## Environmental Risk Assessment for CCA-C and ACZA Treated Wood



Dynamic leaching apparatus used to measure metal loss rates from pressure treated wood

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### Kenneth M. Brooks Ph.D.

**1.0.** Author's qualifications. The author has been studying and modeling the environmental response to a broad spectrum of wood preservatives, including Chromated Copper Arsenate (CCA) and Ammoniacal Copper Zinc Arsenate (ACZA), for over a decade. This work includes publication of numerous peer-reviewed environmental scale risk assessments for the U.S. and Canadian governments. These efforts have addressed the risks and environmental response to many of the commonly used wood preservatives, including CCA-C, ACQ-B, ACZA, creosote and pentachlorophenol. Copies of the documents pertaining to CCA-C and ACZA are appended to these comments. In addition, the author has developed dynamic (flow-through) leaching procedures for evaluating metal losses from pressure treated wood commodities - not sawdust or small blocks of wood. His laboratory currently has the ability to adjust pH values within + 0.1pH units and temperature within + 1.0 degrees C in the large volumes of diluent water required for these dynamic studies. In the case of CCA, the results have been combined with data from other appropriate studies to define metal loss rates from CCA-C treated wood as a function of water temperature, pH, salinity and wood retention. The loss rate algorithms have then been used to construct simple *worst case* computer models predicting concentrations of metal in water and sediments adjacent to treated wood structures. The models have been field tested on numerous occasions and have always been found to be conservative from the environment's point of view. They are used by many local, state and federal agencies to assess the environmental suitability of a broad range of treated wood projects. The results of many of these studies are available in the peer reviewed literature. The following comments focus on aquatic environments. However, much of the information could also be applied to terrestrial landscapes.

**2.0.** Metal loss rates from CCA and ACZA treated wood in aquatic environments. Once an inorganic arsenical preservative is impregnated into the cellular structure of wood, the arsenic, copper and chromium or zinc interact with each other and with the wood components to form insoluble complexes. These insoluble complexes "fix" within and to components of the wood's cellular structure. In CCA preservation, this process can be monitored through the reduction of chromium VI to chromium III. The chromotropic acid test provides an easy method for assessing fixation. Current research indicates that copper forms carboxylate complexes and chromium, as chromium (III) forms arsenate and hydroxide compounds (Bull, 2001). The following comments are intended to help the reader understand these processes:

For CCA, the degree of fixation depends on appropriate conditions. The fixation process is facilitated by increased temperature, to between 140 and 150 °F, and by the presence of a minimum of 22 percent moisture. The higher temperature increases the rate of chromium (VI) reaction with wood components, causing the chromium (VI) to be reduced to chromium (III). This causes the pH of the treated wood to increase to a value consistent with untreated wood. It also results in the formation of insoluble chromium and copper compounds. If the temperature is too high, then the energy of the metal complexes (random motion) is higher than the binding strength and while they find new sites quickly, they frequently break their bonds at those sites. If the wood dries, there is no medium for this reaction to occur in and the CCA preservative will remain unfixed with no reduction of chromium (VI).

- The actual formation of the metal complexes involves a number of mechanisms, each with a different strength (covalent bonds > ionic bonds > van der Waals bonds, etc.). The bonds do not have infinite strength and can be broken by a number of means such as heating the wood to temperatures in excess of 160 °F, physical impact, chemical action, etc.
- The treating process first applies a vacuum to the wood to evacuate as much air from the cell lumens as possible. The preservative is then forced into the wood under high pressure. This allows the preservative to move across the wood cells' surface into their lumens. The pressure cycle in essence opens the door of a box, the CCA preservative enters the box and the door on the box is then sealed when the pressure is released. The point is that the cellular structure of the wood forms a relatively impermeable box that helps to contain the preservative irrespective of the fixation process. In other words, the cellular structure of wood affords diffusion limitations for the migration of zinc, chromium (III), copper (II) and arsenate ions from within the wood structure to the external environment.
- Together, the wood's cellular structure and the formation of insoluble complexes, produce a product that retains the metals allowing minimum movement of preservative from the wood's interior to the outside world. However, the state of CCA metal complexes within the wood is most likely dynamic not static. The bonds that "fix" the metal complexes in the wood are constantly being broken and re-established. The frequency of these actions is undoubtedly related to the temperature of the wood (kinetic energy of the metal complexes) and other factors such as pH, ionic strength, and the presence of any chelators in any water in the lumen. The important point here is that it is the wood's cell structure that contains the ions while they are seeking new sites to bind to.
- In general, and in particular for piling, it is only the outside shell of the wood that is initially preserved. One result of the dynamic state of the preservative within the wood's cells is that metals continue to migrate within the wood in all directions in response to diffusion gradients. This results in a redistribution of the preservative within the wood's interior as well as migration to the outside world. In response to the diffusion of preservative within the wood, initially high concentrations of preservative in the outer layers of wood will naturally decline as the metals diffuse into the interior of the wood. This means that any determination of metal loss rates to the outside world, based on retention assays at some depth beneath the wood's surface, is flawed. The assumption that the decrease in retention at a depth of 0.5 or 1.0 cm resulted from losses to the outside world is simply not valid and grossly overestimates the loss rates. A portion of the reduction in metal concentration in surficial wood layers was caused by metal migration into the interior of the wood as well as leaching to the outside environment.
- The wood's cellular structure is most open to the outside world at the end grain and least open across the face grain. Fortunately, for structural reasons, nearly all wood structures are constructed of components with a very small end-grain to surface area ratio.
- CCA and ACZA wood preservatives are used to extend the life of wood used to construct a variety of structures. These structures are constructed of commodity size pieces of wood with small end-grain to surface-grain ratios (0.008 for a 12 foot long nominal 2 x 6 and

