The affects of dissolved copper on salmon and the environmental affects associated with the use of wood preservatives in aquatic environments

Copper River, Alaska

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1. Background. Models are available for all wood preservatives currently approved for use in freshwater and/or saltwater. The assumptions used to derive these models are based on worst cases. Opponents to the use of pressure treated wood and others attempting to understand the environmental response to these products frequently conclude that because preservatives do lose small amounts of copper to aquatic environments, and because small increases have been observed in sedimented copper concentrations, treated wood is inappropriate for use in water. The purposes of this paper are:

a. To explore the response of salmonids to low concentrations of dissolved copper;
b. To discuss the implications of DRAFT 2003 U.S. EPA recommendations to States having NPDES authority for establishing copper water quality criteria;
c. To describe short- and long-term loss rates of copper from pressure treated wood;
d. To predict increases in water column concentrations of copper using both proximity and box model assessments; and
e. To put copper contributions from pressure treated piling into proper perspective by comparing them with other inputs to aquatic environments;

2. Acute affects of copper on fathead minnows and salmon. Acute affects of copper on fish and invertebrates have been reviewed by Brooks (1998, 2000). The toxicity of copper is primarily associated with cupric ion and copper hydroxides (Cu^{+2}, CuOH and Cu_2OH_2). The potential for copper to bind with biotic ligands is a function of the bioavailability of the metal, which is mediated by natural constituents in aquatic systems which either compete with copper for biologically important binding sites or which bind copper to larger molecules and/or particles. Until recently, the US Environmental Protection Agency (EPA) has based water quality criteria for copper on hardness, expressed in equivalents of $CaCO_3$. The reasoning was that other physical parameters, such as pH, which affects the ionic state of free copper, covaried with hardness. However, hardness does not account for other mediating factors such as dissolved organic carbon (DOC), which is also known to bind copper and therefore to reduce its bioavailability. Sciera *et al.* (2004) varied hardness between 10 and 40 mg CaCO3/L; pH between 6.5 and 8.0 and DOC between 0 and 10 mg/L to demonstrate a range of 96-hr LC_{50} values varying between 2.9 and 427.3 μg dissolved Cu/L in fathead minnows (*Pimephales promelas*). In general, bioassays have been conducted in ion-free water amended with Ca and Mg to achieve the specified hardness. Dissolved Organic Carbon (DOC) has not been reported in most bioassays, but generally appeared to be very low or zero. Sciera *et al.* (2004) used multifactor regression analysis to conclude that DOC was the dominant factor causing the wide spread in their LC_{50} determinations.

Sorensen (1991) observed acute intoxication (96 hr-LC_{50}) in adult salmonids at dissolved copper concentrations varying between 60 and 680 μg Cu/L. Chapman (1978) reported affects levels for steel head (*Oncorhynchus mykiss*) and chinook salmon alevins, swim-up fry, parr and smolts. The 200-hr LC_{10} describes the concentration of copper that kills ten percent of the fish in 200 hours (8.3 days). He found that juvenile stellhead were more sensitive to copper than juvenile chinook. Steelhead parr were most sensitive with a 200 hr LC_{10} of 8 μg/L. Steelhead alevins (19 μg/L) and swim-up fry (9 μg/L were slightly more robust. Swim-up fry of chinook salmon were the most sensitive life stage of this species with a 200-hr LC_{10} of 14 μg Cu/L. Finlayson and Wilson (1989) developed a chronic copper benchmark that they considered appropriate to protect all life stages of chinook salmon in the Sacramento River, California. At a hardness of 64 mg $CaCO_3$/L, their algorithm indicates adequate protection at 8.59 μg Cu/L. Acute toxicity values (96-hr LC_{50} in μg Cu/L) values for two salmonids are provided in Table 1 together with the hardness values at which the tests were conducted.

Table 1. Benchmarks describing acute copper toxicity in salmonids.

Species	96-hr LC_{50} (μg Cu/L)	Reference
Brown trout (*Salmo trutta*)	61.5 @157.8 mg $CaCO_3$/L	Baldigo and Baudanza (2001)
Chinook salmon (*Oncorhynchus tshawytscha*)	19.0 @ 24 mg $CaCO_3$/L	Chapman (1978)

3. Chronic affects of copper on salmon. Little (1983) reported detection limits of numerous organic compounds by a variety of fishes that varied between 10^{-5} and 2.9 x 10^{-20} moles. They reported that low concentrations of single amino acids are able to evoke spontaneous (unconditioned) and conditioned responses in numerous species. Conditioned responses to shock reinforced introductions of single amino acids could be achieved in four or five trials. These conditioned responses have been shown to last for longer than 3 months. This is the basis for NOAA fisheries attempts at the Manchester Research Station to condition endangered salmon stocks being maintained in their hatchery-nursery system by introducing macerated salmon in concert with water previously exposed to predators (squawfish, blue herons, etc.).

Olfactory perceptions are important to fish for feeding, predator avoidance, schooling, migration, recognition of natal spawning grounds and mating (recognition of the same species). Impairment of a fish's olfactory response has potential adverse affects on individuals and populations of fish. For instance, Wisby and Hasler (1954) captured coho salmon (*Oncorhynchus kisutch*) returning to Issaquah Creek and the East Fork of Issaquah Creek. They occluded the nares (olfactory organs) from a portion of the fish with cotton and then reintroduced them back into the environment below the confluence of the two streams. Eighty-nine percent of fish with intact nares (N = 73) chose the correct branch whereas only 60% the fish with occluded nares (N = 70) chose the correct branch. Lorz and McPherson (1976) confirmed this loss of migratory fidelity by exposing 18 month old coho salmon (*Oncorhynchus kisutch*) to varying copper concentrations. Exposure to 5 μg Cu/L for 165 days resulted in a 30% reduction in downstream migration.

Giattina *et al.* (1982) reported copper avoidance in rainbow trout (*Oncorhynchus mykis*) at 4.4 to 6.4 μg Cu/L in soft water (28 mg $CaCO_3$/L). However, these same trout were attracted to 334 to 386 μg Cu/L. Drummond *et al.* (1973) observed reduced feeding of brook trout (*Salvelinus fontinalis*) lasting only 24 hours following long-term exposure to 6 μg Cu/L. Un-acclimated chinook salmon (*Oncorhynchus tshawythscha*) have been shown to significantly avoid copper concentrations as low as 0.8 μg Cu/L in water having hardness equivalent to 25.3 mg $CaCO_3$/L at pH = 7.5 and T = 10.2 ^oC. (Hansen *et al.* 1999a). The avoidance reaction was impaired at copper concentrations $\geq$ 44 μg Cu/L. This last finding is important because it demonstrated that chinook salmon did not avoid lethal concentrations of copper. The authors noted that chinook salmon acclimated to water containing 2.0 μg Cu/L, did not avoid higher copper concentrations. This suggests that chinook salmon will not elicit an avoidance reaction in natural environments, where the authors acknowledge that background concentrations are commonly as high as 4.0 μg Cu/L. The reasons for the lack of avoidance of copper at high concentrations was further explored by Hansen *et al.* (1999b) who described histological evidence demonstrating a significant reduced number of olfactory sensors in chinook salmon exposed to $\geq$ 50 μg Cu/L and that the numbers of *small-dendrite* receptors was significantly decreased after a four hour exposure to 25 μg Cu/L. The authors noted that olfactory rosette receptors have been reported to regenerate following 8 to 42 days recuperation in clean water following short-term exposure to high copper concentrations, but that the demonstrated olfactory impairment may affect important responses including homing response of anadromous salmonids, predator avoidance and feeding.

