

**Literature Review, Computer Model and Assessment
Of the Potential Environmental Risks Associated with
Copper Naphthenate Treated Wood Products
Used in Aquatic Environments**

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Literature Review, Computer Model and Assessment Of the Potential Environmental Risks Associated with Copper Naphthenate Treated Wood Products Used in Aquatic Environments

1. Background. Copper naphthenate (CuN) has been used as an industrial biocide since the beginning of the 20th century (Minich and Goll, 1948). The active ingredient in CuN is a combination of copper salts and naphthenic acid. Naphthenic acid is found in crude oils at concentrations of 0.5 to 2.0 percent. These acids are known as cyclopentane or cyclohexane carboxylic acids. Naphthenic acids are represented by a family of compounds with typical product molecular weights ranging from 210 to 330 grams/mole (Brient *et al.* 1995). Buchanan and Solomon (1990) reported that CuN is relatively insoluble in water (< 1.5 mg/L). For purposes of pressure treating wood for use in freshwater, the preservative is dissolved in oils meeting the requirements of AWPA Standard P-9 (AWPA 1996).

Copper naphthenate is an unrestricted pesticide registered by the U.S. EPA for general use in treating wood (40 CFR section 152.170). The unrestricted status of copper naphthenate means that an applicator's license is not required by end users. For this reason, CuN is typically used to treat field cuts and borings during the construction of treated wood projects. All of the other common wood preservatives (CCA, ACZA, ACQ-B, pentachlorophenol and creosote) are restricted pesticides and end users must have a pesticide applicator's license to apply the preservative. This unrestricted status is applied in recognition that:

- Copper naphthenate wood preservatives are not Toxicity Category I acute toxicants;
- This preservative does not cause significant subchronic, chronic or delayed toxic effects; and;
- Copper naphthenate does not pose a serious hazard to man or the environment.

Copper naphthenate treated wood is not characterized as a hazardous waste (40 CFR Part 261). This means that CuN treated wood waste is not subject to TCLP testing. This greatly simplifies the disposal of CuN treated wood waste.

II. Aquatic toxicity and risk assessment benchmarks for copper naphthenate. Brooks (2000b) reviewed the toxicity of dissolved and sedimented copper in freshwater environments. The reader is referred to that document for an in-depth discussion of the aquatic toxicity of copper.

Dissolved copper and complexed copper naphthenate. The US EPA's Office of Prevention, Pesticides and Toxic Substances Product Chemistry Guideline 63-10, "*Dissociation Constant*", requires the active ingredient be sufficiently soluble in water to test for dissociation constants. Because copper naphthenate has such low water solubility, the EPA has not required this data. Based on this information, it is assumed that the migrating preservative will remain in the associated (CuN) form while in the water column. Toxicity data for copper naphthenate dissolved in a dimethylformamide solvent, developed by the U.S. Army Environmental Hygiene

Agency (AEHA, 1988), is summarized in Table (1). The lowest 96-hr LC₅₀ was 250 µg CuN/L for rainbow trout (*Oncorhynchus mykiss*). The 96 hr No Observed Effect Concentration (NOEC) for this species was 56 µg CuN/L.

Table 1. Toxicity data for copper naphthenate dissolved in dimethylformamide to a variety of aquatic organisms. All values are in micrograms copper naphthenate per liter (mg CuN/L). Data from AEHA (1988).

| Test Species | Type Test | Mean (mg/L) | Mean (µg/L) | 0.1 x Mean LC ₅₀ or NOEC |
|-------------------------|------------------------|-------------|-------------|-------------------------------------|
| <i>Rainbow Trout</i> | 96 hr LC ₅₀ | 0.25 | 250 | 25 |
| <i>Rainbow Trout</i> | 96 hr NOEC | 0.056 | 56 | 56 |
| <i>Bluegill sunfish</i> | 96 hr LC ₅₀ | 1.50 | 1500 | 150 |
| <i>Bluegill sunfish</i> | 96 hr NOEC | 0.56 | 560 | 560 |
| <i>Daphnia magna</i> | 48 hr LC ₅₀ | 1.10 | 1100 | 110 |
| <i>Daphnia magna</i> | 48 hr NOEC | 0.56 | 560 | 560 |

The bioavailability of CuN was significantly increased in the bioassay tests summarized in Table (1) because the compounds were dissolved in dimethylformamide. Copper naphthenate has very low water solubility and is expected to quickly complex with dissolved and/or particulate organic matter in natural aquatic environments. The anticipated reduction in toxicity associated with these complexes has not been studied. Therefore, Brooks (2002) collected twenty-liters of effluent from each of the three treatment replicates and the untreated control on Day 0.5. This material was stored and transported at 4°C the next day to Environment Canada’s Pacific Environmental Science Center (PESC), where 21-Day Chronic toxicity tests were conducted using *Daphnia magna*. Copper concentrations in the effluent provided to PESC were measured independently by that laboratory along with a suite parameters including water hardness.

Preliminary range finding tests indicated a 48-hr LC₅₀ of 59.4 µg Cu/L. EPA (2001) provides a Species Mean Acute Value (SMAV) of 20.12 µg total Cu/L at a hardness of 100 mg CaCO₃/L and 19.31 µg/L for only dissolved copper at the same hardness. Mastin and Rodgers (2000) reported 48-h LC₅₀ copper toxicity to *Daphnia magna* associated with herbicide use at 11.3 to 29.4 µg Cu/L suggesting that the combination of copper and other ingredients in the tested herbicides acted synergistically in one case and antagonistically in another with respect to this ostracod. The mode of action for the synergism or antagonism was not discussed. The point that should be taken from this is that the 48-hr LC₅₀ measured in the copper naphthenate effluent during this study was 59.4 µg total Cu/L – nearly three times the SMAV reported by EPA (2001). This suggests that the organic and inorganic components in the leachate from copper naphthenate treated wood act antagonistically with the copper to reduce the leachate’s acute toxicity to less than that associated with copper alone.

The 21-day chronic tests did not reveal significant reductions in neonate production at 1% effluent in which the copper concentrations were 4.56 to 5.92 µg Cu/L. Significant reductions were observed in two of six replicates at 5% leachate concentration where the copper concentration was 22.95 µg Cu/L. Unfortunately data for intermediate concentrations were not available. Therefore all that could be concluded from the tests was that the NOEL likely lies between 5.92 and 22.95 µg Cu/L. The U.S. EPA chronic standard at the observed hardness of

133.2 ± 5.17 mg CaCdO₃/L is 13.02 µg Cu/L – which is mid-range between the no effect and chronic effect concentrations reported by PESC.