essentially 8 for a piling with one end buried in sediment and the other above water in the air). They are not constructed of small blocks of wood with high end-grain to face grain ratios and they certainly are not constructed of sawdust, in which the cellular structure of the wood has been destroyed and the bound metals detached by mechanical impact.

- For purposes of understanding the environmental response to treated wood products, researchers need to focus their attention on studies that have examined the loss of metal from the material actually used in construction not from small blocks of wood or from sawdust. With respect to aquatic environments, the only studies that are appropriate for quantifying metal loss rates in water are those that measure metal concentrations from wood treated to AWPA specifications for use in aquatic environments in diluents that are characteristic of the real world. The concentrations of metals in diluents have no useful meaning unless they can be converted to loss rates from the wood per unit time. Place a treated board into water for one hour and you get one concentration of metal. Leave it there for a day and you get another concentration. Neither value is useful for understanding the environmental performance of the product unless the concentrations can be converted to some loss rate (i.e. in  $\mu g \operatorname{Cu/cm^2-day}$ ). Based on the preceding discussion, the following criteria could be used to identify those leaching studies that are useful for assessing metal loss rates to aquatic environments:
  - The wood should be treated to AWPA specifications for use in marine or freshwaters;
  - The wood samples should have small end-grain to surface grain ratios, or the end grain should be sealed;
  - Tests using sawdust, such as required by SPLP and TCLP or small blocks of wood without sealed end-grain are of little use for assessing metal loss rates to aquatic environments;
  - For CCA, preservative fixation should be demonstrated using the chromotropic acid test. Otherwise, almost any value can be obtained;
  - Leaching conditions with pH values outside a range of perhaps 5.0 to 9.0 have little applicability to the real world. When buffers are required to achieve a desired test pH, they should be similar to those anticipated in the real world. The numerous criticisms and problems associated with the work of Warner and Solomon (1990), who used a citric acid - sodium hydroxide buffer system are an example. This author recommends the use of inorganic acids such as the sulfuric:nitric acid combination specified for SPLP testing to mimic naturally reduced pH conditions;
  - Salinity should be between zero and perhaps 40 parts per thousand;
  - Appropriate temperatures lie between perhaps 5 and 35 degrees centigrade.
  - In the least, the studies should be static renewal. This author prefers dynamic tests to insure that high metal concentrations in the diluent do not reduce diffusion gradients to the point where they inhibit further metal migration from the test samples;
  - If bioassays are contemplated, then water hardness and pH should be established at or above the minimum EPA requirements for the test organism(s).