Hansen *et al.* (1999c) demonstrated un-acclimated rainbow and brown trout avoidance of very low concentrations of mixtures of metals (nominally 1.2 μg Cu/L, + 0.11 μg Cd/L, 0.32 μg Hg/L and 5.0 μg Zn/L). The avoidance could have resulted from additive or synergistic interaction of the metals, or it could be that the fish were responding to a single metal in the mixture. The authors did not adequately discuss the interactive effects of the mixture of metals. Sprague (1964) observed un-acclimated Atlantic salmon avoidance of 2.3 μg Cu/L or 53.4 μg Zn/L. Important to the assessment of ACZA, which loses copper and zinc at essentially the same rate, Sprague (1964) demonstrated that unacclimated Atlantic salmon avoided Cu-Zn mixtures containing as little as 0.42 μg Cu/L and 6.1 μg Zn/L suggesting that the metals acted synergistically. These authors also found that rainbow trout acclimated to the simulated ambient metal mixture (12 μg Cu/L; 1.1 μg Cd/L; 3.2 μg Pb/L; and 50 μg Zn/L) preferred clean water when given that option and avoided higher concentrations.

Baldigo and Baudanza (2001) assessed avoidance by brown trout to water pumped from a reservoir treated with copper sulfate to control algae. This highly replicated study is one of the few reviewed studies that quantified many of water quality endpoints important for determining the toxicity of copper. The water had pH = 7.0; TOC = 134.6 μM/L; chloride = 135 μM/L; Mg = 45.7 μM/L; Ca = 112.1 μM/L and K = 13.9 μM/L. Measured copper concentrations of 9.7 to 183.3 μg Cu/L were generally higher than the designed concentrations of 0 to 152 μg Cu/L. Their results indicated that the estimated threshold for avoidance of dissolved copper was ~55 μg/L, which is only slightly less than the 61.5 μg Cu/L 96-hr LC_{50} determined by these authors in the same water. The lack of response may be due to elevated copper concentration (9.7 μg Cu/L) in the rearing and control water, which was pumped from an aqueduct leaving the West-of-Hudson Catskill reservoir system. Marr *et al.* (1995a, 1995b) have shown that brown trout acclimated to elevated mixtures of metals (including copper) suffered fewer mortalities than un-acclimated populations. This study is important to this review because it documents the potential for increased tolerance to metals associated with acclimation and the mediating effect that dissolved organic carbon and hardness have on chronic and acute copper toxicity.

McKim and Benoit (1971) found that 9.5 μg Cu^{2+}/liter was a safe concentration for brook trout (*Salvelinus fontinalis*) in Lake Superior. Drummond *et al.* (1973) assessed the affects of short term exposure to 0.7 to 24 μg Cu/L on this same species in water having total hardness of 44 to 46 mg/L and pH of 7.54 to 7.75 mg $CaCO_3$/L. They found significant increases in fish activity at all increased copper concentrations above zero. Mean coughing rates were significantly ($p < 0.01$) increased at $\geq$9.0 μg Cu/L but not at 6.0 μg/L. Most importantly, they found that the addition of copper decreased feeding activity. Fish acclimated quickly at 6 μg

Cu/L and 100% resumed normal feeding behavior after 24 hours of exposure. Brook trout acclimated to higher concentrations of copper more slowly. Eighty-seven percent of the trout resumed feeding after 6 days exposure to 12 μg Cu/L and 100% were feeding after 14 days exposure. However, their feeding behavior was described as sluggish.

Hara *et al.* (1976) demonstrated reduced recognition of water containing 10^{-5} M L-serine (an amino acid associated with fish skin) when exposed to 8 μg Cu/L. This study is somewhat confused by the authors' statement that the rearing and trough water contained an average of 20 μg Cu/L. Rehnberg and Schreck (1986) conducted similar experiments with coho salmon (*Oncorhynchus kisutch*) in water having hardness equivalent to 30.5 mg $CaCO_3$/L and pH = 6.72. They observed lack of avoidance of L-serine introduced at 10^{-8} M at all tested copper concentrations. The lowest copper concentration tested was 6.35 mg Cu/L (10^{-8} M Cu). Sauier *et al.* (1991) exposed 14th day post-fertilization and post hatching rainbow trout to water having a hardness of 61.8 to 64 mg $CaCO_3$/L and 22 μg Cu^{+2}/L for 41 and 37 weeks respectively to assess the affects of long-term chronic exposure to high copper concentrations. The authors then gave the fish a choice of swimming upstream into their own rearing water or into water containing a heterospecific pheromone. Control fish significantly preferred their own rearing water that contained <5 μg Cu/L, whereas the copper exposed fish did not show a preference. Olfactory responses were not significantly different between the control and either treatment group different following 10 weeks of post test conditioning of all cohorts in ambient water not spiked with copper. This long-term 22 μg Cu^{+2} /L challenge of olfactory responses suggests significant short term effects – followed by recovery after 2 to 10 weeks in water containing 5 μg Cu/L. The observation of these fishes ability to discriminate the subtle pheromones in their own rearing water in the continuous presence of 5 μg Cu/L suggests that concentrations this low did not have an adverse affect on the test results. Chronic response of salmonids to dissolved copper are summarized in Table 2. Rjerselius *et al.* (1993) have demonstrated that it is the cupric ion that has the greatest affect on olfactory response in salmonids. The proportion of copper in the free cupric ion state is dependent on a number of mediating factors including water hardness, alkalinity, pH, dissolved organic carbon, etc. U.S. EPA copper water quality criteria are currently based on hardness, which is included in Table 2.

Table 2. Thresholds above which salmon have been shown to avoid dissolved copper.

Species	Avoidance Threshold (μg Cu/L)	Hardness (mg $CaCO_3$/L)	Reference
Rainbow trout (*Oncorhynchus mykiss*)	0.1	89.5	Folmar (1976)
Rainbow trout (*Oncorhynchus mykiss*)	6.4	23.0 – 27.0	Giattina *et al.* (1982)
Rainbow trout (*Oncorhynchus mykiss*)	70.0	112.4	Black and Birge (1980)
Rainbow trout (*Oncorhynchus mykiss*)	8.0	90.0	Hara *et al.* (1976)
Rainbow trout (*Oncorhynchus mykiss*)	<22 μg Cu^{2+}/L	61.8 – 64.0	Saucier *et al.* (1991)
Atlantic salmon (*Salmo salar*)	2.4	20.0	Sprague *et al.* (1965)
Brown trout (*Salmo trutta*)	55.0	157.8	Baldigo and Baudanza (2001)
Coho salmon (*Oncorhynchus kisutch*)	<6.4*	30.5	Rehnberg and Schreck (1986)

Summary for copper affects on salmonids. Nearly all natural bodies of water contain some copper, which constitutes about 0.006% of earth's crust and is typically found at concentrations of 2 to 100 μg Cu/g dry soil and 1.4 to 10.0 μg/L in water. While not discussed in this report, rivers carrying high concentrations of suspended solids also tend to have elevated concentrations of dissolved metals, including copper. The point being that fish and other aquatic organisms are continually exposed to copper with is an essential trace element for most plants and animals. At elevated concentrations, copper becomes toxic. The mass of dissolved copper has been recognized as an inappropriate endpoint for assessing biological effects because the metals toxicity is mediated by a number of organic and inorganic constituents found in natural water bodies. For salmonids, acute toxicity has traditionally been measured by 96-hr LC_{50} bioassays in laboratory water with only hardness recognized as an important parameter. The results of these bioassays vary between 19 and 61.5 μg dissolved Cu/L depending on hardness and perhaps on species of salmon. Current trends in evaluating copper toxicity focus on inclusion of the many factors which mediate or exacerbate the metal's toxicity through use of the *Biotic Ligand Model* or the development of site specific *Water Effects Ratios*. It should be emphasized that either approach is applied on a site specific basis. In general, it appears that application of the WER approach leads to higher WQC than the existing hardness approach. However, in waters having low concentrations of sulfide and dissolved organic carbon coupled with low pH, the *Biotic Ligand Model* will likely demonstrate copper toxicity at lower concentrations than the hardness approach has historically indicated.