For purposes of this analysis, the U.S. EPA chronic dissolved copper criterion given in equation (1) will be used as a risk benchmark. This is a four day average chronic criterion, which will be compared with predicted water column copper concentrations within a few centimeters of copper naphthenate treated piling on the second day following immersion to assess risk in freshwater environments.

$$\text{Equation (1) EPA chronic Cu criterion} = \leq 0.960 * \exp^{\{0.85456 * [\text{Ln}(\text{hardness})] - 1.465\}}$$

Toxicity of sedimented copper naphthenate. No direct information describing the toxicity of sedimented copper naphthenate was available in completing this assessment. However, Herman *et al.* (1994) studied microbial remediation of oil sands tailings and observed a Microtox EC₅₀ of 30% (v/v) for a commercial naphthenic acid (NAS) mixture (100 mg NAS/L).

Degradation of copper naphthenate. Herman *et al.* (1993, 1994) showed that natural microflora, including *Acinetobacter calcoaceticus*, *Pseudomonas fluorescens* and *Kurthia sp.*, were capable of degrading both commercial mixtures of NAS and to a lesser extent more complex mixtures of extractable organic acids found in oil sands tailings. The NAS was rendered non-toxic following three days of microbial remediation. Cosmacini (1972) examined the biodegradation of sodium naphthenate in fresh water and found that initial concentrations of ca. 4.5 mg/L were reduced to levels indistinguishable from zero in his published graph within nine days. Chim *et al.* (1974) found that naphthenic acids did not inhibit microbial degradation in activated sludge at concentrations less than 500 mg/L. Herman *et al.* (1993) and Herman *et al.* (1994) found that indigenous bacterial cultures present in oil sands tailings could utilize commercial mixtures of naphthenic acids as a sole source of carbon converting approximately 50% of the carbon into CO₂.

Assuming that the environmental fate of copper naphthenate is similar to that found by Cosmacini (1972) for sodium naphthenate suggests a half-life of approximately 3 days. Because of their slow loss rates from pressure treated wood (Brooks, 1996, 1997a, 1997b, 1997c, 1998a, 1998b, 2000a, 2000b), sediment accumulation of the active ingredients in wood preservatives occurs over periods of years. These time frames are long in comparison with a half-life of three days for copper naphthenate. This assumption leads to the conclusion that the naphthenate component will degrade leaving the copper behind in sediments. It would be helpful to this risk assessment if more information describing the environmental fate of sedimented copper naphthenate were available. This risk assessment will examine the accumulation of copper in nearfield sediments and determine the biological risks on that basis.

Washington State (WAC 173-204) has developed *Apparent Effects Threshold* sediment standards for marine environments. Similar standards have not been developed in North America for freshwater sediments. Brooks (2000a) discussed the literature describing sediment copper toxicity and reviewed available benchmarks used in assessing this issue. He developed the recommendations given in Table (2) for assessing the risks associated with anthropogenic inputs of copper to aquatic environments. These benchmarks will be used for assessing the risks to biota living in sediments near copper naphthenate treated wood.

Table 2. Recommended benchmarks for assessing the environmental risks associated with sedimented copper lost from pressure treated wood (Brooks 2000a).

| Sediment and Water Column Characteristics | Acceptable levels of Sedimented Copper |
|---|--|
| 1. Coarse grained sediment (silt & clay <10%) Total Organic Carbon < 0.2% Moderate to low pH (5.5 to 6.5) Low hardness and alkalinity (15 to 25 ppm CaCO ₃) | 30 µg Cu/g dry sediment |
| 2. Intermediate sediments (silt & clay between 10% and 25%) Total Organic Carbon between 0.2% and 1.0% Neutral pH (6.5 to 7.5) Moderate hardness and alkalinity (35 to 100 ppm CaCO ₃) | 55 µg Cu/g dry sediment |
| 3. Low energy, well buffered streams and lakes (fines > 25%) Total Organic Carbon >1.00% Greater than neutral pH (pH > 7.5) High hardness and alkalinity (> 100 ppm CaCO ₃) | 100 µg Cu/g dry sediment |

III. Copper naphthenate leaching rates from pressure treated wood. Brooks (2002) conducted two flow-through leaching studies using three sections of 60 cm long Douglas fir poles treated to 0.080 pounds of copper per cubic foot (pcf) of wood in the outer treated zone and three piling sections treated to 0.140 pcf. The poles and piling had circumferences of 62.6 to 78.0 cm. Diluent water had a mean pH 6.55 ± 0.11 and temperature of 9.86 ± 0.38 °C in the pole study and a pH of 7.17 ± 0.07 and temperature of 15.16 ± 0.16 in the piling study. Untreated Douglas fir controls were included in each study. Flow rates in the two studies were 172 ± 1.89 L/day in the pole study and 53.5 ± 4.26 L/day in the piling study. Effluent was collected on leaching days 0.5, 1.5, 2.5, 4.5, 7.5, 10.5, 15.5, 22.5 and 30.5 days following immersion. Long-term preservative loss rates will be determined in the future following six months of continual immersion. Copper concentrations in the effluent were determined at the Battelle Marine Science's Laboratory using ICP-AES following EPA Method 200.7 (EPA, 1994). Copper concentrations in the effluent were converted to copper loss rates per square centimeter of immersed wood per day.

The data for both studies were submitted to the Advanced Non-Linear Regression routine in Statistica™ 6 software with $\text{Log}_{10}(\text{Copper Loss})$ as the dependent variable and time, pH, temperature and retention as the independent variables. A constant term describing long term copper loss rates was also included in the exponential model. Independent variables with non-significant coefficients were iteratively eliminated from the model starting with the highest p-value. The final model, is provided in Equation (2). Within the narrow range of values examined, neither temperature nor pH was a significant factor. Also note that preservative loss rates were not significantly different between retentions of 0.08 and 0.14 pcf. That means that this algorithm can be used where either poles or piling will be in contact with surface freshwaters.

The constant term in Equation (2) was not significant at $\alpha = 0.05$, but it was at $\alpha = 0.10$. This term was left in the model based on the hypothesis that as long as there is unfixed CuN in the piling, some amount will likely migrate from the wood. The coefficient of determination for this solution was 0.90 and a normal probability plot of the residuals indicated that they were normally distributed. The results of this exercise are summarized graphically in Figure (1).

