of appropriate values for V_v)

Accumulation of copper in freshwater sediments. Copper is an immutable element that does not degrade in sediments. If sedimented copper were to move downstream with the bedload, then the second law of thermodynamics suggests that concentrations would decrease, not increase. In this risk assessment, it is assumed that the copper remains in the immediate vicinity of the piling and that those concentrations are not mediated by the addition of new sediment. The accumulation of copper, as a function of distance from the piling, can be obtained by integrating the near term copper loss algorithm from time = 0.0 to 4.5 days and adding the result to the long term copper loss algorithm integrated from 4.5 days to infinity.

$$\text{Copper accumulation/dh} = \int_{t=0}^{t=4.5} \mu\pi R_p V_v \text{ x } 265.14 \text{ x } \exp^{(-0.924 \text{ x day} - 0.239 \text{ x pH})}/[(R_p + 0.2618D)V_{ss}]dt$$

plus

$$\text{Copper accumulation/dh} = \int_{t=4.5}^{t=4} \mu\pi R_p V_v \text{ x } 4.25 \text{ x } \exp^{(-0.0175 \text{ x day})}/[(R_p + 0.2618D)V_{ss}]dt$$

$$\text{Total Copper accumulation/dh } (\mu g/cm^2) = \beta R_p V_{ss}(225.28 + 282.46 \times \exp^{-0.239 \times pH}) / [(R_p + 0.2618D)V_{ss}]$$

There is an obvious flaw in this methodology because over an infinite period of time, all of the copper would be lost from the piling and that value is independent of the receiving water pH. However, most treated wood projects will last for a maximum of perhaps 75 years and all of the copper will not have leached out of the piling. The pH factor was left in the equation because it relates to the rate at which copper is added to the sediments. Piling placed in areas of low pH will lose more copper to the sediments during the anticipated maximum life span of a project.

The copper is assumed to be bioturbed into the upper two centimeters of a sediment column whose dry density is Δ. Equation (9) describes the sediment copper concentration algorithm used in this risk assessment. The units are in micrograms of copper per cubic centimeter of dry sediment in the upper two centimeters of the sediment column.

Equation (9) Copper conc.(μg Cu/cm^3 dry sediment) = $R_p V_{ss}(353.87 + 443.69 \times \exp^{-0.239 \times pH}) / [\Delta(R_p + 0.2618D)V_{ss}]$

Accumulation of DDAC in sediments. As described in Equation (6) and Figure (10), the DDAC loss rate decreases rapidly with very low losses after the first several days. Seven days following immersion of the ACQ-B preserved wood, the DDAC loss is only 0.002 $\mu g/cm^2$ or about 0.00006 times the first day's loss. DDAC degrades in microbially active sediments with an apparent half-life of approximately 14 to 49 days (Schoenig, 1997). The length of the pulse of DDAC is short in comparison with the half-life and therefore no long term accumulations of DDAC in sediments are anticipated. This risk assessment is based on the accumulation of DDAC in sediments over an infinite period of time. Because the DDAC loss time is short, sediment concentrations will quickly peak within a few weeks and because the half-life is short, they will then quickly degrade. Following the first week of immersion, sedimented DDAC concentrations will rapidly decline by a factor of 2.7 to 32 within ten weeks. For these reasons, no correction is made for microbial degradation in this assessment.

Integrating Equation (6) from $t = 0$ to $t = 4$ and substituting the result into the expression for deposition the predicted DDAC concentration in sediments.

$$\text{DDAC concentration} = \mu\pi R_p V_v \times 77.25 \times \int_{t=0}^{t=4} \exp^{(-1.534 \times day)} / [2\Delta(R_p + 0.2618D)V_{ss}]dt$$

Equation (10) DDAC concentration = $\beta 79.07 R_p V_v / [\Delta(R_p + 0.2618D)V_{ss}]$ in mg DDAC/kg

Predictive computer model for 0.4 pcf ACQ-B preserved wood used in freshwater environments with steady state current speeds. The results of the preceding analysis have been incorporated into a *Microsoft EXCEL for Windows*™ spreadsheet. Copies of the files are enclosed in the pocket at the back of this document. The following paragraphs provide specific definitions and instructions.

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

User Entry	Value
1. Preservative retention (kg/m^3)	6.2
2. Average Piling Radius (cm)	**User entry**
3. Piling Age In Days	**User entry normally = 0.5**

4. Salinity (parts per thousand, ppt)	0.0
5. Settling Velocity (0.05 for silt; 0.0005 for clay in cm/sec)	0.005
6. Average Maximum Tidal Speed (cm/sec)	0.0
7. Steady State Current Speed (cm/sec, measured at slack tide)	**User entry**
8. Marine Sediment Copper Quality Standard (mg/kg)	390 ppm
9. Freshwater Sediment Copper Benchmark (mg/kg)	**User entry**
10. Freshwater Chronic Copper Standard (μg/L)	$\exp^{(0.8545*\lvert\ln(\text{hardness})\rvert - 1.465)}$
11. Water Hardness (mg $CaCO_3$/L)	**User entry**
12. Marine Water Copper Standard (μg/L)	3.11
13. Sediment Density (g/cm^3)	**User entry**
14. Water column background copper concentration (μg/L)	**User entry**
15. Sediment background copper concentration (μg/g)	**User entry**
16. Freshwater pH	**User entry**
17. Freshwater and marine water DDAC benchmark (μg/L)	49
18. Freshwater and marine sediment DDAC benchmark (mg/kg)	10

Notes:

1. Treated wood retention in kilograms-m^{-3}. AWPA defines minimum ACQ-B retention's to insure adequate performance. AWPA Standards (1996) require retention's of 40 kg-m^{-3} for piling and lumber submerged in marine environments, and 6.2 kg-m^{-3} for southern yellow pine and hemlock-fir used in direct contact with fresh water. This risk assessment is only for use with an ACQ-B retention of 6.2 kg/m^3 in freshwater.

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

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

The radius of Class A piling will typically range between 10 and 20 centimeters. Unless the project specifies larger or smaller piling, a value of 15 cm is recommended.

3. Treated wood age in days. Enter the time since immersion, in days. For newly constructed projects, this should be 0.5. Predictions of water column copper and DDAC concentrations will be for 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 26 to 30 ppt. Fresh water has a nominal salinity of 0.0 ppt. Salinity in estuaries influenced by major rivers can vary significantly between 3 or 4 ppt and 24 to 26 ppt. Contact the local Sea Grant Office for an accurate site specific estimate. For preliminary evaluations use the following values:

Fresh Water	**Salinity = 0.0 ppt**
Marine Water	**Salinity = 30 ppt**
Estuarine Water	**Salinity = 15 ppt**

5. Settling Velocity refers to the vertical velocity of suspended sediment to which copper and DDAC are likely to adsorb (silt and clay). This model assumes that metals are adsorbed to heavy clay and that the settling velocity is 0.005 cm/sec. If a sediment grain size analysis shows significant clay content (>60%) and high total organic carbon (TOC), then it might be appropriate to reduce this value to 0.0005 cm/sec. 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 0.005 cm/sec be used. This will give a conservative (from the environment's point of view) estimate.

6. Average Maximum Tidal Speed. This risk assessment model is for freshwater influenced only by steady state currents. A separate model is provided for environments where tidal currents affect water speeds. This entry should equal zero.

7. Steady State Current Speed (cm/sec). For purposes of this freshwater model, steady state currents should be consistent with those expected during construction of the project. Absent predictive data, take three measurement of current speed at mid depth using a window shade drogue or current meter and calculate the mean.

8. Marine Sediment Copper Quality Standard (mg/kg). Enter the jurisdictional marine 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).

9. Freshwater Sediment Copper Benchmark (mg/kg). Use an appropriate jurisdictional sediment quality standard or select the most appropriate benchmark from the following recommendations.

Physicochemical Characteristics	**Sedimented Copper Benchmark**
1. Coarse grained sediment (silt & clay <10%) Total Organic Carbon < 0.5% Moderate to low pH (5.5 to 6.5) Low hardness and alkalinity (25 to 35 ppm $CaCO_3$)	35 µg Cu/g dry sediment
2. Intermediate sediments (silt & clay between 10% and 25%) Total Organic Carbon between 0.5% and 1.5% Neutral pH (6.5 to 7.5) Moderate hardness and alkalinity (35 to 100 ppm $CaCO_3$)	65 µg Cu/g dry sediment
3. Low energy, well buffered streams and lakes (fines > 25%) Total Organic Carbon >1.25% Greater than neutral pH (pH > 7.5) High hardness and alkalinity (> 100 ppm $CaCO_3$)	100 µg Cu/g dry sediment

10. Fresh water, chronic, copper standard (µg/L). The U.S. EPA provides both chronic and acute copper standards for freshwater. 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 EPA chronic copper standard is used in this model because significant decreases in copper losses from newly installed ACQ-B treated wood occur within a matter of days, not hours. The chronic standard is a function of water hardness measured as the calcium and magnesium salts present in water. For purposes of this standard, hardness is measured in milligrams per liter of calcium carbonate ($CaCO_3$). The standard is determined using Equation (2).