As noted by Brooks (1997, 2000) chronic effects associated with compromise of salmons' olfactory responses have been well documented at concentrations of 4.4 to 6.4 μg Cu/L in soft water with hardness < ca. 30 mg $CaCO_3$/L. Salmonids acclimated to water with no copper will demonstrate olfactory effects at even lower concentrations of 0.1 to 2.4 μg Cu/L when exposed to rapid increases in the metal. The literature also indicates that salmon acclimated to 2.0 μg dissolved Cu/L do not demonstrate the same changes in olfactory mediated responses as fish acclimated in water containing no copper – at least not at copper concentrations in the 5 to 15 μg/L range. As noted above, copper is ubiquitous in aquatic ecosystems and fish typically encounter concentrations of 0.5 to 1.5 μg/L even in pristine freshwater environments. Therefore, salmon would not be expected to elicit the same behavioral changes to small and/or gradual increases in dissolved copper as has been observed in un-acclimated fish exposed to rapid copper increases in laboratory studies. This hypothesis is strengthened by the existence of very healthy salmon runs in watersheds like Alaska's Copper River where historic dissolved copper concentrations are reported to be in the range of 2 to 23 μg/L.

4. Copper and salmon in Northeast Pacific environments. The appropriateness of suggested regulatory standards must be consistent with empirical evidence in natural environments. This tenant is implicit in the ongoing development of site specific water quality criteria based on the Water Effects Ratios (WER) and the Biotic Ligand Model (BLM). Some typical copper concentrations for salmon producing rivers are provided in Table 3. The Copper River in Alaska (see cover photo) is host to one of the most famous and healthy sockeye salmon runs in North America. United States Geological Service dissolved copper data for this river are summarized in Figure 1. There are numerous streams and rivers carrying low sediment bedloads and low dissolved copper concentrations that also support healthy salmon runs. However, these data clearly demonstrate that healthy salmon runs coexist with dissolved copper concentrations exceeding 2.0 μg/L. That is particularly true for the Copper and Salmon Rivers in Alaska and to a degree for the Columbia River in Washington State.

Reconciling the literature based on bioassays with the real world is actually not terribly difficult in this case. Hansen *et al.* (1999a) observed that chinook salmon acclimated to low dissolved copper concentrations of 2.0 μg/L did not avoid higher concentrations. Nearly all of the databases reviewed in support of this paper contained copper at detectable concentrations of greater than one to two μg dissolved Cu/L. Salmon returning to their natal streams from the Pacific Ocean, where copper concentrations are typically 0.25 to 0.5 μg/L, encounter estuarine and low river reach concentrations of 2 to >10 μg Cu/L. These often natural copper concentrations cannot be avoided by salmon which become acclimated as they migrate through estuaries. The fact that they can navigate complex river systems like the Copper River in Alaska where copper concentrations frequently exceed 2.0 μg/L suggests little or no impairment of their homing abilities. Likewise, downstream migrating sockeye smolts negotiate these same waters, with the same naturally moderately high copper concentrations to sustain one of the most famous salmon runs in North America. The fact that salmon survive and in some cases thrive from Alaska to the Sacramento River in California in waters containing >2.0 μg Cu/L suggests that this ability is not unique to phenotypes resident in Alaska and the animal's ability to acclimate to sublethal concentrations of copper appears in several salmonid species over a broad geographic range. The bottom line is that it appears that olfactory response in salmonids may be temporarily compromised by rapid increases in copper concentrations in the absence of mediating factors (DOC, etc.) but that salmon acclimate to gradual increases in copper concentrations in the real world and that they can thrive in watersheds where concentrations are elevated above 2.0 μg/L.

Table 3. USGS Dissolved copper (μg/L) in Pacific Northwest salmon producing rivers.

River	Dissolved copper	Reference
Sacramento, CA	<11.5 μg/L	Alpers *et al.* (2000)
Columbia River, WA	<3.0; generally 1.8 to 2.2 μg/L	USGS
Copper River Alaska	<23.0; <6.44> μg/L	USGS (see Figure 1)
Salmon River, Alaska	<~60 μg/L; generally 4 to 15 μg/L	
Humtullips River, WA	<30 μg/L	USGS

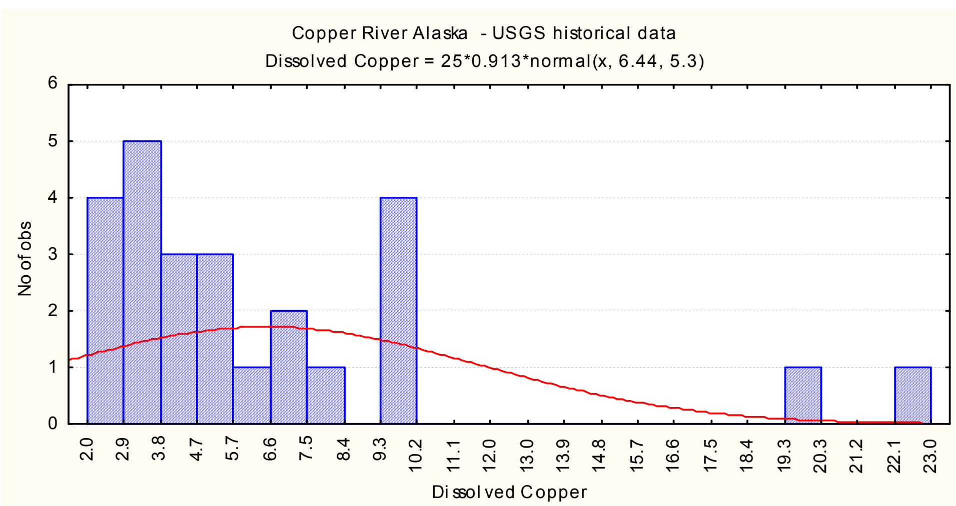


Figure 1. USGS data describing concentrations of dissolved copper (μg/L) in the Copper River, Alaska. Note this histogram includes all recorded data for all years and all stations.

To put the copper issue in proper context, about 9000 dissolved copper datapoints were available in the USGS NAWQZ database for California, Oregon, British Columbia and Alaska from 1996 through 9/30/2003. For some reason, data for Washington State was not available in the USGS database on December 13, 2004. Of these, 146 cases (1.62%) were returned in a query restricted to dissolved copper levels $\geq$ 2.0 µg/L (Figure 2). The highest of these was 6.06 µg/L. Of the 146 cases, 63 were associated with the Sacramento River and/or its tributaries that have been impacted by mining operations and only nine cases were reported outside California. These data suggest that excepting the Sacramento River, dissolved copper in western rivers is not a significant problem – even though these rivers travel through many urban and industrial areas where there are significant inputs of copper.