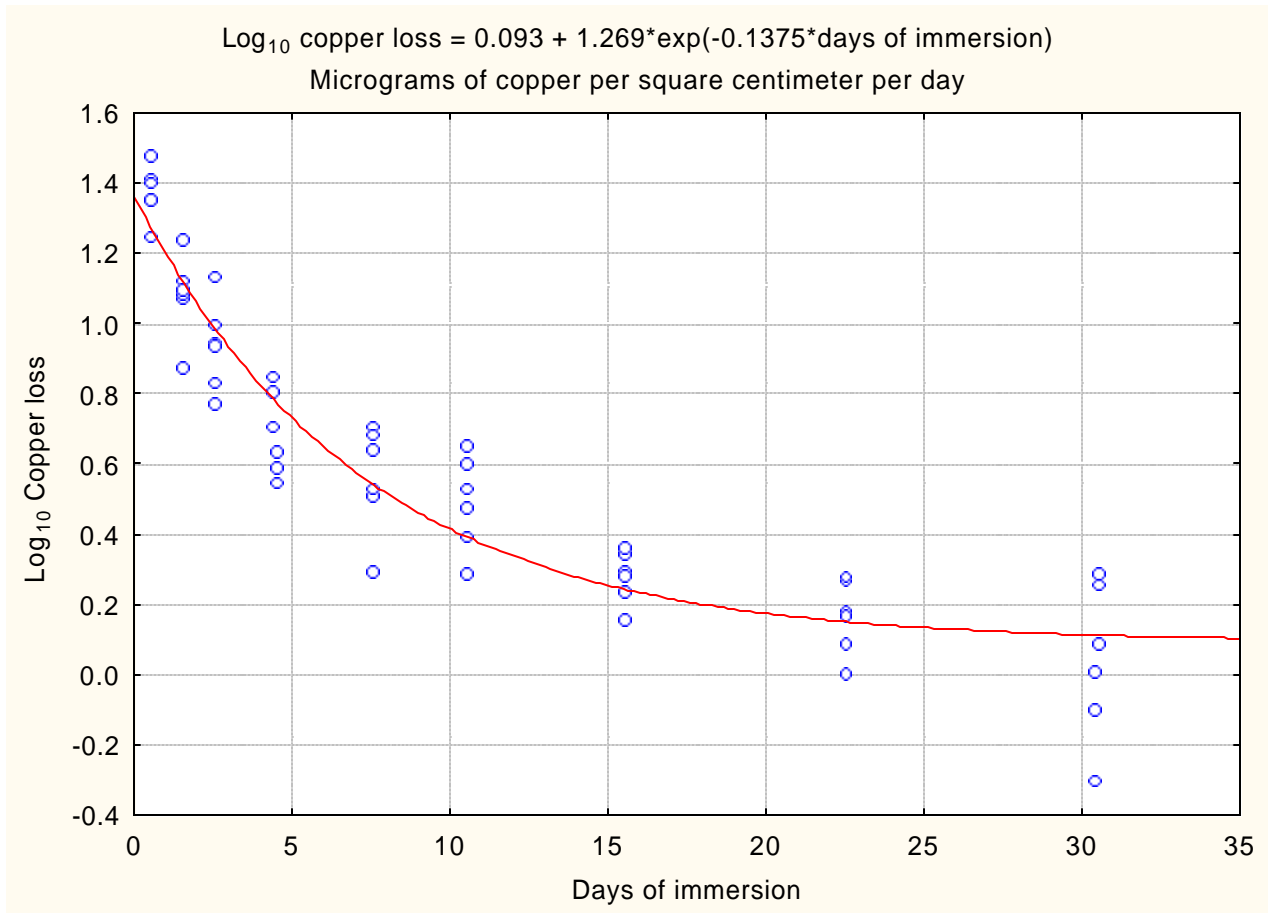


Figure 1. Log₁₀ copper loss rates from costal Douglas fir poles treated to 0.08 pcf Cu and piling treated to 0.14 pcf Cu using copper naphthenate wood preservative. This regression explained 90% of the variation in the database. Receiving water pH was 6.55 for poles and 7.17 for piling.

Equation (2) provides copper loss predictions for copper naphthenate treated poles and piling with retentions between 0.08 and 0.14 pcf Cu. It will be used in developing a risk assessment for copper naphthenate poles and piling immersed in fresh water. It predicts a long-term loss rate of 1.24 μg Cu/cm²-day. This long-term rate should be considered a preliminary finding. Actual long-term copper loss rates will be measured following six months of immersion of the same piling sections used in the study reported herein. These algorithms are accurate at pH values between 6.55 and 7.17. The algorithm may overestimate loss rates at higher pH values and underestimate them at lower pH values. This value is considered conservative from the environment’s point of view because most natural bodies of water have ambient pH values >6.55.

Equation 2. $\text{Log}_{10} \text{ copper loss} = 0.093 + 1.269 \cdot \exp(-0.1375 \cdot \text{days of immersion})$ (μg/cm²-d)

IV. A spreadsheet model predicting treated wood contributions of copper naphthenate to water and sediments. Based on the preceding review, and the analysis presented in this section, a model has been developed to predict water column concentrations of copper naphthenate and sediment concentrations of copper associated with treated wood. The model is intended as a tool

for engineers in the conceptual stages of design, and as a regulatory tool providing site and project specific assessments of the environmental risks associated with copper naphthenate treated wood used in aquatic environments.

The model is reasonably complete and includes 14 easily measured input parameters. However, it does have certain limitations. It is general in nature and does not include provisions for complex, turbulent or chaotic current vectors or mechanically induced redistribution of sedimented copper. Future loss rate studies may require modification of the algorithms used to describe the most important parameters such as receiving water pH.

This model does not include copper accumulation in sediments associated with the mechanical loss of treated wood fibers from structures. Pressure treated wood can be heavier than water and abraded material may sink to the bottom. For economic, as well as environmental reasons, treated wood should be protected from excessive abrasion such as that found in association with float pin piling, ferry dolphins and wingwalls. In addition, this model makes predictions for immersed wood. It does not include algorithms describing preservative lost from overhead structures such as bridges and piers.

In every case, the author has intended to be conservative (from the environment's point of view) in developing assumptions and evaluating the parameters upon which predictions are based. That is to say, if there is an error in this model, the error should cause an overestimation of the concentration of copper naphthenate in the water column and copper accumulation in sediments. This model has not been tested. However, similar models (Brooks 1997a, 1997b, 1997c, 2000a, 2000b) have been field verified and found to be conservative from the environment's point of view in that they always predict higher environmental concentrations of preservative active ingredients than have actually been observed.

Methodology for assessing the risks associated with dissolved copper naphthenate.

Copper naphthenate that is complexed with dissolved or particulate organic matter in the water column is likely to be carried downstream and diluted significantly before being sedimented. For purposes of estimating water column concentrations of copper naphthenate, this model will assume that the copper naphthenate is initially diluted into a volume of water equal to the cross-sectional area of the immersed piling. When piling are located parallel with the current such that the water passing one pile also interacts with the next piling downstream, the model assumes that turbulence increases the mixing volume by an amount equal to the cross-sectional area of a 30 degree cone as illustrated in Figure (2). The highest concentration of dissolved copper naphthenate is assumed to occur at the surface of the downstream most piling. In assessing water column concentrations of copper naphthenate, this model assumes that all copper naphthenate released from the pile is bioavailable in the water column.