Equation (2). Fresh Water Quality Standard = $0.960 \times \exp^{(0.8545*|\ln(\text{hardness})| - 1.465)}$

11. Water Hardness (mg $CaCO_3$/L) . Water hardness is measured as the calcium and magnesium salts present in a sample of water. It is expressed as mg $CaCO_3$/L.

12. Marine Water Copper Standard. The U.S. EPA marine water quality standard for copper is 3.11 µg/L.

13. Sediment Density (grams-cm^{-3}). This value may vary depending on the composition of the sediment. For depositional sediments, values of 1.6 to 1.8 are appropriate. In coarse sediments higher values of 1.8 to 2.4 may be appropriate. Users may use alternate values.

14. Water column background copper concentration (µg/L). Enter either a measured value or one available from local, state or federal databases.

15. Sediment background copper concentration (µg/g). Enter either a measured value or one available from local, state or federal databases. Only the top two centimeters of the sediment column should be analyzed to determine this value. The literature review conducted in support of the risk assessment suggests that the 0.1 M $NH_2OH.HCl$ + 0.01 M HNO_3, pH = 2 extraction, conducted at room temperature for 30 minutes (See Chao, 1972) is most appropriate for determining biologically available copper in sediments. This or a similarly aggressive procedure is recommended for determining background levels of bioavailable copper.

16. Water pH. This value should be an anticipated average during the season (spring, summer, winter, fall) in which construction is anticipated.

17. Freshwater and marine water DDAC benchmark (µg/L). This risk assessment relies on a value of 49 µg DDAC/L as an interim water quality benchmark.

18. Fresh and marine sediment DDAC benchmark (mg/kg). A value of 10 mg DDAC/kg dry sediment, measured in the upper two centimeters of the sediment column, is used as a benchmark in this risk assessment.

Model output. A copy of the computer model printout is provided in Figure (12). Predictions made in this output are for a single southern yellow pine pilling treated to 0.4 pcf with ACQ-B. Predictions are for the day of installation in freshwater flowing at a very slow steady state rate of 0.35 cm/sec. The pH in this water is low at 5.5, the hardness is 50 ppm ($CaCO_3$) and the salinity is 0.0 (freshwater). At the stated level of hardness, the U.S. EPA chronic freshwater copper standard is 6.28 µg Cu/L. With these physicochemical conditions, we have chosen a low sediment copper benchmark of 35 µg Cu/g dry sediment. Model predictions are added to a measured background of 20 µg Cu/g dry sediment and 1.55 µg Cu/L of water. The DDAC water benchmark of 49 µg DDAC/L and sediment benchmark of 10 mg DDAC/g dry sediment weight are used to assess environmental risks. It should be noted that the modeled environment, while not the worst possible case, does represent a realistic near worst case. In most areas of the U.S. excepting perhaps the northeast and high mountain streams, background pH and hardness are likely much higher.

Figure 12. Copper and DDAC Accumulation in Water and Sediments Associated with the use of ACQ Treated Piling

User Entries

1. Retention in kilograms per cubic meter	6.24
2. Average piling radius (centimeters)	15.00
3. Piling Age in Days	0.50
4. Salinity (parts per thousand, ppt)	0.00
5. Settling Velocity (0.05 for silt; 0.00005 for clay)	0.005
6. Average Maximum Tidal Velocity	0.00
7. Steady State Currents (measured at slack tide)	0.30

Intermediate Output

	Cu (Day ≤ 3.0)	Cu (Day > 3.0)	DDAC
Migration (migr/cm2-day)	44.95	4.22	35.83
Mixing Width (cm)	0.00	0.00	0.00
Model Velocity (cm/sec)	0.36	0.36	0.36

Water column Cu & DDAC concentrations

8. Marine Sediment Copper Quality Standard (ppm)	390.00			
9. Freshwater Sediment Copper Benchmark	35.00		**Tidal Flows**	
10. Fresh Water, Chronic, Copper Standard	6.28		**Copper ≤ 3 d**	**DDAC**
11. Water hardness (ppm CaCO3)	50.00	Water Conc. (ppb)		
12. Marine Water Copper Standard	2.90	Marine Water Standard	2.9	49.0
13. Sediment Density (grams/cubic centimeter)	1.3	Fresh Water Standard	6.3	49.0
14. Water background copper concentration (ng/ml)	1.55			
15. Sediment background copper (mg/kg)	20		**Steady state flow (including background)**	
16. Freshwater pH	5.50	Contribution from ACQ	4.59	3.658
17. Fresh and marine water DDAC benchmark (ng/ml)	49.00	Background	1.55	0
18. Fresh and marine sediment DDAC benchmark (mg/kg)	10.00	Total Metal or DDAC	6.14	3.658
		Predicted/EPA Stand.	0.98	0.07

Predicted Sediment copper and DDAC concentrations in micrograms/cm^3 or ppm
The copper concentration includes the background entered in User Input 15

Distance	Cu Accumulation	DDAC Accumulation	Copper Concentration (With Background)	DDAC Concentration	Predicted Sediment Cu concentration /Freshwater Sediment Benchmark	
					With background	Without Background
400	1.245	0.44	20.35	0.12		
375	1.317	0.46	20.37	0.13	0.58	0.010
350	1.398	0.49	20.39	0.14	0.58	0.011
325	0.489	0.52	20.41	0.15	0.58	0.012
300	1.593	0.56	20.44	0.16	0.58	0.013
275	1.713	0.60	20.48	0.17	0.59	0.014
250	1.852	0.65	20.51	0.18	0.59	0.015
225	2.017	0.71	20.56	0.20	0.59	0.016
200	2.212	0.78	20.61	0.22	0.59	0.018
175	2.451	0.86	20.68	0.24	0.59	0.019
150	2.746	0.96	20.76	0.27	0.59	0.022
125	3.123	1.10	20.87	0.30	0.60	0.025
100	3.619	1.27	21.01	0.35	0.60	0.029
75	4.303	1.51	21.20	0.42	0.61	0.034
50	5.305	1.86	21.47	0.52	0.61	0.042
25	6.917	2.43	21.92	0.67	0.63	0.055
10	8.459	2.97	22.35	0.82	0.64	0.067
25	6.917	2.43	21.92	0.67	0.63	0.055
50	5.305	1.86	21.47	0.52	0.61	0.042
75	4.303	1.51	21.20	0.42	0.61	0.034

The intermediate output indicates that under the described conditions, the copper loss rate will be 44.95 µg/cm^2 on the first day of immersion. This value is unusually high because of the low receiving water pH (5.5) chosen for the example. DDAC loss is predicted to be 35.83 µg DDAC/L.

The model predicts that the ACQ-B treated piling will add 44.95 µg Cu/L to the water column within a centimeter of the piling. This contribution is added to the background level to give a total copper concentration of 6.14 µg Cu/L. This concentration is slightly less than the EPA copper standard (6.28 µg Cu/L) at the stated hardness of 50 ppm ($CaCO_3$).

Sedimented copper concentrations, as a function of distance from the perimeter of the piling, are provided in the lower section of the output. Under the worst case conditions described in this output, the ACQ-B treated piling will increase sedimented copper by 2.35 µg Cu/g dry sediment within 10 centimeters of the piling (four inches). The point that should be made is that ACQ-B preserved piling will contribute only very small amounts of copper to sediments in the immediate

vicinity of the project. In addition, it should be noted that under the conditions used to produce this output, the water column concentration of copper is near the U.S. EPA limit and the piling is contributing an insignificant amount of copper to the sediments. This suggests that when water column copper concentrations are maintained within the U.S. EPA criterion, sedimented copper is not a problem. To test this hypothesis, a hardness of 400 mg $CaCO_3$/L, a pH of 8.0, and a background copper level of 60 µg Cu/g dry sediment was tested in the model. In this case, a current speed of only 0.03 cm/sec was required to meet the EPA freshwater criterion. Under those conditions, the piling added an additional 27.88 µg Cu/kg to the sediments at a distance of 10 cm from the piling's perimeter. This increased the total sediment copper burden to 87.88 mg Cu/kg dry sediment. However, the sediment copper benchmark invoked in this risk assessment for these environmental conditions, allows a maximum of 100 µg Cu/g dry sediment. Once again suggesting that if water column concentrations of copper are maintained within EPA limits – even at extremely slow current speeds - then the addition of copper to sediments is unlikely to cause adverse biological effects. It should be stated that there are impacted bodies of water where sediments already carry copper loads high enough to create adverse biological effects. The addition of any copper to these waters would only exacerbate the existing condition.