3.0. Predicting the concentration of metals in aquatic environments near CCA treated

**wood projects.** The literature does contain numerous studies that meet the foregoing requirements and that provide consistent results describing metal loss rates from fixed CCA treated wood to aquatic environments. Nonlinear regression analysis was used by Brooks (2002) to determine metal loss rates from CCA-C treated wood reasonably meeting the requirements given above. The results of several dynamic (flow-through) studies conducted at Aquatic Environmental Sciences were combined with data from Breslin and Adler-Ivanbrook (1998), Kim and Kim (1993), Van Eetvelde *et al.* (1995) and Putt (1993) to develop algorithms describing metal loss rates from CCA-C treated wood as a function of retention, receiving water temperature, pH, salinity and time of immersion. Results from Warner and Solomon (1990) were not included because these researchers used an inappropriate buffer system to adjust pH (see Cooper 1991). The resulting database contained 322 cases describing leachate concentrations of copper, chromium and arsenic associated with the following range of physicochemical conditions:

- ➢ four wood species
- $\blacktriangleright$  CCA-C retentions between 4.5 and 64 kg/m<sup>3</sup>
- ▶ water at salinities between 0.0 and 34 parts per thousand
- ➤ temperatures between 4 and 20 °C
- ▶ pH values ranging between 5.5 and 8.5.
- ➢ Immersion times of 28 to 514 days.

Non-linear regression was used to develop Equation (1), which includes both additive and first order exponential terms describing increased copper losses with increasing temperature, salinity, preservative retention and reduced pH. Equations (2) and (3) describe chromium and arsenic loss rates, which were less sensitive to physicochemical properties in the receiving water.

Equation (1) Copper loss rate (
$$\mu$$
g/cm<sup>2</sup>-day) = 0.036\*Temp (°C) + 0.021\*(Salinity + 0.01)  
- 0.002\*Retention (kg/m<sup>3</sup>) - 0.031\*pH  
+ 6.95\*exp  ${}^{(0.007*Retention (kg/m3) + 0.121*Temp (C))}_{x exp}$ 

Equation (2) Chromium loss ( $\mu g \operatorname{Cr/cm^2-day}$ ) = 0.047\*exp<sup>(-0.013\*Retention (kg/m3)</sup> x exp<sup>0.103\*Temp (C) - 0.031\*Salinity (ppt) - 1.07\*time</sup>

Equation (3) Arsenic loss ( $\mu g As/cm^2-day$ ) = 0.010\*Salinity (ppt) +0.754\*exp<sup>(-0.130\*time)</sup>

Note: In equations (1) through (3), time is immersion time in days

Sensitivity analyses based on Equations (1), (2) and (3) are presented in Figures (1), (2), and (3). With the exception of the temporal predictions in Figure (1), all of the charts are based on metal loss rates during the first day following immersion. These predictions indicate that copper is the most mobile of the three metals under all tested conditions – at least on the first day of immersion. The temporal predictions in Figure (1) indicate that copper and chromium losses declined quickly and reached long-term loss rates asymptotically within about three days. Arsenic loss rates started low at 0.75  $\mu$ g/cm<sup>2</sup>-day, but the As loss rate declined more slowly and

for a longer period of time following immersion. Long term metal loss rates from CCA-C treated southern yellow pine in freshwater at pH 7.5 and 13  $^{\circ}$ C are predicted to be 0.193 µg Cu/cm<sup>2</sup>-day; 0.074 µg As/cm<sup>2</sup>-day and 0.011 Cr/cm<sup>2</sup>-day. Chromium losses were low under all tested conditions.

Within a range of realistic environmental conditions, CCA-C metal loss rates were more sensitive to temperature changes than they were to changes in pH. Figure (3) indicates that copper losses in this dataset increased by 469% as temperature increased from 8 to 20 °C. In contrast, copper loss rates increased from 1.060 to 2.358  $\mu$ g Cu/cm<sup>2</sup>-day (238%) as pH decreased from 8.5 to 5.5 (Figure 2). Interestingly, as shown in Figure (4) chromium loss rates declined in this dataset with increasing CCA-C retention, while arsenic loss rates were little affected and copper losses were only moderately affected.

The sensitivity of long-term metal loss rates to changes in wood species, pH, temperature, salinity and retention is explored in Figure (5). Aquatic organisms are more sensitive to copper than they are to either arsenic or chromium. This fact coupled with the higher long-term copper loss rates from CCA-C treated wood and its higher sensitivity to environmental factors confirms that this is the metal of most concern when assessing environmental risks.

When the data developed specifically to describe metal loss rates from CCA treated structures into aquatic environments is examined, one finds that simple analytical tools lead to reasonably accurate loss rates: i.e. the coefficients of determination for the regression analyses were 80.4% for copper; 64.2% for arsenic; and 36.6% for chromium.



Figure 1. Predicted metal loss as a function of time from wood treated with CCA-C to a retention of 24 kg/m<sup>3</sup> and immersed in fresh water at a temperature of 13  $^{\circ}$ C and pH = 7.5.