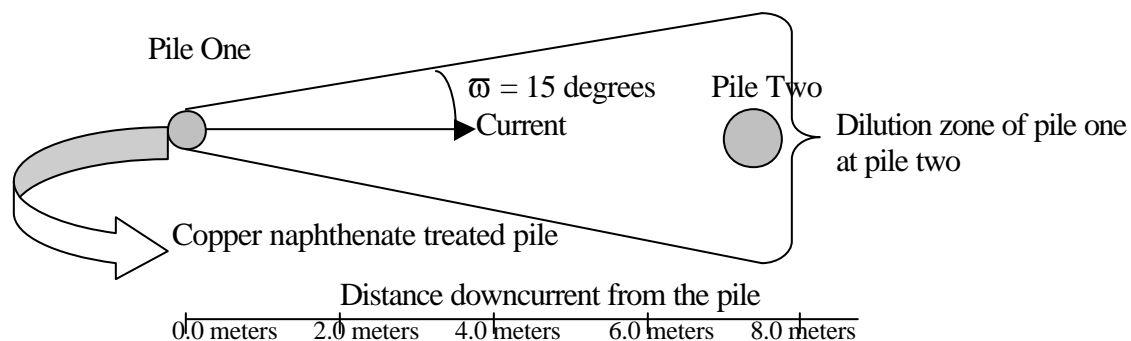


Figure 2. Geometry defining the dilution zone associated with a copper naphthenate treated pile immersed in freshwater. The third dimension is the depth to which the pile is immersed.

The Proximity Model described above is very conservative from the environment's point of view. Box models are more frequently used to predict water column concentrations of contaminants associated with diffuse sources such as treated wood piling. A box model based on the following assumptions is also provided in this assessment:

1. Current speeds are equal at all depths or can be adequately characterized using a mean current speed collected at the average water depth where treated piles are placed. This assumption greatly simplifies the model because both the preservative losses and the volume of the receiving water diluting the preservative are functions of water depth. Therefore the model need only consider the amount of preservative lost to a unit depth of water and the volume of water in that unit depth that passes by the structure with some mean speed V_{ss} .
2. The Box Model used in this assessment assumes that a specified number of piling with a mean average diameter are placed in a box that is defined by the width of the structure orthogonal to the currents; the current speed; and a unit height. This is illustrated in Figure (3).
3. The amount of preservative lost is determined by multiplying the loss rate given in equations (1) or (2) by the total leaching surface area (average piling circumference x number of piling x unit height).
4. The volume of dilution water is the width of the project measured orthogonal to the currents x current speed x a time equivalent to the units in the loss algorithm x unit height.
5. The concentration of copper or copper naphthenate in the receiving water is simply the amount of preservative lost (3) divided by the volume of dilution water (4).
6. This model relies on the benchmarks developed in Section II to assess environmental risk.

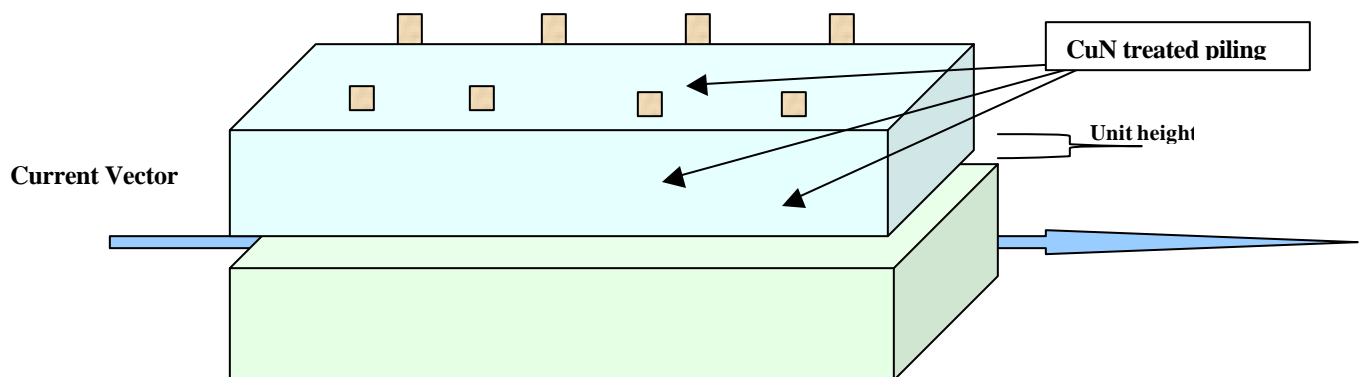


Figure 3. Conceptual drawing describing the box model methodology used to predict water column concentrations of copper naphthenate lost from pressure treated wood.

Methodology for assessing the risks associated with sedimented copper naphthenate.

Based on the chemistry of copper naphthenate, it appears that the organic component will quickly degrade in sediments leaving behind the inorganic copper. Following the worst-case methodology adopted for these risk assessments, it will be assumed that all of the copper naphthenate released from an immersed pile immediately adsorbs to particles similar in size and density to clay. The distribution of sedimented copper naphthenate will then be determined by tracking the fate of the clay in a non-turbulent column of water. Admittedly, this is not a very realistic scenario because much of the CuN will more likely adsorb to particulate organic matter (POM), which has a lower density than clay and would be distributed over wider areas – leading to reduced sediment concentrations. Therefore, this approach represents a worst case. All of the sedimented copper is assumed to remain at the original point of sedimentation and no allowance has been made for resuspension during high water or other factors that would reduce nearfield sediment concentrations.

This model is based on the deposition of clay adsorbed copper naphthenate. The vertical (settling) velocity of clay particles can be obtained through the application of Stokes Law (Shepard, 1963). This law is expressed in Equation (3).

Equation (3) Stokes law for the settling velocities of small particles:

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

Where: g = gravitational constant (980 cm/sec²)

D = particle diameter (≤ 0.00039 cm)

ρ_s = particle density (1.8 to 2.6 gm/cm³)

ρ_w = density of water (0.998 @ 20 °C)

μ = Coefficient of molecular viscosity (10⁻² g/(cm-sec) for freshwater at 20 °C)

Worst-case assumptions require modeling the largest clay particles ($D = 0.00039$ cm) at their highest density (2.6 g/cm³). Under these conditions, Stokes law predicts a settling velocity of 0.0013 cm/sec. This value has been used to predict the distribution of adsorbed copper naphthenate in sediments. Smaller clay particles of equal density would result in wider dispersal of the copper naphthenate resulting in lower sediment concentrations and lower predicted risk.