This piling will also create a DDAC concentration of 3.66 µg DDAC/L in water at the surface of the piling. No background DDAC was measured and none should be expected in nearly all installations not adjacent to sewage treatment plant or industrial outfalls. This concentration is only eight percent of the DDAC benchmark (the NOEL for *Daphnia magna*). Under these worst case conditions, the maximum predicted sediment concentration of DDAC (0.82 mg DDAC/kg dry sediment) is less than ten percent of the sediment DDAC benchmark (10 mg DDAC/kg). The important point is that under all scenarios investigated, where copper concentrations are maintained within the EPA freshwater criterion, DDAC concentrations in the water column and/or sediments were well below a level associated with biological effects as were levels of sedimented copper immediately adjacent to the piling.

ACQ-B projects proposed for small, closed, bodies of water such as ponds. The copper migration rate at pH = 7.0 was integrated from zero to infinity to determine the total copper lost from a 1.0 cm high "slice" of 0.4 pcf ACQ-B preserved piling. The result indicates that over the life of the piling, a total of 0.0267 grams of copper will be lost from each one centimeter height of immersed piling. If we assume that all of that copper remains in the water column and is evenly diluted within the one cm high "slice" of water by mechanical mixing (rainfall, faunal activity, wind, etc.) and diffusion, then it will take 3,979 liters of dilution water to meet the U.S. EPA chronic copper standard of 6.7 µg Cu/L at 55 mg $CaCO_3$/kg hardness. At a water depth of one centimeter, it takes 398 square meters to equal 3,979 liters of water. Therefore, for each piling immersed in such a pond, 398 square meters of surface area or 0.097 acres per piling is needed. That is ten piling per acre of pond – assuming that the pond's depths are equal everywhere. In fact, piers, etc. are frequently placed in the shallow parts of the pond and the total pond volume is likely much larger than would be determined by measuring the length of immersed piling and the surface area. Most of this copper will likely end up in the sediments – decreasing the water column concentration. As a point of interest, if all of the copper released from ten piling, submerged to a depth of 3 meters in a pond having a sediment surface area of 3,980 m^2 were mixed into the upper two centimeters of sediment with density equal to 1.8 grams/cm^3, the sediment concentration would be increased by 0.000001 µg Cu/g dry sediment.

Summary for the use of 0.4 pcf ACQ-B preserved southern yellow pine in freshwater and evaluation of generalized risks. This risk assessment is designed to provide site and project specific assessments. However, based on the examination of a broad range of typical conditions, the following general statements can be made:

1. If water column concentrations of copper, immediately adjacent to the piling, are maintained at levels below the U.S. EPA chronic freshwater copper standard, then only very small amounts of copper will be added to sediments. These small additions must be summed with background sediment copper levels to assess risks. Freshwater sediment quality standards were not available for this risk assessment. However, three sediment benchmarks have been proposed until standards are developed. These benchmarks are keyed to environmental physicochemical parameters including water hardness and pH and sediment grain size and total organic carbon. They range from 35 µg Cu/kg dry sediment in soft water with low pH and coarse sediments to 100 µg Cu/kg dry sediment in hard water with pH above 7.5 and sediments rich in silt, clay, and total organic carbon.

2. Based on this analysis, it appears that DDAC, lost from 0.4 pcf ACQ-B preserved wood has no significant potential to effect biological resources when water column concentrations of copper are maintained below the U.S. EPA chronic freshwater copper standard.

3. In typical applications (pH > 7.0, hardness > 75 mg ($CaCO_3$)/kg , background water column copper < 1.5 µg Cu/L), a minimum current speed of 0.5 cm/sec is required to insure that water column concentrations immediately adjacent to the piling are not exceeded. If a row of piling is placed adjacent to each other in a line parallel to the currents, the minimum current speeds required to meet the EPA chronic standard are given in Table (20). This is obviously a worst case analysis since piling are seldom placed immediately adjacent to each other in a line parallel to the currents. More typically, in a pier or wharf project, piling would be spaced two to three meters apart and would not fall in a line parallel to the currents. This worst case analysis suggests that for a typical residential dock, with two opposing piling supporting the dock, a minimum current speed of 0.3 cm/sec is required during the first day to meet the EPA standard. Copper losses from ACQ-B preserved piling fall rapidly and should reach undetectable concentrations in nearly all piling applications within a week or two.

Table 20. Minimum current speeds required to meet the U.S. EPA chronic copper standard at hardness = 75 mg/kg ($CaCO_3$), water pH = 7.0 and with a background copper level of 1.5 µg/L as a function of the number of piling placed immediately adjacent to each other in a line parallel to the currents.

Number of piling paralleling the currents	Minimum required current speed
1.00	0.2
2.00	0.3
3.00	0.5
4.00	0.6
5.00	0.8
6.00	0.9
7.00	1.1
8.00	1.2
9.00	1.4
10.00	1.5

Hardness = 75.00 mg $CaCO_3$/L
Water pH = 7.00
Background Copper = 1.50 µg/L

The Corps of Engineers (1996) has taken a different approach in conducting a Biological Assessment (BA) for the use of treated wood in the lower Columbia River used by several endangered stocks of salmon. The Corps of Engineers (1996) used a box model to evaluate the biological risk to Columbia River resources posed by the construction of ACZA treated structures

containing 24, 100 and 350 piling. Physicochemical conditions used in the assessment were conservatively determined from available monitoring data. This BA assumed that background copper was 2.0 μg/L, hardness = 50 mg/kg and pH = 7.5. Copper loss from ACZA is similar to that for ACQ-B and some insight can be gained from the proposed Biological Assessment. The Corps of Engineers (1996) found that when current speeds exceeded 0.3 cm/sec, projects involving 24 or fewer ACZA treated piling should not be expected to adversely effect aquatic resources. Projects involving 100 or fewer piling should not require further review when current speeds exceed 1.0 cm/sec and projects involving 350 pilings should not require further review when current speeds exceed 10 cm/sec.

Based on the analysis included in the Columbia River BA and this risk assessment, it appears that projects involving fewer than 100 piling, installed in moving water, have little potential to adversely effect aquatic resources. Projects involving more than 100 piling should require an individual risk assessment, as should ACQ-B projects, involving more than 10 piling per acre of surface area, proposed for construction in small ponds or lakes. It should be noted that the COE recommendations on the use of treated wood in the lower Columbia River were less restrictive than are the recommendations made in Brooks (1997a, 1997b or 1997c). This author's recommendations are:

1. Projects installed in areas where currents are less than 0.5 cm/sec in densities exceeding ten piling per surface acre should require an individual risk assessment using this or a similar model.

2. Projects involving fewer than 100 piling can be permitted without additional risk assessment when current speeds are $\geq$ 1.0 cm/sec.

3. Projects involving more than 100 piling should be required to complete an individual risk assessment. These risk assessment documents are free and the cost for gathering data is small.

4. Projects in areas known to have elevated background concentrations of copper (>50 μg Cu/kg sediment or more than 2.5 μg Cu/L) should be required to complete an individual risk assessment.

Risk Assessment Part II. Anticipated environmental levels of copper resulting from the use of 0.4 pcf ACQ-B treated piling used in constructing large surface area projects, such as bulkheads (ACQbrisk.xls). Significant quantities of treated wood may come into contact with water when sawn lumber is used to construct bulkheads. The possible length of these bulkheads and low water circulation found in some residential canals suggest that this application may represent a worst case use, deserving special consideration. Copper loss rates from ACQ-B treated wood will be modeled as before. There is an assumption that copper loss from sawn lumber is equivalent to that reported by Jin (1997) for piling. This assessment is for a newly installed bulkhead of length *l*. The following assumptions have been made in constructing the model.

i. that the volume of the receiving water is large in comparison with the total amount of ACQ-B preserved wood being immersed. As previously described, the surface area of the receiving freshwater should be greater than 400 square meters per piling. Because marine organisms are more sensitive to copper, ACQ-B piling placed in estuaries should meet the marine copper standard of 3.11 μg Cu/L. This requires that the receiving water surface area cover at least 857 square meters per installed piling. This standard would be appropriate where piers are constructed in tidal lagoons with very poor flushing rates (<< one per day).

ii. that detoxification processes due to natural chelation, complexation and sedimentation are long compared with the speed of the current and uptake by aquatic organisms

iii. that released copper adsorbs to the heavy clay fraction of the suspended particulate load and that that these adsorption nuclei settle with a velocity of 0.005 cm/sec. Critics might argue that in some environments, there is little suspended particulate organic or inorganic matter to act as adsorption nuclei. They may be true. However, the result would be that the copper remains in solution or that it complexes with dissolved organic matter (DOM). In either case, the result would be significant reductions in the predicted sediment concentrations because the copper would be dispersed over a much larger area due to the very slow settling velocity.

iv. for determining water column concentrations of copper, it is assumed that all of the copper released from the treated wood remains in the water column. For determining sediment concentrations of copper, it is assumed that all of the copper released from the treated wood is deposited in the sediments.

v. this assessment can be used in freshwater influenced by tidal currents as well as steady state currents.