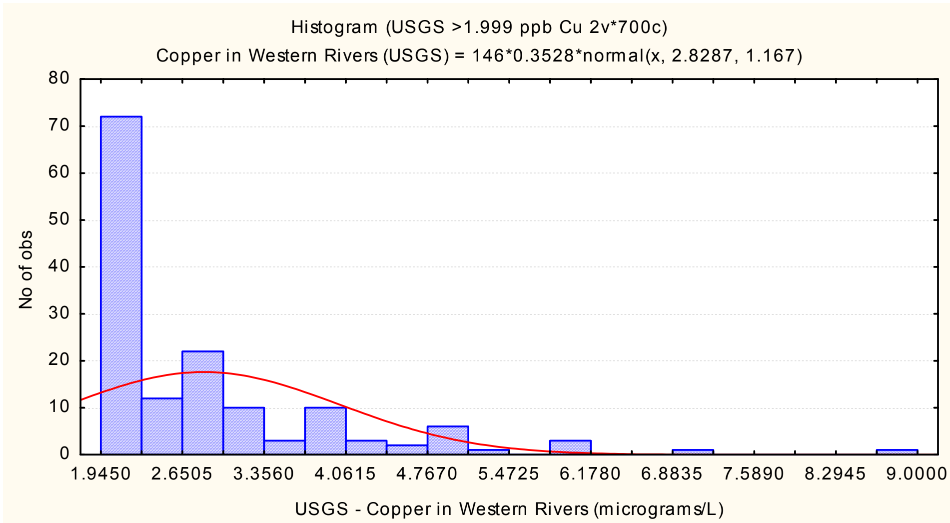


Figure 2. Histogram describing the frequency of dissolved copper concentrations $\geq$ 2.0 µg/L recorded in the USGS NAWQA database for California, Oregon, British Columbia and Alaska from 1996 to September 2003.

5. Copper water quality criteria. The existing acute and chronic EPA copper water quality criteria (WQC) for dissolved copper (i.e. that passing a 0.45 µM filter) are hardness based in freshwater. Table 3 includes definitions for acute and chronic criteria. Typical freshwater acute values range from 4.6 µg Cu/L at 25 mg $CaCO_3$/L to 18.5 at 100 mg $CaCO_3$/L and chronic values range between 3.5 and 11.4 µg Cu/L at the same hardness values.

Table 3. U.S. Environmental Protection Agency copper water quality criteria.

a. Freshwater.
   i. Acute. This is a one-hour average not to be exceeded more than once every three years on average.

   Freshwater acute Cu WQC = 0.960*exp$^{0.9422[\ln(\text{hardness})] - 1.464}$

   ii. Chronic. This is a four-day average concentration not to be exceeded more than once every three years on average

   Freshwater chronic Cu WQC = 0.960*exp$^{0.8545[\ln(\text{hardness})] - 1.465}$

b. Marine
   i. Acute. This is a one-hour average not to be exceeded more than once every three years on average.

   Marine acute Cu WQC = 4.8 µg dissolved Cu/L

ii. Chronic. This is a four-day average concentration not to be exceeded more than once every three years on average

Marine chronic Cu WQC = 3.1 μg dissolved Cu/L

In November 2003, the EPA published a *2003 Update of Ambient Water Quality Criteria for Copper* (EPA 822-R-03-026, November 2003). The document provides updated guidance to States and authorized Tribes to establish water quality standards under the Clean Water Act (CWA) to protect aquatic life from copper. These guidelines are not presented as new regulatory WQC by EPA. Therefore, regulatory implementation is apparently being left up to individual States and Tribes once the recommendations are finalized. How those jurisdictions respond to these DRAFT recommendations is problematic and will likely vary across the country.

5.1. **Freshwater and the Biotic Ligand Model.** In recognition of an emerging understanding that there are numerous constituents in natural bodies of water that mediate metal toxicity, EPA has sponsored development of a *Biotic Ligand Model* (BLM) first published by DiToro *et al.* (2001), which is recommended for setting site specific freshwater standards in the draft update. Accurate use of the BLM requires determination of pH, dissolved organic carbon (DOC), percent humic acid, temperature, Ca, Mg, Na, K, SO_4, Cl, dissolved inorganic carbon (DIC) and sulfide. These data have not routinely been collected and are not typically available in historical archives. However, EPA has used available data meeting their data quality objectives to arrive at the following National Criteria Statements for freshwater and marine environments.

Freshwater acute. Freshwater aquatic organisms and their uses should not be affected unacceptably if the 24-hour average dissolved copper concentration does not exceed the BLM-derived site-LC_{50} divided by two more than once every 3 years on average.

Freshwater chronic. Except where a locally important species is very sensitive, freshwater aquatic organisms and their uses should not be affected unacceptably if the 4-day average concentration of dissolved copper does not exceed the BLM-derived site-water LC_{50} divided by the Final Acute-Chronic Ratio (FACR).

Note: In Section 5.3.2 of the EPA guidance, an FACR of 3.23 was calculated as the geometric mean of the ACRs (Acuyte Chronic Ratios) for sensitive freshwater species, *C. dubia, D. magna, D. pulex, O. tshawytscha,* and *O. mykiss* along with one saltwater ACR for *C. variegates.* Importantly, EPA's current calculation of the FACR includes the ACR for two salmonids (chinook salmon and rainbow trout).

An example of the use of this approach is available for one of Aquatic Environmental Sciences research ponds (Montgomery's Pond) in which the BLM was used to assess copper toxicity. The water in this pond has low hardness of 15.8 mg $CaCO_3$ leading to a chronic copper WQC of 2.11 μg Cu/L using the existing hardness based standard. The BLM predicted an LC_{50} of 11.2 $\pm$ 1.9 μg Cu/L for *Daphnia magna* and 237$\pm$ 35.5 μg Cu/L for *Pimephales promelas*. The lower value of 11.2 divided by an FACR of 3.23 gives a chronic WQC of 3.47 μg Cu/L.

Implementation of the freshwater standard. The BLM is designed to develop site-specific criteria for stream reaches. This can be a difficult task because the specific water quality parameters affecting the model are not steady state and vary as a function of stream-flow and season. Furthermore, the number of input parameters required to run the BLM and the paucity of historical data increase the expense of accomplishing this task. EPA is currently addressing these issues and further guidance is supposed to be available in the future. It seems likely that these 2003 DRAFT recommendations for freshwater will not be widely adopted until these difficulties are resolved.

5.2. **Development of the new saltwater marine standards.** Genus Mean Acute Values (GMVA) values (96-hr LC_{50}) for summer flounder and cabezon were reported at 12.7 and 86.4 µg Cu/L. Other vertebrate fish species are more tolerant with GMVAs ranging from 117 to 4,743 µg Cu/L. The larval stages of most species are most sensitive and the larvae of the common blue mussel (*Mytilus edulis*) is 11.5 µg Cu/L. GMVAs for other invertebrates ranged from 12.6 for the Pacific oyster (*Crassostrea sp.*) to 6,448 µg Cu/L for the brackish water clam, *Rangia cuneata*.