The Microsoft Excel™ model presented below can be used to assess the environmental risks associated with the use of copper naphthenate treated wood used in freshwaters flowing with constant speed such as upland streams, lakes and rivers at elevations above those where water levels are influenced by marine tides. This model is not appropriate for use in marine waters where tides create harmonically varying current speeds. However, copper naphthenate is not approved for use in saltwater. The following statements summarize the assumptions used in constructing the model:

- i. the volume of the receiving water is large (> 400 square meters per piling) in comparison with the total amount of preserved wood being used;

- ii. the released copper naphthenate adsorbs to the heavy clay fraction of the suspended particulate load with a vertical settling velocity of 0.0013 cm/sec;
- iii. copper naphthenate concentrations in the water column are determined in the immediate vicinity of the piling. No allowances are made for diffusion;
- iv. copper naphthenate accumulates in sediments and the organic fraction degrades quickly (half-life \cong 3 days) in comparison with copper accumulation in sediments.
- v. There is no bedload movement in streams and the copper remains at its original point of sedimentation;
- vi. there is no additional deposition of new sediment. The addition of new sediment would reduce the concentration of accumulated copper naphthenate;
- 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 over time. This model assumes that copper accumulates only in 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 concentration of copper naphthenate will be reduced in the real world.

Water column concentrations of copper naphthenate lost from piling in fresh water environments dominated by steady state currents. A conservative model for copper naphthenate concentrations in lotic systems assumes that preservative lost from a piling is 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.

$$\text{Equation (4) Dilution volume} = 2R_p V_{ss} * 86,400 \text{ ml/day or } 2R_p V_{ss} 86.40 \text{ liters/day}$$

Where: R_p = the radius of the piling (cm)

V_{ss} = the current speed (cm/sec)

86,400 = number of seconds in one day to match the CuN loss time

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 copper migration rate (M_{Cu}) developed in Equation (2) and correcting for the surface area in a unit height of water ($2\pi R_p M_{Cu}$) gives a conservative prediction of the water column concentration of copper lost from a single pile that has been simplified in Equation (5).

$$\text{Equation (5) Copper in water} = 0.045 * 10^{1.269 * \exp(-0.138 * \text{time (days)}) / V_{ss}} \text{ (}\mu\text{g Cu/L)}$$

Deposition rates of copper naphthenate to sediments in freshwater environments.

This dilution model assumes that water is passing a piling with constant velocity. Turbulence associated with the piling creates the geometry described in Figure (4).

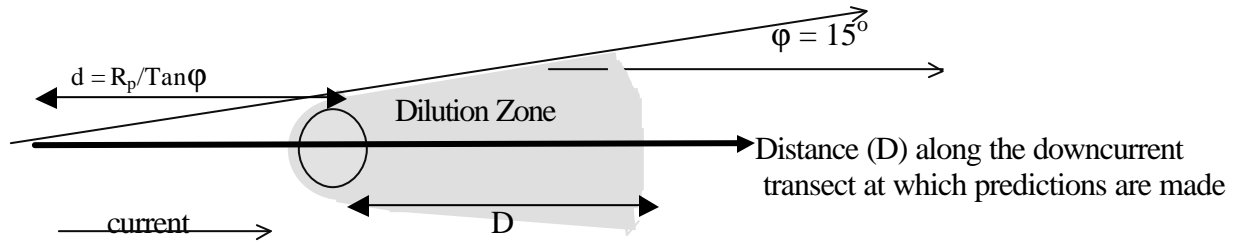


Figure 4. Dilution zone geometry used to predict preservative concentrations in sediments associated with the use of 0.14 pcf copper naphthenate preserved piling.

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

- dA = the incremental area
- R_p = radius of the piling
- D = Distance downstream from the surface of the piling
- dD = the incremental distance along transect D
- ϕ = the angle representing turbulent mixing = $15^\circ = 0.2618$ radians
- d = displacement of origin = $R_p / \text{Tan}\phi = 3.73 * R_p$

Simplifying, we obtain $dA = 2(D + 3.73 * R_p) * 0.2618 * dD$. 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 copper naphthenate is assumed to be adsorbed. Both are expressed in cm/sec. The expression then becomes:

$$dA/dh = 0.524 * (D + 3.73R_p) * V_{ss}/V_v$$

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

$$\text{Copper deposition (}\mu\text{gCu-cm}^{-2}\text{day}^{-1}\text{)dh} = 2\pi R_p M_{Cu} dh/dA = 2\pi R_p M_{Cu} V_v / (0.524 * (D + 3.73R_p) * V_{ss})$$

The sediment deposition rate of copper is predicted by substituting the copper loss rate (M_{Cu} = Equation 1) developed earlier into this expression.

$$\text{Equation (6) Cu deposition} = 11.77 * R_p V_v 10^{(0.093 + 1.268 * \exp(-0.138 * \text{time (days)})) / ((D + 3.73R_p) * V_{ss})} \text{ (}\mu\text{g/cm}^2\text{-day)}$$

- Where: R_p = radius of the piling;
- day = the number of days post immersion
- D = the distance (cm) from the downstream perimeter of the piling
- V_v = settling velocity = 0.0013 cm/sec
- V_{ss} = the steady state current velocity

The accumulation of copper on any day can be determined by solving Equation (1) from day = 0 to day = t . For this risk assessment, the project life was taken as 35 years. In most lotic environments, copper will be redistributed to low levels during winter high flows and a more appropriate accumulation would be 365 days. However, to be conservative, the longer time frame was used. The ratio of the 35-year loss to the first days loss (Day 0.5) was numerically determined to be 20.7 and the total accumulation is provided in Equation (7), which has been simplified and the sediment dilution factor of 2.0 cm sediment depth x sediment density (?) added.

$$\text{Cu concentration at the end of 35 years} = \frac{9,632.5 * R_p * V_v * 10^{(0.093 + 1.268 * \exp(-0.138 * 0.5))}}{2.0 * \rho * (D + 3.73 R_p) * V_{ss}} \text{ (}\mu\text{g Cu/g dry sediment)}$$

$$\text{Equation (7) Cu concentration at the end of 35 years} = 4,816.2 * R_p * V_v / (D + 3.73 R_p) * V_{ss} \text{ (}\mu\text{g Cu/g)}$$

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

$$\text{Depositional footprint's length} = V_{ss} dh / V_v$$

Where: 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 = 0.0013 cm/sec.

This expression can also be used to determine the maximum distance at which copper will accumulate downstream from the piling. For instance, if the height of the immersed piling is 5 meters, the steady state current speed is 2.5 cm/sec, then the maximum distance downstream at which copper is predicted to be deposited is 9,615 meters.

V. Predictive computer model for 0.08 to 0.14 pcf copper naphthenate preserved wood used in freshwater environments. The results of the preceding analysis have been incorporated into a *Microsoft EXCEL for Windows™* spreadsheet (Figure 5). A copy of the model is enclosed in the pocket at the back of this document. The following paragraphs provide specific definitions and instructions.