Currents. Currents in tidally influenced estuaries may extend well into the region dominated by fresh or brackish water. They 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 model is used to include tidal currents in this analysis. We assume that tidal flows are harmonic with a frequency of 12 hours. The instantaneous tidal current can be modeled by the harmonic:

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

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

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

where $V_{maximum}$ is measured in cm/sec 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 dominated by tidal currents.

In addition, three replicate measurements of water speed should be taken at mid depth and the mean used as a measurement of the steady state current speed. In areas influenced by both steady state and tidal currents, these measurements should be made at slack tide. We will refer to this steady state speed as V_{ss}.

The "Distance" developed in this analysis is the average distance that a particle is carried, by the tides, in one direction, before its velocity is reversed and it is carried back toward the point of origin (source). The average tidally driven velocity is $0.64V_{maximum}$ (3.82 hours/6 hours). The appropriate velocity to be used in this model (cm/sec) can then be determined using Equation (11). This procedure will integrate the effects of both steady state and tidal currents influencing a site at the time the measurements are taken.

Equation (11). $\mathbf{V_{model} = V_{ss} + 0.64*V_{maximum}}$

Lumber surface area leaching ratio applicable to bulkhead construction. 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 2" x 6" board, the total leaching surface is 2.54 x the area of one side of the larger face. 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^2/cm^2 of exposed face. These ratios are somewhat small for 2" x 8" and larger boards. For purposes of this model, it is assumed 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 (12). 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 (12). $\mathbf{Surface\ Area\ Leaching\ Ratio = 1.84\ exp^{-0.01346 \times Board\ Width\ (cm))}}$

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 specific 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:

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

Transit time in this equation can be replaced with an equivalent expression:

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

Substituting this into the previous expression and simplifying gives Equation (13).

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

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

Water column concentrations of copper associated with large surface area projects such as bulkheads treated with ACQ-B preservative. 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 Water Concentration = Copper Migration Rate (μg per second) x Exposure Time x Leaching Surface Ratio/Mixing Width

where exposure time = bulkhead length/V_{model}

$$\text{Copper Water Concentration} = 265.13 \times \exp^{-0.924 \times \text{days} - 0.239 \times \text{pH}} \times 1.84 \exp^{-0.01346 \times \text{Board Width (cm)}} / (86{,}400 \times 2.5 \times 10^{-3} \times (V_{ss} + 0.64(V_{maximum} - V_{ss}))^2)$$

or, after converting this to μg/L ($x10^3$), we obtain Equation (14).

Equation (14) $$\textbf{Copper Water Concentration} = 2259.960 \times \exp^{-0.924 \text{ days} - 0.239 \text{ pH} - 0.01346 \text{ Board Width (cm)}} / (V_{ss} + 0.64(V_{maximum} - V_{ss}))^2$$

Note that this expression assumes that the water depth out to the edge of the Mixing Width is constant. Vertical mixing would further dilute metal losses associated with bulkheads located on relatively steep shorelines. No vertical mixing is assumed in this model. In addition, no metal losses to sediment are accounted for in the expression. This seems reasonable because the times associated with water transport along even long bulkheads (100 meters) by slow currents (5 cm/sec) are short (2,000 seconds) in comparison with vertical velocities (0.005 cm/sec) for heavy clay adsorption nuclei. An adsorbed copper molecule would settle an average of 10.0 cm during transit along a 100 meter long bulkhead at 5 cm/sec, suggesting that the copper remains in the water column – albeit likely bound to organic or inorganic particles.

Sediment concentrations of copper associated with the use of 0.4 pcf ACQ-B treated lumber in bulkheads. This bulkhead model will assume that copper is lost from dimension lumber at the rates previously determined for piling. The lost copper is assumed to adsorb to suspended heavy clay. The fate of the adsorbed copper is then determined by examining the fate of the suspended heavy clay particles. In real environments, significant quantities of the copper may remain solubilized in the water column and/or become adsorbed to finer clay fractions or particulate organic matter. Copper associated with smaller grain sizes will be distributed over larger areas at much lower concentrations than predicted here. For that reason these predictions are considered conservative from a 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 $\text{Velocity}_{model} + \text{Velocity}_{mixing}$ where we assume that the two vectors are orthogonal. Velocity_{mixing} is determined from Equation (15) and equals:

Equation (15) $$\textbf{Velocity}_{mixing} = 2.5 \times 10^{-3} \times (\textbf{Velocity}_{model})^2$$

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

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

An additional correction must to included in the relationship to describe the aspect ratio of the leaching area to the area of deposition. This Aspect Ratio Correction Factor (ARCF) is:

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

If we assume that the settling copper is distributed over an area equal to ARCF x $Velocity_{verticle}/Velocity_{horizontal,}$ then we can model copper deposition to the sediments in the following manner:

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

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

or $$Deposition_{copper} = (265.13 \times \exp^{-0.924 \times days - 0.239 \times pH} \times 1.84 \exp^{-0.01346 \times \text{Board Width (cm)}}) \times \text{bulkhead length} \times Velocity_{verticle} / [86{,}400 \times \{6.25 \times 10^{-6} \times (Velocity_{model})^4 + (Velocity_{model})^2\}^{1/2} \times \{\sin(\tan^{-1}(Velocity_{mixing}/Velocity_{model}))\}]$$ (μg Cu/cm²/day for the first 4.5 days)

This expression is appropriate for the first 4.5 days of immersion. A similar relationship is required to model copper deposition after the first 4.5 days:

$$Deposition_{copper} = (4.25 \times \exp^{-0.0175 \times days} \times 1.84 \exp^{-0.01346 \times \text{Board Width (cm)}}) \times \text{bulkhead length} \times Velocity_{verticle} / [86{,}400 \times \{6.25 \times 10^{-6} \times (Velocity_{model})^4 + (Velocity_{model})^2\}^{1/2} \times \{\sin(\tan^{-1}(Velocity_{mixing}/Velocity_{model}))\}]$$ (μg Cu/cm²/day after the first 4.5 days)

Assuming that $6.25 \times 10^{-6} \times Velocity_{model}{}^4$ is << 1 for small current speeds representing worst case conditions; and simplifying these equations, we obtain the final form of the sediment deposition model.

Equation (16) $$\mathbf{Deposition_{(days < 4.5)} = 0.0056 \times \exp^{-0.924 \times days - 0.239 \times pH - 0.01346 \times \text{Board Width}} \times \text{bulkhead length} \times Velocity_{verticle} / (Velocity_{model} \times \sin(\tan^{-1}(2.5 \times 10^{-3} \times Velocity_{model}))}$$

and

$$\mathbf{Deposition_{(days \geq 4.5)} = 0.000091 \times \exp^{-0.0175 \times days}) - 0.01346 \times \text{Board Width}} \times \text{bulkhead length} \times Velocity_{verticle} / (Velocity_{model} \times \sin(\tan^{-1}(2.5 \times 10^{-3} \times Velocity_{model}))}$$

Copper Accumulation. 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 ACQ-B treated structure will remain in the bioturbed top two centimeters of the sediment column. The total copper accumulated in the sediments per unit of immersed piling height can be obtained by integrating Equations (16) over the periods of time for which they are each appropriate leading to Equation (17).

Eq. (17) $$\mathbf{Accumulation_{(Cu\ in\ seds)} = (225.28 + 282.46 \times \exp^{-0.239 \times pH}) \times 1.84 \times \exp^{-0.01346 \times \text{Board Width (cm)}}}$$

x bulkhead length x $Velocity_{verticle}$ /(86,400 x ($Velocity_{model}$ x sin($\tan^{-1}$(2.5x10^{-3} x $Velocity_{model}$))))

Predicted concentrations of copper in the water column and sediments associated with the use of 0.4 pcf ACQ-B treated lumber used to construct bulkheads and other large surface area structures in freshwater environments including those influenced by tidal currents. The results of the preceding analysis have been incorporated into a *Microsoft EXCEL for Windows*™ (Version 5.0) spreadsheet. A copy of the file is enclosed in the pocket at the back of this document (ACQbrisk.xls). Figure (13) presents the results of a typical analysis **and the** following paragraphs provide specific definitions and instructions.