The Final Acute Value (FAV) was derived by dividing the geometric mean of the four lowest GMVAs (12.3 µg Cu/L) and then arbitrarily reducing this to 6.19 as a further precaution to protect commercially and recreationally important mussels (*Mytilus sp.*). The Criterion Maximum Concentration (CMC) of 3.1 µg dissolved Cu/L was then taken as half the FAV. Due to lack of qualifying data, EPA was unable to develop a Final Acute Chronic Ratio for saltwater organisms and in what can only be described as a smoke and mirrors discussion adopted the freshwater ACR of 3.23 for use in saltwater. For saltwater, the FAV for mussels (6.188 µg Cu/L), divided by the ACR of 3.23 giving a marine chronic standard of 1.9 µg dissolved Cu/L. It would be interesting to investigate the health of the ubiquitous *Mytilus* genera in marinas where bottom paints on boats create continuous concentrations >1.9 µg dissolved Cu/L.

Implementation of the saltwater criteria. When coupled with the severe economic implications for stormwater, sewage treatment facilities, ports, recreational marinas, U.S. Navy facilities and industry, the lack of existing marine ACR data and EPA's inadequate justification for the proposed CMC decreases the likelihood that this WQC will be implemented until more saltwater data is available.

5.3. **Water Effect Ratio (WER).** EPA-822-R-01-005 describes a *Streamlined Water-Effect Ratio Procedure for Discharges of Copper* (WER) to be used for developing site specific values for aquatic life criteria in marine and freshwater. This is an empirically based methodology that compares copper affects on aquatic life in site water spiked with copper to similar bioassays conducted in laboratory water at the same hardness. The WER is the lower of the site-water EC_{50} divided by the laboratory water EC_{50} or the site water EC_{50} divided by the documented Species Mean Acute Value from the literature. The geometric mean of two (or more) sampling event WERs is concluded to be the site WER.

This process is analogous to the BLM in that it integrates *all* of the physicochemical and biological factors affecting copper toxicity at a site with results from traditional laboratory bioassays to develop a factor that is then multiplied by the appropriate acute or chronic dissolved copper WQC to define a site-specific WQC. The BLM requires measurement of those factors most important for influencing copper's toxicity and uses a computer program to predict lethal accumulations of copper on important biotic ligands. From an empiricists point of view, the WER is more appealing. However, the BLM is less expensive and faster.

Copper WQC developed using the WER have increased site specific criteria by 1.5 to 5.0 µg Cu/L above existing chronic (3.1 µg/L) or acute (4.8 µg/L) marine WQC. However, larger increases in WQC of 7.9 to 15 µg Cu/L have been established for harbors in New York, New

Jersey and Connecticut (Seligman and Zirino, 1998). A site specific WQC for San Francisco Bay of 6.25 μg Cu/L is under review by EPA. Development of site specific WERs is economically feasible for major ports, large cities and/or industries, their development by proponents of small projects outside the boundaries of existing site specific WQC is problematic due to the time and expense involved. The streamlined WER procedure appears to mitigate these costs. However, this review was unable to determine the acceptability (by USACE in administering Section 10 Permits or by States having NPDES authority) of site specific WQC developed using the streamlined procedures. Under any circumstances, the acceptability of treated wood projects should be based on comparison of predicted copper concentrations associated with the project in comparison with national, regional or site specific WQC applicable to all stakeholders and not to some separate standard.

5.4. **Summary with respect to EPA's DRAFT 2003 copper recommendations.** Movement to site specific copper WQC will undoubtedly improve their efficiency and protectiveness. The more empirically based WER approach is appealing and the issuance of streamlined methods for developing site specific criteria will strengthen implementation. However, the process remains expensive for small project proponents outside areas where site specific WQC have been established. These rural and/or recreational projects will likely fall outside urban and/or industrial areas where local governments and/or associations of industries develop local or regional WERs. It is uncertain how much it would cost to develop a WER for a small project and furthermore, it is uncertain how State governments would receive, process and publish locally or individually developed effects ratios. Similarly, implementation of the BLM for developing site specific WQC is fraught with uncertainty. State governments may require data collected several times a year to account for inherent variability associated with season, freshwater flows, etc. It should be anticipated that implementation of these approaches will continue by local governments prompted by consortia of industries and other affected users of aquatic environments. I suspect that application of these approaches to suburban and/or rural areas by small local jurisdictions or individuals is years away. In light of that, the proposed reduction in the marine chronic WQC to 1.9 μg Cu/L will impose unacceptable costs on local governments, ports, marinas, stormwater dischargers and the military. It appears unlikely that this will be implemented at least until these major users are covered by site specific criteria and this could become another blue versus red (rural versus urban) issue for coastal states.

6. Copper loss rates from waterborne preserved wood products. Chromated Copper Arsenate (CCA) and Ammoniacal Copper Zinc Arsenate (ACZA) are approved for use in marine and freshwater environments. In general CCA is used to treat southern yellow pine on the east coast and ACZA is used to treat Douglas fir on the west coast. Creosote treated wood is used throughout the United States in marine environments and is used extensively in and over freshwater in many areas of the country for bridge construction. Copper Azole (CA-B), Ammoniacal Copper Quat (ACQ) and Copper Naphthenate (CN) and Pentachlorophenol (Penta) are available for use over and in freshwaters only. Waterborne preservatives using copper will form the focus of what follows. Copper loss rates for most currently available waterborne preservatives are provided in Table 4. Loss rates for Copper Azole are being developed but are not yet complete.

Table 4. Copper loss rates (μg Cu/cm²-day) from CCA-C, Copper naphthenate, ACQ-B in freshwater and from ACZA in saltwater. Loss rates are given for 0.5, 2.0 and 30 days following initial immersion.

Preservative	Loss Algorithm	Losses ($\mu g/cm^2$-day) at the following times of immersion 0.5 days	2.0 days	30 days
CCA-C	=0.036*Temp+0.021*(Salinity +0.01) - 0.002*E5 - 0.031*pH+6.95*(EXP(-0.007*Retention + 0.121*Temp))*EXP(0.015*Salinity - 0.284*pH-1.379*Time)	3.34	0.69	0.22
Copper naphthenate	$10^{-0.008 +1.44*ex[(-0.147*time(days)}$	17.40	8.32	1.98
ACQ-B	Copper loss ($\mu g/cm^2$-day) for days < 4.5 = 265.14 x $\exp^{(-0.924 \times day - 0.239 * pH)}$ Copper loss ($\mu g/cm^2$-day) for days $\geq$ 4.5 = 4.25 x $\exp^{(-0.0175 \times day)}$	35.41	8.85	2.52
ACZA in seawater	Under development	18.65	12.0*	2.01*

*New copper loss rate algorithms for ACZA are under development. These values are based on averages computed from raw data collected in the first set of experiments.

All of the loss rates described in Table 4 were conducted on commodity size products (sections of piling and 2” x 6” and 4” x 4” sawn lumber) in dynamic test conditions which have been found to increase the observed loss rates in comparison with those determined under static conditions. These products were produced using *Best Management Practices* (BMP) published by the Western Wood Preservers Institute (WWPI/CITW 1996).

During a recent meeting with NOAA and Stratus Consulting, the graph shown in Figure 3 was presented describing tests conducted on CCA-C piling treated to 40 kg/m^3 using a stepped series of possible BMP practices. One of the participants asked why the most aggressive possible BMP was not routinely used to produce wood destined for use in aquatic environments. This question was explored by predicting the increased water column concentration of copper associated with each BMP. The results, determined using a box model describing increases in dissolved copper associated with the use of 25 piling spaced 2.0 m on center located in an area of very slow currents flowing at 2.0 cm/sec, are provided in Table 5. The predicted increase in dissolved copper concentrations are 0.036 μg/L (36 parts per trillion) for wood fixed at ambient air temperature and passing the chromotropic acid test; 0.015 μg/L for wood fixed in a steam bath; and 0.007 μg/L for wood fixed in steam and then washed as it was pulled from the fixation chamber. The added costs of steam fixation and the additional process water produced during the washing are not justified by the 29 part per trillion (0.029 μg Cu/L) improvement in water quality. None of the increases in copper associated with this project could be detected using modern analytical techniques and all of the values are within the natural variability of marine or freshwater environments. The most important element of the CCA-C BMP is that fixation must be assured using the chromotropic acid test and all of these treatments met any reasonable environmental performance standard.