User Entries. Ten user entries are required to run the model. These are shaded in blue in Figure (5). Each of these entries is discussed in the following paragraphs:

- 1. Treated wood retention in pounds/ft³.** AWWA defines minimum copper naphthenate retention to insure adequate performance. Depending on wood species and hazard zone, AWWA Standards C2 and C3 (1996) require retentions of 0.06 to 0.14 lbs/ft³ for piling and lumber submerged in freshwater environments. The model was developed using wood that had been treated to a nominal retention of 0.08 and 0.14 lbs/ft³. Data supporting copper naphthenate treated wood use in marine environments has not yet been developed

and submitted to AWWA and there is no current AWWA Standard for marine use of copper naphthenate. The model covers the range of probable uses and no user entry is required.

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 be determined from the relationship: $Circumference = \pi * 2r$ or $R_p = circumference / 2\pi$ (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. To assess the chronic risks associated with newly constructed projects, this should be 2.0 days.
4. **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 historic data, take three measurements of current speed at mid depth using a window shade drogue or current meter and calculate the mean. In the example illustrated in Figure (7), a low speed of 0.5 cm/sec has been modeled.
5. **Settling Velocity** refers to the vertical velocity of suspended clay to which dissolved copper naphthenate is likely to adsorb. This model assumes that copper naphthenate adsorbs to the heaviest clay particles (3.9 microns diameter) with a settling velocity of 0.0013 cm/sec. Entering a lower settling velocity will result in lower sediment concentration predictions and a higher settling velocity will increase the predictions. The pre-entered value should be valid for nearly all cases and should not be changed without substantiating evidence for a different adsorption nuclei size.
6. **Water hardness.** This value is necessary in order to calculate the U.S. EPA freshwater chronic copper quality standard. Hardness is determined in mg/kg ($CaCO_3$) by an analytical laboratory using EPA 200.7. A 500 ml sample should be collected at mid depth in an HDPE bottle. The cost is about \$40.00/sample. In the example, the entered hardness is 55 mg $CaCO_3/L$.
7. **pH.** This is the standard pH measured electrometrically using EPA 150.1 or SM 4500 H+. Ideally, the measurement should be made *in-situ*. A 250 ml sample collected in amber glass can be held for 24 hours prior to laboratory analysis. The cost is about \$20.00 for laboratory analyses. In the illustrated case, the ambient pH is 6.55.
8. **Background water copper concentration.** Dissolved copper is normally measured using inductively coupled plasma (ICP) in accordance with EPA 200.7. A one-liter filtered (0.45 μm) water sample should be collected in a properly cleaned HDPE bottle to which 5 ml of HNO_3 has been added. The sample can be held for six months under these conditions. The cost is approximately \$45.00 if the sample has not been acidified. A detection limit $\leq 1.0 \mu g Cu/L$ should be required. In the example, a background concentration of 0.8 $\mu g Cu/L$ has been modeled. This value is added by the model to the predicted contribution from the treated wood to estimate the total dissolved copper concentration following immersion of the treated wood.

Copper naphthenate conc. in water and copper conc. in sediments associated with pressure treated wood

User Entries

1. Piling Retention in pounds per cubic foot
2. Average piling radius (centimeters)
3. Treated wood age in days
4. Mean current speed (cm/sec)
5. Settling Velocity (0.0013 cm/sec for clay)
6. Water hardness (mg CaCO3/L)
7. Water column pH
8. Background water copper concentration (mmg/L)
9. Background sediment copper (mg/kg)
10. Freshwater chronic copper standard
11. Freshwater sediment copper standard
12. Sediment density (g/cm^3)

| |
|--------------|
| 0.08 to 0.14 |
| 15.00 |
| 2.00 |
| 0.50 |
| 0.0013 |
| 55.00 |
| 6.55 to 7.17 |
| 0.80 |
| 12.00 |
| 6.12 |
| 55.00 |
| 1.60 |

Intermediate Output

| | |
|----------------------------------|--------|
| Exponential factor | 0.759 |
| Cu migration (microg/cm^2 - day) | 11.355 |

Proximate water column risk assessment

| | |
|-------------------------------------|-------|
| Water Column Cu Conc.(mmg/L) | 0.83 |
| Background copper (from E12) | 0.80 |
| Predicted total Cu conc. (mmg Cu/L) | 1.63 |
| Water copper standard (mmg Cu/L) | 6.12 |
| Ratio (Cu Concentration/Standard) | 0.135 |

Box Model User Entries

13. Width of Box (meters)
14. Number of piling in each row
15. Distance between rows of piling (m)

| |
|---|
| 4 |
| 1 |
| 2 |

Box Model Water Column Risk Assessment

| | |
|---------------------------------------|-------|
| Water Column CuN Conc. (mmg/L) | 0.86 |
| Allowable # of piling per meter width | 42.93 |

Sediment Risk Assessment

| Distance (cm) | Cu conc. P1 (microg/cm^3) | Cu Conc. P2 (microg/cm^3) | Total Cu from piling (microg/cm^3) | Background Cu (microg/cm^3) | Total Sediment Cu (microg/cm^3) | Sediment Standard (mg/kg) | Ratio: conc/stand |
|---------------|---------------------------|---------------------------|------------------------------------|-----------------------------|---------------------------------|---------------------------|-------------------|
| 10 | 1.54 | | 1.54 | 12.0 | 13.54 | 55.00 | 0.40 |
| 25 | 1.25 | | 1.25 | 12.0 | 13.25 | 55.00 | 0.39 |
| 50 | 0.96 | | 0.96 | 12.0 | 12.96 | 55.00 | 0.38 |
| 75 | 0.78 | | 0.78 | 12.0 | 12.78 | 55.00 | 0.38 |
| 100 | 0.65 | | 0.65 | 12.0 | 12.65 | 55.00 | 0.37 |
| 125 | 0.56 | | 0.56 | 12.0 | 12.56 | 55.00 | 0.37 |
| 150 | 0.49 | | 0.49 | 12.0 | 12.49 | 55.00 | 0.37 |
| 175 | 0.44 | | 0.44 | 12.0 | 12.44 | 55.00 | 0.37 |
| 200 | 0.40 | 1.54 | 1.94 | 12.0 | 13.94 | 55.00 | 0.41 |
| 225 | 0.36 | 1.25 | 1.62 | 12.0 | 13.62 | 55.00 | 0.40 |
| 250 | 0.33 | 0.96 | 1.29 | 12.0 | 13.29 | 55.00 | 0.39 |
| 275 | 0.31 | 0.78 | 1.08 | 12.0 | 13.08 | 55.00 | 0.39 |
| 300 | 0.29 | 0.65 | 0.94 | 12.0 | 12.94 | 55.00 | 0.38 |
| 325 | 0.27 | 0.56 | 0.83 | 12.0 | 12.83 | 55.00 | 0.38 |
| 350 | 0.25 | 0.49 | 0.74 | 12.0 | 12.74 | 55.00 | 0.38 |
| 375 | 0.24 | 0.44 | 0.68 | 12.0 | 12.68 | 55.00 | 0.37 |

Figure 5. Spreadsheet model predicting the environmental concentrations (mg/L) of copper associated with 0.08 to 0.14 pcf copper naphthenate treated wood immersed in freshwater at pH values between 6.55 and 7.17.