Notes for the output from a:ACQbrisk.xls in Figure (13). The basis for this analysis is a newly installed, 100 meter long bulkhead, with 2"x8" ACQ-B treated sheathing, installed in a moderately well flushed (current = 4.0 cm/sec) freshwater environment with hardness = 125 mg/kg and pH = 8.0. The background levels of copper are 1.0 µg/L in the water and 10 mg/kg in the sediments. These physicochemical parameters are assumed to mimic those typical of rivers in the southeastern United States.

Predicted water column copper concentration. The model output predicts copper losses on the first day of 24.69 µg/cm^2/day. This copper is diluted in a mixing width of 100 cm during transit along the length of the bulkhead. On the first day, the project increases the water column concentration by 10.18 µg/L. When added to the background, the predicted water column concentration is just below (11.183 µg/L) the U.S. EPA chronic standard at 12.333 µg Cu/L. Water column predictions for water adjacent to the bulkhead on any given day following immersion can be obtained by entering the day in question in User Entry Number 3. On the second day following construction, the predicted copper concentration associated with the bulkhead is reduced to 2.55 µg/L.

Predicted sediment copper levels. A total of 0.83 mg Cu/kg dry sediment will be added to the upper two centimeters of the sediment column by this bulkhead. This deposition is along the shore to a width equal to the mixing width (100 cm). As in the piling model, sediment concentration predictions are for $t = \infty$. However, measured copper levels will approach predicted concentrations within approximately two weeks.

Waves, bioturbation, and other mechanical disturbances will likely further reduce the predicted sediment burden. In any case, the ACQ-B treated wood is increasing the sediment copper concentration by only a minor amount. As was found with the piling model, as long as the water column concentration of copper is maintained below the EPA chronic standard, ACQ-B treated piling will not add significant amounts of copper to sediments. Sedimented copper associated with these types of projects is only a problem when background levels already exceed an appropriate standard or benchmark.

Generalized risks associated with the use of ACQ-B treated wood in the construction of freshwater bulkheads. Evaluation of these risks under a number of different conditions suggests that water hardness has the greatest influence on the minimum current speeds required to maintain water column copper concentrations less than the U.S. EPA freshwater copper standard. Table (21) assumes a neutral pH (7.0) and a background copper concentration of 2.0 µg Cu/L.

Figure 13. ACQbrisk.xls Copper Losses from 0.4 pcf ACQ-B Treated Bulkheads.

User Entries	
1. Retention in kilograms per cubic meter	6.2
2. Average piling radius (centimeters)	
3. Structure Age in Days	0.5
4. Salinity (parts per thousand, ppt)	0
5. Settling Velocity (0.05 for silt; 0.00005 for clay)	0.005
6. Average Maximum Tidal Velocity	0
7. Steady State Currents (measured at slack tide)	4
8. Marine Sediment Copper Quality Standard (ppm)	390
9. Maximum Marine Sediment Impact Zone Cu Std.	390
10. Fresh Water, Chronic, Copper Standard	12.33
11. Water hardness (ppm CaCO3)	125
12. Marine Water Copper Standard	3.11
13. Sediment Density (grams/cubic centimeter)	1.8
14. Bulkhead Length (cm)	10000
15. Board Width (cm) (2x6 = 14, 2x8 = 19. 2x12 = 29.2)	19
16. Freshwater Sediment Benchmark	100
17. Background water copper concentration (ng/ml)	1.0
18. Background sediment copper concentration (mg/kg)	10
19. Freshwater pH	8.0

Intermediate Output	Day ≤ 4.5	Day > 4.5
Migration (migr/cm2-day)	24.69	4.21
Age Factor	0.98	0.98
Mixing Width (cm)	100.00	100.00
Model Velocity (cm/sec)	4.00	4.00
Geometry Factor	1.40	1.40
Mixing Velocity (cm/sec)	0.04	0.04

Water Copper Cu Conc. Associated with ACQ-B Bulkheads

	without background	with background
Water Conc. (ng/ml)	10.183	11.183
Marine Water Standard	3.110	3.110
Fresh Water Standard	12.333	12.333

Predicted Sediment Copper Levels in micrograms/square cm sediment surface	2.99
Predicted Sediment Copper Concentration (mg/kg in the upper 2 cm of sediment column)	0.83
Predicted Sediment Copper Concentration Including Background (mg/kg)	15.58

Table 21. Minimum current speeds (cm/sec) required to maintain receiving water copper concentrations below the U.S. EPA freshwater chronic copper criteria. This table assumes neutral pH (7.0) and a background copper concentration of 2.0 μg Cu/L. The table is for a bulkhead of any length – assuming that the receiving water volume is large in comparison with the leaching surface area.

Hardness expressed in mg $CaCO_3$/L	Minimum current speed (cm/sec)
25	10
50	7
75	6

100	5
≥125	4

Risk Assessment Part III. Environmental risks associated with the use of 0.4 pcf ACQ-B treated piling in environments influenced by tidal currents (ACQprisk.xls). This risk assessment is appropriate for evaluating the use of 0.4 pcf ACQ-B preserved piling used in environments influenced by tidal (harmonic) currents. The heads of estuaries with strong freshwater influence or river channels located at an elevation where marine tidal currents influence their flow provide examples of situations where this model is appropriate.

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

Sediment Grain Size (SGS) considerations. The clay (< 3 microns) fraction sequesters copper more efficiently than do coarse grained sediments. In addition, sediments containing high proportions of 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 copper) in localized areas.

This model is based on the deposition of copper by following the fate of the silt-clay to which it is adsorbed. A quantitative assessment of this 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 (18).

Equation (18) Stokes law for the settling velocities of small particles:

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

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 copper is adsorbed to heavy clay particles with vertical velocities in sea water (10° C) of 2 x 10^{-2} to 10^{-5} cm/sec. An intermediate value of 5 x 10^{-3} cm/sec will be used in computing clay 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 much more spread out and significantly lower. The EXCEL Spreadsheet includes provisions for user defined settling velocities and this value can easily be changed.

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

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

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

$$\text{Distance} = 3.82\ (\text{hours}) \times V_{maximum} = 1.3752 \times 10^4\ (\text{sec}) \times V_{maximum}$$

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

In situations where local currents are a function of both steady state and tidally driven factors, three current measurements should be taken approximately three hours apart. In addition to the measurements required to determine $V_{maximum}$, the third measurement should be taken at slack tide. This measurement is V_{ss}. The appropriate velocity to be used in this model (cm/sec) can then be determined using Equation 19.

Equation (19). $$\mathbf{V_{model} = V_{ss} + 0.64*V_{maximum}}$$

Diffusion. An examination of potential diffusion constants (D) reveals very low values ($D \sim 1.5 \times 10^{-4}$). Substituting these values into an appropriate diffusion equation, such as Equation (20), suggests that in most open systems, diffusion plays little part in the distribution of copper. The diffusion distances are on the order of a few centimeters per hour, which we expect to be small in comparison with currents and turbulence.

Equation (20). $$\mathbf{C_{(x,t)} = C_o e^{-(x\ exp2)/4Dt}/2(\pi Dt)^{1/2}}$$

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

In the following analysis, it is assumed that copper is deposited in a circular pattern around the construction site. While this might be viewed as unrealistic, worst case scenarios will involve very low current velocities associated with backwaters and eddies. In these environments, horizontal mixing associated with wind driven waves, anthropogenically induced mechanical mixing and shoreline geomorphology may play a significant part in the distribution of suspended material. Therefore, in worst case situations, a circular distribution pattern may very well provide a reasonable assessment of the broad scale distribution of contaminants.

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

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

$dr = [V_{model}/V_{vert}]dh$ where: dh = incremental piling height and V_{vert} = vertical particle velocity (0.005 cm/sec for heavy clay)

The distance from the periphery of the pile at which particles impact the bottom is $r = h(V_{model}/V_{vert})$ and therefore,

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

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

$$\text{Deposition (D)} = M/dA = m2\pi R_p dh / 2\pi[h(V_{model}/V_{vert}) + R_p](V_{model}/V_{vert})dh$$

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

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

Equation (21). $\mathbf{D = mR_p/[(r + R_p)(V_{model}/V_{vert})]}$

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

Risk assessment model for piling used in freshwater areas influenced by tidal currents. This dilution geometry has been combined with the copper loss algorithms developed earlier to produce a Microsoft Excel™ spreadsheet based computer model (ACQprisk.xls).