Table 5. Box modeling describing increases in dissolved copper associated with the placement of five bents of five CCA-C preserved piling (25 total) on 2.0 m centers in water flowing at 2.0 cm/sec. Three successively aggressive BMP procedures were used to produce the piling evaluated in Figure 3. Data are for the first day of immersion.

BMP Process	Predicted copper increase (µg/L)
Fixed under cover at ambient temperature	0.036
Fixed in a steam fixation cylinder	0.015
Fixed in a steam fixation cylinder & washed	0.007

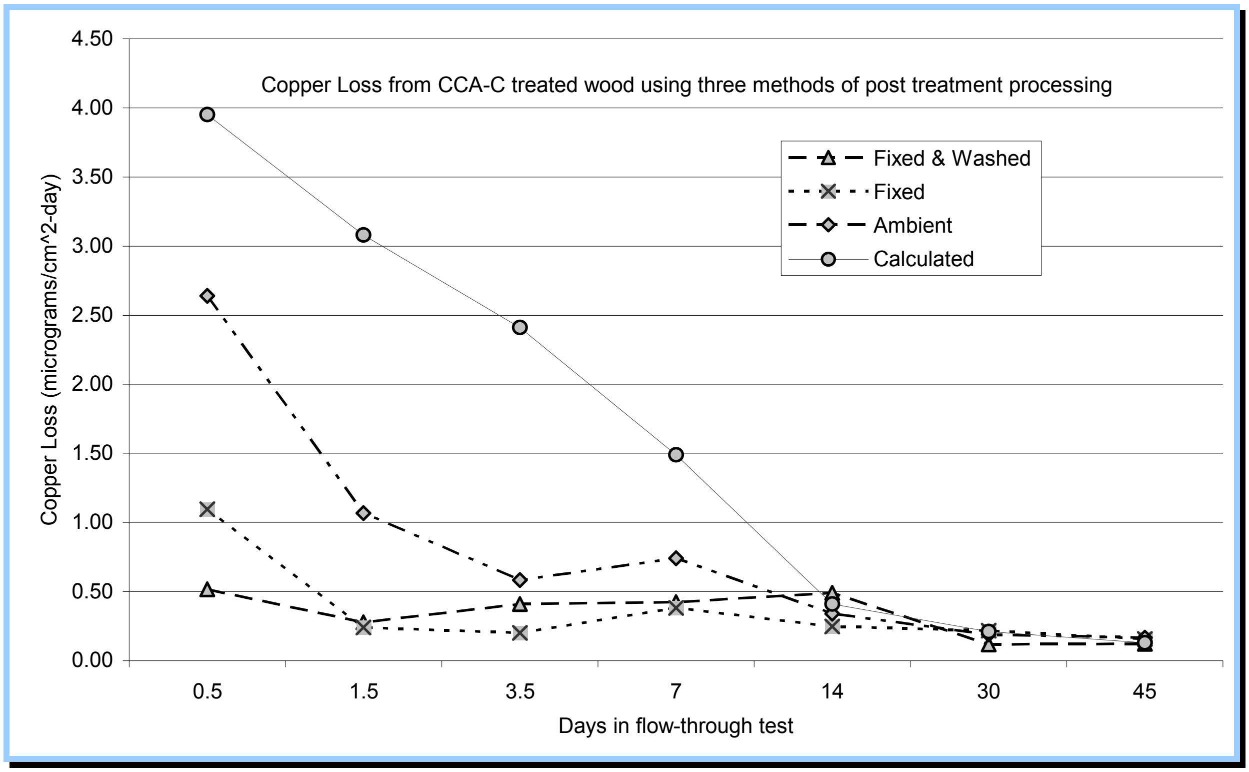
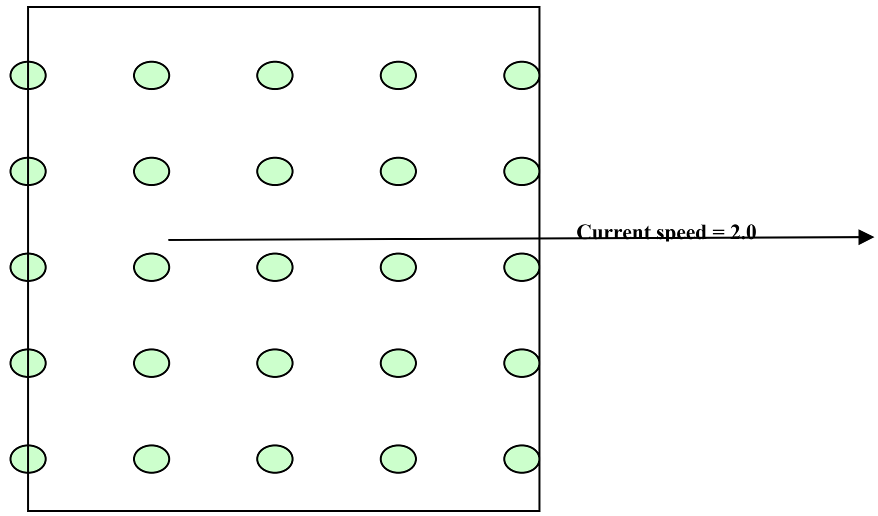


Figure 3. Copper loss from southern yellow pine piling treated to 40 kg/m^3 and fixed at ambient temperatures or in a steam fixation cylinder with and without a final freshwater washdown. The pre-BMP algorithm presented in Brooks (1996) is provided for comparison.

Currently available models are being modified to include both proximity predictions applicable within 2 cm of a single piling and box models. Figure 4 describes the box model used in these assessments. The structure (bridge, dock, restaurant, etc.) is being constructed on 25 pressure treated piling placed in five bents of five piling each. The dilution zone (width of the box) is assumed to extend one meter either side of the outside piling. This model assumes a poorly circulated body of water flowing at 2.0 cm/sec. Most streams and rivers flow at 10s of cm/sec and tidal flows generally average 5 to 10 cm/sec. Current speeds of 2.0 cm/sec might be found in small lakes or in the backwaters of slow-flowing rivers. Freshwaters are assumed to have pH = 6.5 and marine waters are assumed to be at 30 parts per thousand salinity. The temperature of both environments was assumed to be 15 ^{o}C and the wood was assumed to be treated to AWPA specifications for the environment being modeled.



a. Copper input to the box is equal to π x piling diameter x number of piling x copper loss rate.
b. Dilution volume is equal to the box width x current speed
c. Water depth is not a factor because the emersed length of piling equals the dilution water depth and they cancel.
d. For comparison with the acute standard, models compute the copper loss at $t = 0.5$ days and for comparison with the chronic standard, losses are computed at $t = 2.0$ days, which is half the stipulated four day average.

Figure 4. Box model used to assess dissolved copper concentrations associated with a treated wood project using 25 piling that average 30 cm in diameter and that have been treated with four waterborne preservatives containing copper.