9. **Background sediment copper concentration.** Sediment copper is normally measured using ICP analyses in accordance with EPA 6010. A detection limit of ≤ 2.0 mg Cu/kg dry sediment should be achieved. A 4 oz. sample is normally collected into a precleaned widemouth glass jar. Collect only the top two centimeters of sediment using an acetone washed stainless steel spatula. The sample can be held frozen for six months. The cost is typically \$40.00 including a Strong Acid Sample Digestion (EPA 3050) in accordance with EPA 3000 series. In this case, a background concentration of $15.0 \mu\text{g Cu/g}$ dry sediment is modeled. This value is added to the predicted sediment concentration for comparison with the benchmark.
10. **Freshwater chronic copper standard.** This value is automatically calculated by the spreadsheet based on the water hardness (Entry 6) entered by the user. The value is expressed in $\mu\text{g Cu/L}$. In this case, the EPA standard is $6.12 \mu\text{g/L}$.
11. **Freshwater sediment copper standard.** The entry should be chosen from the descriptions given in Table (2) of this report. In this case, the lowest recommended value of $34 \mu\text{g Cu/L}$ is modeled.
12. **Sediment density.** This is the density of the sediment in grams/cm^3 . The modeled density of 1.6 g/cm^3 is reasonably approximation. No change should be made without specific data.
13. **Width of Box (meters).** This is the width of the area that is orthogonal (at right angles) to the current flow. The geometry is described in Figure (4). The value is computed by the model based on the number of rows their width orthogonal to the currents.
14. **Number of rows of piling.** This entry is included to facilitate use of the Box Model. It is simply the number of rows of piling used in the project.
15. **Distance between rows of piling.** This is the distance between piling bents.

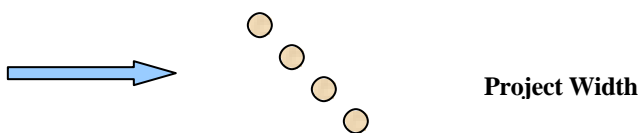


Figure 6. Geometry used to determine a projects width (User Entry 15).

Intermediate Output. The first entry in this section simply calculates the exponential factor associated with the age of the piling in the loss algorithm. The second output row describes the migration of copper from copper naphthenate pressure treated wood in $\mu\text{g CuN/cm}^2\text{-day}$ as a function of time following immersion.

Proximate water column risk assessment. This section of the output, located in the middle of the right side of the printout, is devoted to assessing the environmental risks associated with copper naphthenate dissolved in the water column. The first output is the predicted copper concentration within a centimeter of the treated wood's surface. The second row reflects the background copper entered by the user in User Entry (8). These contributions are summed in the third row. The forth row is the EPA chronic copper standard and the last row in this section describes the ratio of predicted copper to the standard. Values less than 1.0 indicate little or no

of the copper or sediments. This worst-case analysis also assumes that there is no additional accumulation of sediment that would dilute the copper.

Distance (cm). This is the distance (cm) downcurrent from the downcurrent face of the piling at which the prediction is being made.

Copper concentration piling (1). This is the predicted sediment concentration of Cu ($\mu\text{g/g}$ dry sediment) as a function of distance from the first in a series of any number of piling.

Copper concentration piling (2). This is the predicted sediment concentration of Cu ($\mu\text{g Cu/g}$ dry sediment) associated with a second piling. In this case the piling is located two meters (200 cm) downcurrent from the first piling. As many piling as are placed parallel to the currents can be entered in subsequent columns to develop a thorough understanding of cumulative effects. However, the contributions from upstream piling diminish significantly at distances greater than ca. 4.0 meters.

Total copper from piling (mg Cu/g). This value is simply the sum of the predictions made for the piling in previous columns.

Background copper (mg Cu/g). This is the background concentration of copper observed in sediments and entered in User Entry (9).

Total sediment copper (mg Cu/g). This value represents the predicted sediment concentration at the end of 35 years following project construction assuming that high annual flows do not redistribute and dilute the copper further from the piling.

Sediment standard (mg Cu/g). This is the benchmark determined by examining the environmental characteristics of the water body in the vicinity of the project and entered in User Entry (12).

Ratio: Concentration/Standard. This is the predicted maximum sediment copper concentration divided by the chosen standard. In general, a distance of 25 to 30 cm from the downstream piling has been chosen as an appropriate point at which to make this assessment. Ratios less than one (1.0) indicate that the project is acceptable.

Sediment summary. The results of modeling a large number of projects and scenarios indicates that if water column concentrations of copper are maintained at less than the U.S. EPA chronic copper standard, then the contribution of copper to sediments will be negligible in every instance. However, the addition of copper to sediments already exceeding reasonable benchmarks is a questionable practice and in these instances, an alternative pressure treatment may be appropriate.

VI. Summary and generalization of the environmental risks associated with the use of 0.14 pcf copper naphthenate pressure treated wood in freshwaters where the ambient pH is ≥ 6.55 .

The foregoing risk assessment is designed to provide site and project specific assessments. Table (3) was constructed using the Box Model and provides a summary of the maximum number of piling that can be installed parallel to the current vector without exceeding EPA chronic water quality criterion at 55 mg CaCO₃ hardness with a background copper concentration of 0.8 µg/L. The ambient pH is assumed to be ≥ 6.55 . Ambient pH values less than this are rarely encountered. Table (3) assumes that the rows of piling are placed two meters (6 feet) apart. The Proximity Model (Figures 5 and 7) indicates that water column concentrations will exceed the chronic EPA standard within a centimeter of the pilings surface when current speeds are ≤ 0.08 cm/sec. Few wharves and other large structures are being constructed on wooden piling today because concrete and steel have greater load bearing capacities. Most real treated wood projects involve two to five piling bents spaced at least four meters apart. This includes rural bridges, small ferry terminals, marinas and personal use docks and floats. Based on the results presented in Table (3) and the Proximity Model, small projects, located in nearly all natural bodies of water, present little or no risk to aquatic ecosystems.

Table 3. Maximum number of piling allowable to remain below the U.S. EPA chronic copper water quality criterion at a hardness of 55 mg CaCO₃/L on the first day of immersion of 30 cm diameter copper naphthenate piling treated to between 0.08 and 0.14 pcf copper in the treated wood. The table is accurate at ambient pH values ≥ 6.55 . The piling are assumed to be in rows spaced two meters apart.

| Current Speed (cm/sec) | Allowable number of piling per row paralleling the currents |
|-------------------------------|--|
| 0.1 | 10 |
| 0.3 | 20 |
| 0.5 | 51 |
| 1.0 | 103 |
| 2.5 | 257 |
| 5.0 | 515 |

Current speeds in streams and rivers are generally greater than 5 to 10 cm/sec and are typically greater than 0.5 cm/sec in lakes greater than perhaps 200 acres. Ponds and other small bodies of water that are replenished by annual streams or stormwater may have stagnant water during periods of calm wind. However, wind driven current speeds in these small bodies of water can also typically exceed 0.5 cm/sec.