Figure 2. Predicted metal loss as a function of pH from wood treated with CCA-C to a retention of 24 kg/m<sup>3</sup> and immersed in fresh water at a temperature of 13  $^{\circ}$ C.



Figure 3. Left - metal loss as a function of temperature in freshwater (retention =  $24 \text{ kg/m}^3$ ) and pH = 7.0. Right - wood treated to  $40 \text{ kg/m}^3$  and immersed in seawater at 30 parts per thousand.



Figure 4. Left - metal loss as a function of retention in freshwater (retention =  $24 \text{ kg/m}^3$ ) at a temperature of  $13 \,^{\circ}\text{C}$  and a pH of 7.0. Right - wood treated to  $40 \,\text{kg/m}^3$  and immersed in seawater at 30 parts per thousand.



Figure 5. Box and whisker plots describing long-term metal loss rates from CCA- C treated wood over a range of pH, temperature and salinity. Four different wood species are included in the database.

**4.0. Predicting the concentration of metals in aquatic environments near ACZA treated wood projects.** Based on data presented in Stanley (1994b), Brooks (1997) developed metal loss algorithms and models for ACZA treated wood. Metal loss rates from ACZA treated wood are a function of salinity, time after treatment and retention rates. The following loss algorithms are from Brooks (1997b). All losses are in  $\mu g \text{ cm}^{-2} \text{ day}^{-1}$ .

Saltwater Copper Losses =  $32.5 \text{ x exp}^{-1.114 \text{ x Days}}$ Fresh Water Copper Losses =  $1908.6 \text{ x exp}^{-0.429 \text{ x Days} - 0.383 \text{ x pH}}$ Fresh and Saltwater Arsenic Losses = 0.099Zinc Fresh Water Losses =  $166.6 \text{ x exp}^{-1.02 \text{ x Days} - 1.054 \text{ x pH}}$ Saltwater Zinc Losses =  $31.074 \text{ x exp}^{-2.667 \text{ x Days}}$ 

**5.0.** Summary comments regarding metal loss rates from CCA-C and ACZA treated wood structures into aquatic environments. The literature describing metal loss rates from arsenically treated wood (CCA-C and ACZA) is complex. Reviewers must be careful to ask specific questions and to use studies appropriate to those questions when seeking answers. For instance, the work of Stanley (1994a), which was conducted at pH values of 5, 7, 9 and in 0.10M HCl. Only those portions of this study which examined loss rates at environmentally realistic pH values between 5 and 9 are useful in understanding the environmental response to these products. There are no natural environments that are appropriately modeled by 0.10M HCl. Similarly, a

paper by Warner and Solomon (1990) has repeatedly been criticized in the literature because of their use of a sodium hydroxide – citric acid buffer system and their unrealistic pH values of 3.5 and 4.5. Similar cautions should be appended to the analysis of soil or sediment data in which aggressive extraction techniques have been used. If the question being asked regards human or environmental health, then the extraction techniques should assess bioavailable metal – not total metal.

**6.0.** Predicting the environmental response to immersed structures constructed of CCA-C and ACZA. Several models (Brooks 1996, 1997, and USACE 1997) have been developed for predicting environmental concentrations of dissolved metals in aquatic environments near CCA or ACZA treated structures. The Brooks models have been field verified on several occasions for other preservatives (creosote and ACZA) and always found to be somewhat conservative from the environment's point of view. In other words they predict slightly more preservative in water and sediments than is actually found. USACE (1997) and Brooks (1996, 1997a, 1997b) rely on metal loss algorithms developed by Brooks.