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

User Entry	Value
1. Retention In Kilograms/Cubic Meter	6.2
2. Average Piling Radius (Centimeters)	User Entry
3. Treated Wood Age In Days	User Entry
4. Salinity (parts per thousand, ppt)	User Entry
5. Settling Velocity (0.05 for silt; 0.0005 for clay in cm/sec)	0.005
6. Average Maximum Tidal Speed (cm/sec)	User Entry
7. Steady State Current Speed (cm/sec, measured at slack tide)	User Entry
8. Marine Sediment Copper Quality Standard (mg/kg)	390
9. Freshwater sediment benchmark (mg/kg)	User Entry
10. Fresh Water, Chronic, Copper Standard ($\mu g/L$)	$\exp^{(0.8545*\lvert\ln(\text{hardness})\rvert - 1.465)}$
11. Water Hardness (mg/kg $CaCO_3$)	User Entry
12. Marine Water Copper Standard ($\mu g/L$)	3.11
13. Sediment Density (grams/cubic centimeter)	2.2 grams-cm^{-3}
14. Freshwater pH	User Entry
15. Background water column copper concentration ($\mu g/L$)	User Entry

16. Background sediment copper concentration (mg/kg)	User Entry

Notes:

1. Treated wood retention (kg/m^3). AWPA Standards (1996) requires a minimum ACQ-B retention of 6.2 kg/m^3 for southern yellow pine and hemlock-fir piling and lumber in contact with freshwater. This retention applies only to the treated zone which is typically the outer 1.5 inches for southern yellow pine piling and _" for lumber.

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

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

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

3. Treated wood age in days. Enter the time since immersion, in days. For newly constructed projects, this should be 0.5. Predictions of water column copper concentrations will be for the period within half an hour of slack tide on the day identified in this entry.

4. Salinity (parts per thousand). Salinity in open ocean environments is typically 34 ppt. In areas like Puget Sound it is lower at 28 to 30 ppt. Fresh water has a nominal salinity of 0.0 ppt. Salinity in estuaries influenced by major rivers can vary significantly between 2 or 3 ppt and 24 to 26 ppt. Contact your local Sea Grant Office for an accurate estimate. In estuaries, the appropriate value may be very site specific. The following values are recommended for preliminary evaluations where site specific information is not available:

Fresh Water	**Salinity = 0.0 ppt**
Marine Water	**Salinity = 30 ppt**
Estuarine Water	**Salinity = 15 ppt**

5. Settling Velocity (cm/sec) 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 heavy clay with a settling velocity of 0.005 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 0.005 cm/sec be used. This will give a conservative (from the environment's point of view) estimate.

6. Average Maximum Tidal Velocity (cm/sec). 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 (cm/sec 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 (mg/kg). 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. The user can assign alternate standards.

9. Freshwater Sediment Copper Benchmark (mg/kg). Use an appropriate jurisdictional sediment quality standard or select the most appropriate benchmark from the following recommendations.

Physicochemical Characteristics	**Sedimented Copper Benchmark**
1. Coarse grained sediment (silt & clay <10%) Total Organic Carbon < 0.5% Moderate to low pH (5.5 to 6.5) Low hardness and alkalinity (25 to 35 ppm $CaCO_3$)	35 µg Cu/g dry sediment
2. Intermediate sediments (silt & clay between 10% and 25%) Total Organic Carbon between 0.5% and 1.5% Neutral pH (6.5 to 7.5) Moderate hardness and alkalinity (35 to 100 ppm $CaCO_3$)	65 µg Cu/g dry sediment
3. Low energy, well buffered streams and lakes (fines > 25%) Total Organic Carbon >1.25% Greater than neutral pH (pH > 7.5) High hardness and alkalinity (> 100 ppm $CaCO_3$)	100 µg Cu/g dry sediment

10. Fresh water, chronic, copper standard (µg/L). The U.S. EPA defines fresh water copper standards for chronic or acute effects. 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 ACQ-B 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 mg $CaCO_3$/L. The standard is determined using Equation (2).

Equation (2). Freshwater copper chronic standard = $0.960 \times \exp^{(0.8545 \times |.\ln(\text{hardness})| - 1.465)}$

11. Water Hardness (mg $CaCO_3$) . Water hardness is measured as the calcium and magnesium salts present in a sample of water. It is expressed as mg $CaCO_3$/L.

12. Marine Water Copper Standard (µg/L). The U.S. EPA saltwater dissolved copper criterion is 3.11 µg/L in marine environments. Users may enter alternate values.

13. Sediment Density (grams-cm^{-3}). This value may vary depending on the composition of the sediment. For depositional sediments, values of 1.6 to 1.8 are appropriate. In coarse sediments higher values of 1.8 to 2.4 may be appropriate. Users may use alternate values.

14. Water pH. This value should be an anticipated average during the season (spring, summer, winter, fall) in which construction is anticipated.

15. Background water column copper concentration (μg/L). Enter either a measured value or one available from local, state or federal databases.

16. Sediment background copper concentration (μg/g). Enter either a measured value or one available from local, state or federal databases. Only the top two centimeters of the sediment column should be analyzed to determine this value. The literature review conducted in support of the risk assessment suggests that the 0.1 M $NH_2OH.HCl$ + 0.01 M HNO_3, pH = 2 extraction, conducted at room temperature for 30 minutes (See Chao, 1972) is most appropriate for determining biologically available copper in sediments. This or a similarly aggressive procedure is recommended for determining background levels of bioavailable copper.

Recommended model input. When site specific information is not available, the values provided in Table (22) can be used.

Table 22. Recommended input parameters during preliminary evaluations or when specific information is unavailable.

User Entry	Fresh Water	Marine	Estuarine
1. Treated wood retention (kg/m^3)	6.2	Not Recommended	6.2
2. Average piling radius (cm)	15.0		15.0
3. Treated Wood Age (days)	0.5		0.5
4. Salinity (parts per thousand, ppt)	0.0		<5.0
5. Settling Velocity (0.05 for silt; 0.0005 for clay in cm/sec)	0.005		0.005
6. Average maximum Tidal Speed (cm/sec)	0.00		10.0 (north)
			5.0 (south)
7. Steady State Currents (cm/sec measured at slack tide)	5 to 30		2 to 10
8. Marine Sediment Copper Quality Standard (mg/kg)	390		390
9. Freshwater Sediment Benchmark (mg Cu/kg dry sediment)		See Table ( )	
10. Fresh Water, Chronic, Copper Standard	(automatically computed from hardness entry)		
11. Water Hardness (ppm $CaCO_3$)	75		100
12. Marine Water Copper Standard		Not Applicable	
13. Sediment Density (grams/cubic centimeter)	2.0		1.8
14. Water pH	7.5		8.0
15. Board Width (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. Background water column copper concentration (μg/L)	1.5		1.0
17. Background sediment copper concentration (mg/kg)	10.0 in unpolluted areas		

Model Output. Water column copper concentrations associated with ACQ-B treated piling installed in areas influenced by tidal currents. The Microsoft EXCEL ™ spreadsheet (ACQprisk.xls) accompanying this assessment 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.

Water column concentration of copper. By integrating Equation (16) from half an hour before slack tide to half an hour after slack tide, we find that the average tidal speed during

this period is 0.06451 x $V_{maximum}$. Multiplying by a factor of 1,000 to convert from µg/ml to ng/ml and combining this factor with copper leaching rates for Day ≤ 4.5 given in Equation (4), we obtain:

$$\text{Copper Water Concentration (C)} = 1000 \times 265.13 \times \exp^{-0.924 \times \text{days} - 0.239 \times \text{pH}} \times 2\pi R_p / [24(\pi(1800 \times 0.0651 V_{max} + R_p)^2 - R_p^2 + 3600 R_p Vss)]$$

or:

Equation (22) Copper water concentration (C) = $\mathbf{69410.87 \times \exp^{-0.924 \times \text{days} - 0.239 \times \text{pH}} \times R_p / [3.14 \times (117.18 V_{max} + R_p)^2 + 3600 R_p Vss - 3.14 \times R_p^2]}$

Where:

exp = 2.718
time = age of the project in days
R_p = piling radius in centimeters
V_{max} = Maximum Tidal Current Speed
V_{ss} = Steady State Current Speed

This model assumes that the volume of the water body is large in comparison with the total amount of copper lost from the structure. It does not make predictions for small volume, closed water body conditions. These were discussed in Part I of this risk assessment.