Predicted increases in dissolved copper on the day of construction are summarized in Table 6. Increases in concentrations of copper are slightly higher within 2 cm of individual piling than they are on the downcurrent perimeter of the box. Also note that predicted increases in dissolved copper are consistent with the loss rates associated with each preservative (Table 4). However, even on the first day, the copper increases are all ≤ 0.6 µg/L adjacent to an individual piling and ≤ 0.48 µg Cu/L on the downcurrent perimeter of the box. Projects of this size are rarely constructed in a single day and the data provided in Table 7 predicting increases in copper concentrations following the first 15 days of immersion are more indicative of potential environmental effects. All of the increases in dissolved copper are less than 34 parts per trillion (0.034 µg/L). Increases this small cannot be detected within the natural variability of either freshwater or marine environments. That point is substantiated by several model verification studies conducted for CCA-C and ACZA pressure treated wood projects in the Pacific Northwest and in Florida where no significant increases in dissolved metal have been observed adjacent to treated wood structures constructed in either freshwater or marine environments. The point is that the loss rates are so small as to be undetectable in the real world. Copper is known to bioconcentrate in mussels by factors of 2,491 to 7,730 (EPA 2003) and VanderWeele (1996) has shown that mussel tissue content was proportional to the ambient copper concentration within one month of Exposure. Brooks (2004) observed copper concentrations of 0.775 to 1.906 µg Cu/L in Sequim Bay water immediately adjacent to an ACZA structure and 1.690 µg/L at a reference location. Tissues excised from mussels growing directly on the ACZA treated structure contained 1.653 µg Cu/g wet weight in comparison with 1.647 µg Cu/g in reference location mussels – a difference of 0.006 µg Cu/g dry tissue weight. The differences were not significantly different. However, assuming that the 0.006 µg Cu/g wet tissue weight increase observed in mussels growing on the ACZA treated piling was real and not due to random chance, this would imply that the water column concentration of copper was (5,110* 0.006/1000) or

0.030 μg Cu/L higher on the piling than at the reference location. This is very close to the predicted value of 0.027 μg Cu/L predicted in Table 7.

Table 6. Predicted water column concentrations of copper (μg Cu/L) on the first half day of immersion within a few cm (proximity model) of a single treated piling and on the downcurrent side of the box described in Figure xx in a slow current speed of 2.0 cm/sec. pH is assumed to be 6.5 and water temperature = 15 °C.

Preservative	Proximity Model (2 cm from single piling)	Box model (25 piling spaced 2 m on center)
CCA-C (freshwater)	0.062	0.046
Copper naphthenate (freshwater)	0.316	0.237
ACQ-B (freshwater)	0.643	0.483
ACZA (seawater)	0.340	0.254

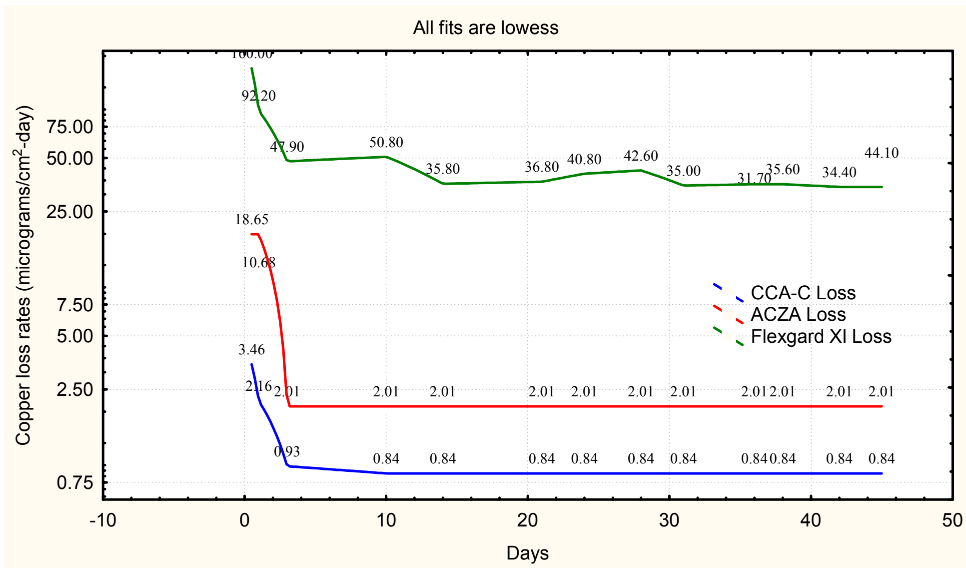
Table 7. Predicted long-term (*t > 15 days*) water column concentrations of copper (μg Cu/L) within a few centimeters (proximity model) of a single treated 30 cm diameter piling and on the downcurrent side of the box described in Figure xx in a slow current speed of 2.0 cm/sec. pH is assumed to be 6.5 and water temperature = 15 °C.

Preservative	Proximity Model (2 cm from single piling)	Box model (25 piling spaced 2 m on center)
CCA-C (freshwater)	0.006	0.003
Copper naphthenate (freshwater)	0.052	0.027
ACQ-B (freshwater)	0.059	0.034
ACZA in seawater (freshwater)	0.040	0.027

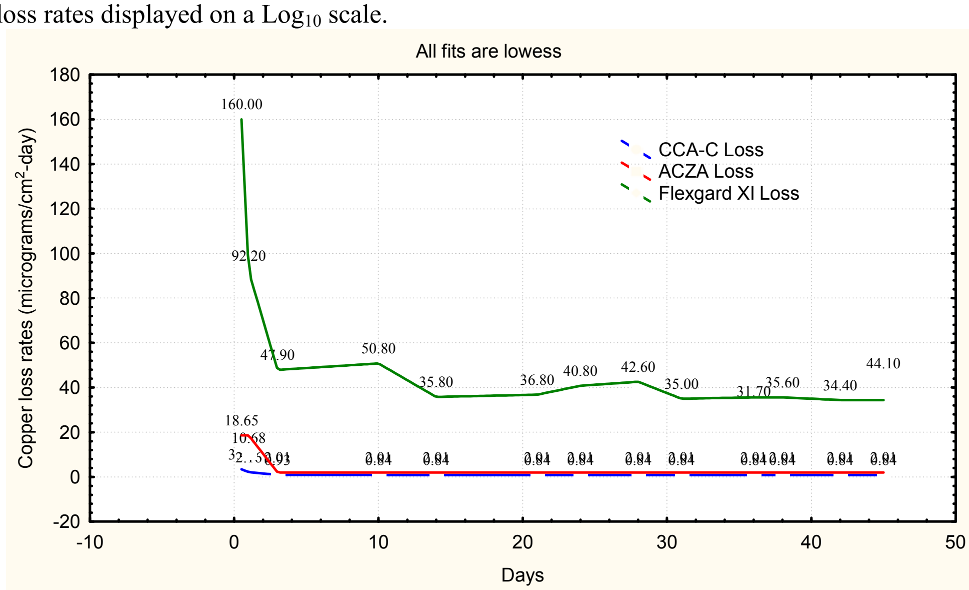
6.0. Putting copper losses from pressure treated wood into perspective. As previously noted copper is ubiquitous in earth's crust and its surface and ground waters. Copper has also been an important metal to civilizations for thousands of years and in the 21st century there are many uses of this metal and therefore many competing users for the allowable environmental load. Relatively high concentrations of copper are found in sewage treatment plant effluents (household water from homes containing copper pipes and industrial inputs), stormwater (particularly from highway runoff), industrial effluents (metal manufacturing, shipyards, etc.), agricultural inputs (from pesticide use and increased soil erosion) and nonpoint sources such as antifouling paints used on boats in marine environments. In addition, historic mining operations have resulted in acid leaching of copper from mine tailings that have affected several rivers and watersheds in western states. These many sources make copper a ubiquitous contaminant in heavily urbanized and/or industrialized areas.