It should be emphasized that Table (3) was constructed to reflect CuN concentrations on the first day of immersion. Concentrations will decline exponentially with time and would likely be undetectable following the first few days of immersion. Copper naphthenate pressure treated wood associated with projects containing fewer than 100 piling are unlikely to have any measurable effect on aquatic environments that would also not be present with other construction materials such as steel, concrete or untreated wood.

It is the opinion of this author that projects involving greater than 100 copper naphthenate treated piling should be subjected to a detailed site specific risk assessment. It is likely that such a risk assessment would be required in compliance with either the National Environmental Protection Act (NEPA) or State Environmental Protection Acts (SEPA).

VII. Abrasion of copper naphthenate treated wood piling. 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 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 (8).

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 untreated interior wood structure becomes available to fungi and boring organisms.

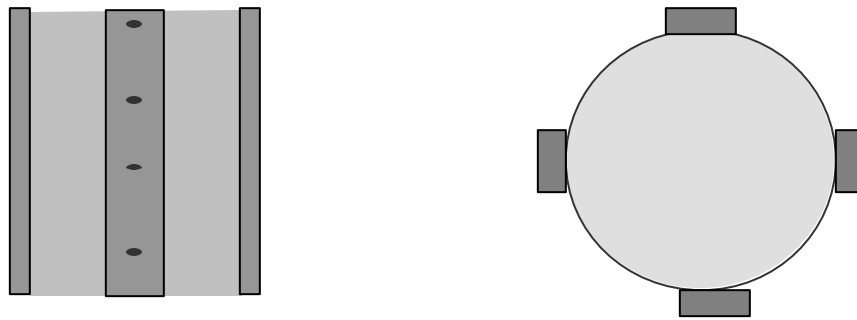


Figure 8. Use of half-inch thick strips of high-density polyethylene to reduce abrasion on wooden piling. The strips are nailed every six to eight inches using galvanized nails driven slightly below the surface of the bumper.

VIII. Treatment of complex structures. There is an endless variety of placements for copper naphthenate treated wood in actual structures. Output from the copper naphthenate risk assessment model predicts sediment copper concentrations along a line between piling, as the sum of the contributions from each piling. 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 entire structure in User Input # 2 (Average piling radius) multiplied by $\pi/2 = 1.57$. The anticipated copper naphthenate 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 concentration.

IX. Best Management Practices. The Western Wood Preservers Institute and the Canadian Institute of Treated Wood have developed *Best Management Practices For The Use of Treated Wood in Aquatic Environments* (WWPA – CITW, 1997). Project proponents can specify one or both of the following BMPs and/or government permit writers can condition permits to require them. They are designed to produce a clean product that is free of surface deposits of copper naphthenate and a product that will lose a minimum amount of preservative to the environment. The BMPs require one or both of the following procedures:

- Treat using copper naphthenate, which meets AWWA P8, Section 2. The solvent used shall meet the requirements of AWWA Standard P9, Hydrocarbon Solvent, Type A or Type C, depending on the product being treated and the specifications;
- Solution Filtration – The copper naphthenate solution in use shall be filtered or otherwise kept clean regularly to remove solids which may otherwise be deposited on the wood during treating;
- Follow good housekeeping practices to minimize sawdust and other surface residues on the wood prior to treatment;
- Expansion Bath – This process increases the temperature of the preservative solution surrounding the wood for the purpose of recovering excess preservative and improving surface cleanliness. The expansion bath shall be applied for a minimum of one hour at a maximum temperature of 220 °F or 230 °F depending on the specific commodity.
- The expansion bath shall be followed by a vacuum period using a minimum of 22” for a minimum of two hours;
- Final Steaming – Following the pressure period and removal of the treating solution from the retort, a vacuum shall be applied for a minimum of one hour at not less than 22” to recover excess preservative. Following the vacuum period, the wood shall be subjected to steaming for a two-hour time period for lumber and timbers and three hours for piling per the limitations of the AWWA Commodity Standards. The minimum temperature during steaming shall be 200 °F and the maximum shall be 240 °F to 245 °F depending on the species being treated. After steaming, apply a final vacuum for a minimum of four hours at 22” of vacuum.

X. Risk Assessment Summary. This risk assessment is intended to be conservative from the environment’s point of view. In every case, the author has used conservative assumptions in developing and evaluating the parameters upon which predictions are based. Field verification studies of similar models have always found lower concentrations of wood preservative active ingredients that were predicted by the models.

Copper naphthenate losses from wood treated to 0.08 to 0.14 pcf copper are predicted to be 18.9 µg Cu/cm²-day on the first day of immersion. Initial loss rates decline exponentially and

approach the long-term loss rate of $1.2 \mu\text{g Cu/cm}^2\text{-day}$ in about three or four weeks. The organic components in copper naphthenate and their intermediate compounds are rapidly degraded in natural environments with a half-life of approximately three days.

The toxicity of copper naphthenate has been determined for a number of aquatic organisms. It appears that the copper naphthenate compound is less toxic than copper alone. To be conservative, the U.S. EPA chronic copper standard is applied as a benchmark against which to assess the risks associated with the use of copper naphthenate treated wood in aquatic environments. Because the accumulation in sediments is slow in comparison with the short half-life of naphthenic acid, it is anticipated that copper will accumulate as opposed to copper naphthenate in this compartment. Sediment risks are evaluated using copper benchmarks that depend on a number of sediment physicochemical parameters such as sediment grain size, hardness, pH and total organic carbon. Modeling copper accumulation in sediments indicates that if water column concentrations of copper naphthenate are maintained below the specified benchmark, then sediment accumulations of copper will be less than values considered biologically significant. An exception to this would or could occur where ambient sediment copper concentrations approach or exceed the appropriate benchmark.

The minimum current speeds defined for copper naphthenate in this risk assessment are similar to those determined for other preservatives (Brooks, 1997a, 1997b, 1997c, 1998a and 1998b). It is unlikely that copper naphthenate could be detected in ambient waters following the first two weeks of immersion. Large projects, involving greater than 100 piling, should be required to complete a site specific risk assessment. All treated wood installed in aquatic environments should be produced in conformance with the *Best Management Practices* published by WWPI/CITW (1996). This risk assessment does not predict copper losses from wood not produced using BMPs.

This risk assessment is appropriate for determining the environmental risks associated with the use of piling immersed in freshwater. It should be noted that this risk assessment does not address preservative loss from overhead structures or losses associated with the abrasion of fibers from treated wood. However, overhead losses can be estimated by assuming that the wood is immersed in water.

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