Sediment concentrations associated with 0.4 pcf ACQ-B treated piling installed in freshwater areas influenced by tidal currents. 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 ACQ-B preserved wood projects. Algorithms and parameters driving the model are:

1. Copper loss rates from ACQ-B preserved wood are a function of the time following immersion and pH in the short term. The following algorithms for copper loss rates are used in this model. The output is in µg/cm^2-day.

$$\text{Copper Loss (Day} \leq 4.5) = 265.13 \times \exp^{-0.924 \times \text{days} - 0.239 \times \text{pH}} \ (\mu g/cm^2\text{-day})$$

$$\text{Copper Loss (Day} > 4.5) = 4.5 \times \exp^{-0.0175 \times \text{day}} \ (\mu g/cm^2\text{-day})$$

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, copper is assumed to adsorb to heavy clay particles with a settling velocity of 0.005 cm sec^{-1}.

3. Geometric Correction Factor. This model assumes a circular distribution of adsorbed copper around the piling or complex of pilings associated with tidal currents. 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). Equation (23) defines a Geometry Correction Factor that is included in this model. This factor will focus copper accumulation in an increasingly narrow plume, downstream from the structure, as current speeds increase.

Equation (23) Geometry Correction Factor $\mathbf{(1 + V_{model}/10)}$

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 (24) is used to predict copper deposition.

Equation (24) Deposition (D) = $mR_p/[(r + R_p)(V_{model}/V_{vert})]$

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

Sediment copper accumulation model. The above parameters are combined in the following, intuitive manner to give the final form of the model.

Copper accumulation = Geometry Correction Factor x Copper Deposition

Substitution of the previously determined values for each of these parameters gives the final form of the Sediment Copper Accumulation model in Equation 25.

Equation (25) Copper Accumulation = $(1 + V_{model}/10)$ x $(225.28 + 282.46 \times \exp^{(-0.239\ pH)})$ x R_p

$/[(r + R_p) \times (V_{model}/V_{vert})]$

Where:
- $(1 + V_{model}/10)$ = the Geometry Correction Factor
- 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 = ACQ-B 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.
- pH = the pH of the receiving water

There are some limitations to this model. It does not address metal loading to the sediment associated with abrasion of ACQ-B 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, the copper probably has low bioavailability.

Sediment copper accumulation model output (ACQprisk.xls). Tabular output from the spreadsheet is provided in Figure (14). The project involves installation of new 30 cm diameter piling, treated to an ACQ-B retention of 6.2 kg m^3 in a freshwater environment influenced by tidal currents. The area has weak steady state currents of 0.5 cm/sec that are influenced by even weaker tidal currents of 0.20 cm/sec. Water hardness is 75 mg $CaCO_3$/L with a pH of 7.5. There is a background water column copper concentration of 1.0 µg Cu/L and a sediment concentration of 10 mg Cu/kg dry sediment. The sediment density is 1.8 grams/cm^3. Based on the previous evaluation,

a sediment benchmark of 100 mg Cu/kg dry sediment has been assigned and the U.S. EPA freshwater chronic copper standard at 75 mg/kg is 8.88 μg Cu/L.

Intermediate Output is located in the upper right hand corner of Figure (14). On the first day of installation, these piling are predicted to loose 27.82 μg Cu/cm^2 of immersed, preserved, wood surface. The model velocity is 0.63 cm/sec and the Geometry Factor is increasing the copper concentration in sediments located under downcurrent transecting by a factor of 1.06.

Water column concentrations of copper. The model predicts that the water column concentration of copper within a centimeter of the piling will be increased by 1.89 μg Cu/L. when added to the background, the total copper concentration will be 2.89 μg/L. This is lower than the marine standard and 33% of the U.S. EPA freshwater chronic standard. Within three days, water column concentrations of copper associated only with the treated contribution will decrease to 0.07 μg Cu/L which would likely be undetectable within the natural variability.

Sediment concentrations of copper. Consistent with the previously presented steady state and bulkhead models, these piling contribute only small amounts of copper to the sediments. The accumulated copper increases background levels by 0.38 μg Cu/kg dry sediment in the upper two centimeters of the sediment column. The output is presented for two piling placed 3.75 meters apart (perimeter to perimeter) or 4.00 meters apart (center to center). The contribution from each piling is added to predict the "Total Copper Accumulation" which is then corrected for sediment density to produce a total copper concentration for the two piling (Cu Conc (ppm). In the next column, the piling contribution is added to the background and the total can be compared with the chosen Benchmark. The last column provides the ratio of predicted sediment concentration: benchmark. Values in this column exceeding 1.0 indicate that predicted levels (including the background) exceed the Benchmark. In this case, sedimented copper from the two piling are having a negligible effect on sediment concentrations and the maximum increases of 4.1 percent are likely within the background variability.

Figure 14. Tabular input and output from the Microsoft EXCEL ™ spreadsheet A:\ACQPrisk.

Risk assessment for 0.4 pcf ACQ-B preserved wood used in freshwater influenced by tidal currents

User Entries	
1. Retention in kg/m^3	6.20
2. Average piling radius (cm)	15.00
3. Piling Age in Days	0.50
4. Salinity (parts per thousand, ppt)	0.00
5. Settling Velocity (0.05 for silt; 0.00005 for clay in cm/sec)	0.005
6. Average Maximum Tidal Velocity (cm/sec)	0.20
7. Steady State Currents (measured at slack tide in cm/sec)	0.50
8. Marine Sediment Copper Quality Standard (mg/kg)	390.00
9. Freshwater sediment benchmark (mg/kg)	100.00
10. Freshwater chronic copper standard (ng/ml)	8.88
11. Water hardness (mg CaCO3/kg)	75.00
12. Marine Water Copper Standard (ng/ml)	3.11
13. Sediment Density (grams/cubic centimeter)	1.8
14. Freshwater pH	7.5
15. Background water column copper concentration (ng/L)	1.0
16. Background sediment copper concentration (mg/kg)	10.00

Intermediate Output	
Migration for Days ≤ (migr Cu/cm2-day)	27.82
Age Factor	0.98
Mixing Width (cm)	0.01
Model Velocity (cm/sec)	0.63
Geometry Factor	1.00

Water Column Copper Concentration Associated With ACQ-B Treated Piling	For Days ≤ 4.5
Water conc. Without background (ng Cu/ml)	3.54
Water conc. with background (ng Cu/ml)	4.54
Marine water standard (ng Cu/ml)	3.11
Freshwater standard (ng Cu/ml)	8.88

Predicted sediment copper levels mg/kg dry sediment in the upper 2.0 cm of the sediment column

Distance	Accumulation P1	Accumulation P2	Total Copper Accumulation	Cu Conc. (mg/kg)	Concentration With Background	Sediment Benchmark	Predicted/ Benchmark
400	0.08	0.86	0.95	0.26	10.26	100.00	0.1026
375	0.09	1.38	1.47	0.41	10.41	100.00	0.1041
350	0.09	0.86	0.96	0.27	10.27	100.00	0.1027
325	0.10	0.53	0.63	0.18	10.18	100.00	0.1018
300	0.11	0.38	0.49	0.14	10.14	100.00	0.1014
275	0.12	0.30	0.42	0.12	10.12	100.00	0.1012
250	0.13	0.25	0.38	0.10	10.10	100.00	0.1010
225	0.14	0.21	0.35	0.10	10.10	100.00	0.1010
200	0.16	0.18	0.34	0.10	10.10	100.00	0.1010
175	0.18	0.16	0.34	0.10	10.10	100.00	0.1010
150	0.21	0.14	0.35	0.10	10.10	100.00	0.1010
125	0.25	0.13	0.38	0.10	10.10	100.00	0.1010
100	0.30	0.12	0.42	0.12	10.12	100.00	0.1012
75	0.38	0.11	0.49	0.14	10.14	100.00	0.1014
50	0.53	0.10	0.63	0.18	10.18	100.00	0.1018
25	0.86	0.09	0.96	0.27	10.27	100.00	0.1027
10	1.38	0.09	1.47	0.41	10.41	100.00	0.1041
25	0.86	0.08	0.95	0.26	10.26	100.00	0.1026
50	0.53	0.08	0.61	0.17	10.17	100.00	0.1017
75	0.38	0.07	0.46	0.13	10.13	100.00	0.1013
100	0.30	0.07	0.37	0.10	10.10	100.00	0.1010

Water column and sediment concentrations of DDAC. Didecyldimethylammonium chloride (DDAC) concentrations in all of these applications were far less than toxic thresholds

when copper is properly managed. For a review of this subject, see part one of this risk assessment.

Abrasion of ACQ-B treated wood piling. It should be noted that piling can be subjected to abrasion when they are allowed to come into direct contact with boats, float rings, debris, etc. This risk assessment does not address this mechanical abrasion because it is difficult to predict. It is fairly easy to protect piling from abrasion using half-inch thick high-density polyethylene strips installed down the length of the piling to serve as wearing surfaces. An example of this type of protection is provided in Figure (15).