A thorough analysis of these many sources of copper is beyond the scope of this paper. However, Seligman and Zirino (1998) provide a summary of copper inputs to San Diego Bay, where sediments are contaminated by copper (Brooks, 2004). The Toxics Release Inventory indicates that from 1988 to 1995, the mass of copper released each year to the environment increased from 14,500,000 kg to 19,000,000 kg. Furthermore, the U.S. EPA's National Sediment Quality Inventory found that copper presents a greater risk to aquatic life at more stations (7,000 of 16,000) than any other element or compound measured.

Seligman and Zirino (1998) note that the principal antifouling paints used by the US Navy are ablative copper coatings, which contain 40 to 55% copper and 20% zinc. These coatings are referred to as *ablative* because they are designed to lose copper resulting in high water concentrations at the ship's skin which inhibit the settlement of fouling organisms. This creates an important distinction between copper losses from ablative antifouling coatings and waterborne wood preservatives, which are designed to retain copper through fixation within the wood's cell structure. The end result is that antifouling paints maintain clean hulls on ships; whereas pressure treated wood is frequently heavily fouled. Copper loss rates from these two sources are described graphically in Figure 5a (for detail) and 5b (for perspective). The initial copper loss rate from Flexgard XI is 160 $\mu g/cm^2$-day (Anthony, 1991) in comparison with 18.65 from ACZA and 3.46 from CCA-C. The long-term loss rates are more important with respect to sediment contamination and both treated wood and antifouling paints reach steady state loss rates at the end of about 14 days. To maintain clean hulls, Flexgard XI ablates at a mean rate of 37.4 $\mu g/cm^2$-day, whereas the long term loss rate from ACZA is 2.01 and from CCA-C it is 0.842 μg Cu/cm^2-day (note that loss rates from CCA-C are higher in seawater than in freshwater).



5a. Copper loss rates displayed on a Log_{10} scale.



5b. Copper loss rates displayed on a ratio scale.

Figure 5. Comparison of copper loss rates as a function of time for CCA-C and ACZA preserved wood with losses from ship hulls coated with Flexgard XI™ antifouling paint.

If one assumes that a 600 foot long freighter (small by today's standards) can be modeled as an elliptical cylinder with a draft of 24' and major and minor axes of 600' (length) and 75' (beam), then the ship has an immersed area of 59,869,216 cm^2 and after the first 15 days, it contributes 2,239.1 grams of copper each day while sitting in port. In contrast, a 30 cm diameter CCA-C treated piling immersed in 24 feet of water contributes 0.014 grams of copper per day and the ship is equivalent to 159,114 CCA-C treated piling. ACZA loses more copper than CCA-C and a single piling contributes 0.14 grams of copper per day. Therefore copper losses from the ship each day are equivalent to 15,911 ACZA treated piling sitting in 24 feet of water, which is approximately equal to an entire years worth of production of this product on the Pacific Coast. A spreadsheet detailing these calculations is appended to this paper.

Seligman and Zirino (1998) provide data showing that a Navy shipyard is allowed a daily maximum copper discharge concentration of 33 µg Cu/L and a monthly average of 19 µg Cu/L. Actual discharge concentrations were reported to be much higher with numerous cases between 50 and 300 µg Cu/L. The authors noted that total identified discharges of copper to San Diego Bay are 31,304 kg/year. Two thousand ACZA treated piling, immersed in 24 feet of water, would contribute an additional 101 kg of copper to the Bay each year representing an increase of 0.32%. The contribution from an equal number of CCA-C treated piling would be $1/10^{th}$ this value or 10.1 kg representing a 0.032% increase.

My point in this discussion is not to berate the Navy. This example was simply readily available for this analysis and a similar examination of recreational marinas, civilian ports, stormwater or sewage treatment plant discharges would reveal copper concentrations that dwarf the contribution from several thousand treated wood piling used to construct support facilities for these other activities. It should also be emphasized that where water and/or sediment copper concentrations exceed national, regional or site specific WQC or SQC, currently available models would not recommend use of unsealed pressure treated wood products – regardless the proportional increase associated with the proposed project. The models have been developed as a tool for project proponents and regulators to manage the use of pressure treated wood – not to justify its use in every instance. If the pressure treated wood industry wants to sell products for use in copper impaired environments, then alternative BMPs, such as sealing or wrapping the piling can be considered. However, in unimpaired waters, modeling and field verification studies clearly demonstrate that the contribution of dissolved copper to aquatic environments is so small as to be immeasurable.

7.0. Summary. Copper is ubiquitous in earth's crust and in all surface and ground waters. It is an essential trace element that is added at 2.5 µg/L in Guillard's Medium F/2 to sea water for the optimum culture of marine algae (Strathman, 1987). Society depends on copper in many ways and losses of the metal to aquatic environments can compromise biological integrity – particularly in heavily urbanized and/or industrial areas.

Copper has long been known to affect olfactory reception in salmonids unacclimated to low concentrations. However, this review suggests that salmon encounter concentrations of 1 to 2 µg/L in many rivers and that once acclimated to these low concentrations they do not elicit chronic affects, such as avoidance, to moderate concentrations of copper. This review reveals no basis for setting an absolute standard of 2.0 µg Cu/L based on avoidance of copper in unpublished laboratory bioassays. Rather it appears that salmon acclimated to water containing no copper demonstrate behavior changes when confronted with rapid increases in the metal. In natural and pristine environments, rivers carrying high loads of suspended solids are seen to also have elevated concentrations of dissolved copper and these same rivers support some of the most famous and healthy runs of salmon. If the concentrations of copper were predicted or found to quickly increase by two parts per billion near treated wood structures, then their might be a basis for restricting construction of treated wood projects at certain times of year or in certain locations. However, computer modeling and empirical evidence suggests that the use of waterborne wood preservatives in fresh or marine waters not likely to increase dissolved copper concentrations by detectable amounts. The predicted amounts are a few tens of parts per trillion – not a few parts per billion.

Treated wood contributes copper to aquatic environments and in already impacted areas, its use could exacerbate existing exceedances of WQC or SQC. However, in environments were quality criteria are not already exceeded, the use of pressure treated wood in small to moderate size projects (less than 100 piling) is unlikely to result in any detectable increase in dissolved concentrations of copper. When used in association with moderately flowing salmon streams or in areas with normal tidal flushing, the increase in dissolved copper associated with the use of any of these waterborne preservatives, produced using *Best Management Practices*, is likely to be a few parts per trillion – a thousand times less than the several part per billion increase that might cause chronic effects in even the most sensitive species. The empirically derived estimates made in this paper have been verified on numerous occasions by field studies, which have failed to observe any significant increase in dissolved copper associated with the use of preserved wood.

There is a significant and consistent literature describing metal loss rates from pressure treated wood piling and the environment's response to its use in freshwater and marine environments. Models are available to assess exceptionally large projects or projects proposed for sensitive environments. When coupled with the use of *Best Management Practices* for the production of treated wood products and construction of treated wood projects, there is no evidence in the literature that these products cannot be used in a way that avoids unacceptable risks.

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