The installation of these bumper strips will not only improve the environmental performance of preserved piling, they will also extend the life of the piling because once the piling's preserved shell is breached by abrasion, the interior wood structure becomes available to fungi and boring organisms.

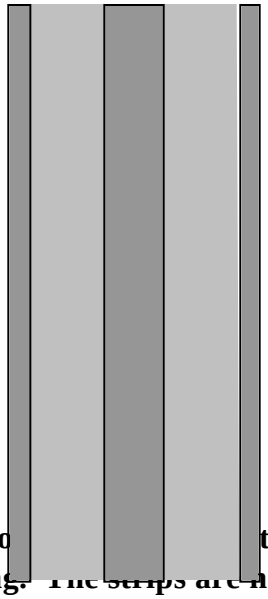


Figure 15. Use o trips of high density polyethylene to reduce abrasion on wooden piling. The strips are nailed every six to eight inches using galvanized nails driven slightly below the surface of the bumper.

Treatment of complex structures. There is an endless variety of placements for ACQ-B treated wood in actual structures. Output from the A:\ACQPrisk.xls model will consider the accumulation from a single pile, along a line between two piling and as the sum of the contributions from a specified number of piling at a point common to all of them. The following paragraphs suggest ways in which the model can be used to predict sediment accumulations 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. A larger (by a factor of $\pi/2$) surface area will be exposed on the perimeter of the dolphin. Copper accumulation around the perimeter of such a structure can be estimated by inputting the radius of the structure in User Input # 2 (Average pilling radius multiplied by $\pi/2 = 1.57$). The anticipated copper accumulation, as a function of distance from the dolphin, can then be read directly. Actual copper accumulation in sediments will probably be negligible in the near field because of mechanical disturbance by the ferry. In this instance, near field, estimates will be too high and far field estimates too low. However, the model will provide insight into the problem.

Pier Structures. The contribution from any number of piling at any point on the benthos can be determined by measuring the distance of the structural member from the point of interest. Determine the sediment accumulation or concentration from the spreadsheet at the measured distance. The sum of all structural components at that point represents the predicted sediment concentrations.

General recommendations for the use of 0.4 pcf ACQ-B preserved southern yellow pine or hem-fir piling used in freshwater environments influenced by tidal currents. In general, ACQ-B treated wood requires only very slow currents in order to maintain water column concentrations of copper at less than the U.S. EPA chronic water quality criteria. Table (23) was constructed with an assumption of neutral pH. Where pH values are > 7.0, slower currents will be required and at lower pH values, higher currents. The background was assumed to be 1.0 µg Cu/L. Minimum values of the *Model Velocity* corresponding to a range of water hardness values are presented in Table (23). Recall that the *Model Velocity* is the sum of steady state and maximum tidal current speeds. In this evaluation maximum tidal and steady state current speeds were assumed to be equal. The U.S. EPA chronic copper criteria are provided at each hardness. Even at 25 mg $CaCO_3$/L, the model velocity required is low at 0.62 cm/sec.

Table 23. Minimum required values of the model velocity required at a range of hardness values (mg $CaCO_3$/L) to maintain copper concentrations less than the U.S. EPA chronic freshwater copper criterion. These values are appropriate for a single piling, placed in water with pH = 7.0 and a background copper concentration of 1.0 µg/L.

Hardness (mg $CaCO_3$/L)	Minimum Model Velocity (cm/sec)	Chronic copper standard (µg/L)
25	0.98	3.47
50	0.49	6.28
75	0.36	8.88
100	0.30	11.35
125	0.23	13.74
150	0.19	16.05
175	0.17	18.31
200	0.15	20.52

Generalized recommendations for this application are similar to those presented in Part I for projects located in areas where only steady state currents are present. Based on the analysis included in the Columbia River BA and this risk assessment, it appears that projects involving fewer than 100 piling, and installed in moving water, have little potential to adversely effect aquatic resources. Projects involving more than 100 piling should require an individual risk assessment, as should ACQ-B projects, involving more than 10 piling/acre in small ponds or lakes. It should be noted that the COE recommendations on the use of treated wood in the lower Columbia River were less restrictive than are the recommendations made in Brooks (1997a, 1997b or 1997c). The author's recommendations are that:

1. Projects installed in areas where currents are less than 0.5 cm/sec in densities exceeding ten piling per surface acre should require an individual risk assessment using this or a similar model.

2. Projects involving fewer than 100 piling can be permitted without additional risk assessment when current speeds are $\geq$ 1.0 cm/sec.

3. Projects involving more than 100 piling should be required to complete an individual risk assessment. These risk assessment documents are free and the cost for gathering data is small.

Projects in areas known to have elevated background concentrations of copper (>50 μg Cu/kg sediment or more than 2.5 μg Cu/L) should be required to complete an individual risk assessment.

Summary and Conclusions. Copper is a ubiquitous metal found in all aquatic environments. It is also a micronutrient essential to the proper functioning of living cells. At elevated levels, copper becomes toxic to a variety of aquatic fauna and flora. The bioavailability and toxicity of this metal have been well studied and the U.S. Environmental Protection Agency has published national fresh and saltwater copper criteria. The review conducted in support of this risk assessment suggests that these criteria are conservative from the environment's point of view and provide adequate protection for the most sensitive species. The EPA chronic standard has been adopted as a benchmark against which to judge the environmental suitability of ACQ-B treated wood used in aquatic environments.

Washington State has adopted a marine sediment copper standard and that standard is used as a benchmark in this risk assessment. Freshwater sediment quality standards have not been developed. Three benchmarks, dependent on water and sediment physicochemical properties, have been adopted for the purposes of this risk assessment. The range of these benchmarks is consistent with Threshold Effects Levels reviewed by Jones (1997).

Data describing the loss of copper and DDAC from 0.4 pcf ACQ-B treated poles is used in this risk assessment to predict the loss of copper and DDAC as a function of time of immersion and pH. That analysis suggests that initially moderate copper losses from ACQ-B treated wood decline very rapidly to low levels within a week. Initially, losses of DDAC are similar to copper in magnitude. However, these losses decline even faster and approach zero within several days.

The risk assessment indicates that copper is the metal of concern. If copper concentrations are maintained below the EPA chronic freshwater standard, then only small amounts of copper are added to sediments and DDAC concentrations in water and sediments will be below anticipated Threshold Effects Levels.

The environmental risks associated with the use of 0.4 pcf ACQ-B preserved wood have been evaluated by quantifying the additional metal loading associated with the use of these products in freshwater environments, and comparing the resulting concentrations with appropriate benchmarks. Three Microsoft™ EXCEL models are provided with this risk assessment:

(I) ACQ(ss).xls for 0.4 ACQ-B treated piling used in lakes, rivers and streams;

(II) ACQbrisk.xls for 0.4 ACQ-B treated lumber used to construct bulkheads and other large surface area projects in freshwater where either steady state or tidal currents dominate;

(III) ACQprisk.xls for 0.4 pcf ACQ-B treated piling used in freshwater environments influenced by tidal currents.

These risk assessments provide project proponents and regulatory agencies with a tool for evaluating the risks associated with specific 0.4 pcf ACQ-B projects in specific environments. Testing of similar models developed for creosote, CCA-C and ACZA indicates that they are conservative from the environment's point of view. Predictions have generally exceeded observed levels of PAH or metals in the water column and sediments by 20 to 30%. Specific testing of the ACQ-B model has not yet been accomplished.

Throughout this analysis, conservative assumptions have been used. Leaching rates from ACQ-B treated products have been shown to decrease exponentially with time. We have used leaching rates observed in freshly treated wood (Day = 0.5) to determine risks. We have assumed minimal mixing in aquatic environments. In all instances we have assumed that the metals leached into the water are in their most toxic form and that there is no detoxification by natural processes. This analysis indicates minimal risks when 0.4 pcf ACQ-B preserved piling is used in moving water. The model does demonstrate the potential for exceeding the U.S. EPA chronic copper standard when bulkheads are installed in poorly circulated or closed bodies of water. General guidelines for the use of ACQ-B preserved wood have been provided.

The predictions and recommendations made in this study presume that wood products are properly treated and fixed. That assumption will only be valid if the treated wood industry continues an aggressive environmental quality control program, and if regulators and the consuming public demand high quality, environmentally sensitive, products for the projects they permit and build. Recently *completed Best Management Practices for the Use of Treated Wood in Aquatic Environments* (WWPI, 1996) provide project proponents and regulators with an effective tool to insure that only well fixed treated wood enters aquatic environments.

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

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