6.1. Predicting environmental concentrations of copper, chromium and arsenic in aquatic environments near CCA treated structures. The proximity model of Brooks (1996) has subsequently been modified to include the metal loss algorithms described in Section 3.0. The dilution algorithms for these models are based on *worst case analyses*. For piling placed in lotic or lentic environments, the model assumes that the dilution water is defined by the diameter of the piling and the average current speed on the day of installation. The dilution volume for harmonically driven systems is more complicated and the reader is referred to Brooks (1997a) for details. Figure (6) describes the predicted concentration of copper in the water column within a few centimeters of a piling treated to  $24.0 \text{ kg/m}^2$  and immersed in water having a pH of 5.5 and temperature of 15 °C as a function of current speed. Current speeds in most rivers and streams are > 5 to 10 cm/sec. Along shore current speeds in lakes are typically 2.0 to 5.0 cm/sec. In estuaries, current speeds vary greatly from <1.0 to 100 cm/sec or more depending on tidal exchanges geomorphology, etc. The point is that current speeds are > 0.5 cm/sec in most of these environments and at this slow speed, single treated piling is expected to raise the concentration of dissolved copper in water located within a few centimeters of the piling by less than 0.2 µg Cu/L. It is unlikely that increases in dissolved copper this small can be measured because all surface water caries copper and the natural variability is much larger than the predicted increase. Predictions for arsenic and chromium can be made using equations (2) and (3). The results indicate that a 30 cm diameter placed in freshwater having a pH of 6.5, temperature =  $15 \,^{\circ}$ C, salinity = 0.0 and hardness equivalent to 55 mg CaCO<sub>3</sub>/L, the piling will lose 4.08 µg Cu/cm<sup>2</sup>-day: 0.106 µg Cr/cm<sup>2</sup>-day: and 0.71 µg As/cm<sup>2</sup>-day. Assuming that the water is flowing at a speed of 0.5 cm/sec, which would be characteristic of small ponds and lakes, the predicted increase in the concentration of dissolved metal within a few centimeters of the piling would be 0.296  $\mu$ g Cu/L; 0.008  $\mu$ g Cr/L and 0.05  $\mu$ g As/L.



# Figure 6. Copper concentration within 2.0 cm of a Class A piling treated to 24.0 kg/m<sup>2</sup> with CCA-C in water having an ambient pH of 5.5 and a temperature of 15 °C.

The bottom line is that these worst case models do not predict significant increases of metals near individual piling or small groups of piling in open water bodies. Different dilution algorithms are provided by Brooks (1997a) for bulkheads. The models predict higher concentrations of dissolved and sedimented metal associated with CCA treated bulkheads, particularly when large sections of bulkhead are constructed over short periods of time in poorly flushed residential canals. The question to be answered is whether or not the observed increases in dissolved metals pose significant threats to aquatic resources.

6.2. Assessing the potential for arsenic and chromium bioconcentration and biomagnification by aquatic biota near CCA-C treated structures. The metals contained in CCA are all natural parts of the earth's lithosphere. The average crustal concentrations are: copper is ca. 50  $\mu$ g Cu/g; 125  $\mu$ g Cr/g; and arsenic 7  $\mu$ g As/g with natural concentrations as high as 100  $\mu$ g As/g. These elements are found everywhere, particularly in aquatic environments and it is well known that they bioconcentrate in fish and shellfish.

6.2.1. **Arsenic bioaccumulation.** Because inorganic trivalent arsenic is a potent toxicant in mammals (including man) at even moderate concentrations, there is considerable data describing its bioaccumulation. Penrose, *et al.* (1977) examined the arsenic budget in a sea urchin-alga system and concluded that organic arsenic is rapidly excreted by most organisms and

therefore, while there may be significant bioconcentration of arsenic from surrounding waters, there is no apparent biomagnification in food chains. Organisms containing high levels of arsenic in their tissues tend to be those that are prone to incidental ingestion of sediment particles while feeding.

Bioconcentration of arsenic from ambient water has also been reported by Schroeder and Balassa (1966), Lunde (1970, 1975) and Fowler *et al.* (1975). High levels of arsenic in marine animals are reported by USDA (1980) from around the world. Reported levels of arsenic, expressed as a proportion of wet tissue weight, for some typical marine species are provided in Table (1) based on data from USDA (1980). Woolson (1977) reported that arsenic concentrations are 10 to 100 times higher in marine fish and shellfish than in fresh water species.

### Table 1. Arsenic content of aquatic animal life (in parts per billion). USDA (1980).

#### Marine

Fresh

Crab	27,000 - 5	52,500
Clams (all species)	900 - 1	12,720
Oysters (Crassostrea virginica)	600 - 4	42,750
Lobster (Panulirus borealis)	3,200 -	9,600
Tuna	710 -	4,600
Water		
Trout	69 -	149
Perch (Perca fluviatilis)	600	
Bass (Micropterus salmoides)	70 -	930
Channel catfish (Ictalurus punctatus)	0 -	3,100

Penrose and Woolson (1974) reviewed studies by Fernandez del Riego, Seydel and Lunde which suggested that arsenic was not biomagnified in food chains. Work by Boothe and Knauer (cited in Penrose and Woolson, 1974) and Black and Penrose (cited in Penrose and Woolson, 1974) suggested that arsenic ingested in food is rapidly excreted by marine organisms. Woolson (1975) summarized his review of arsenical bioaccumulation by noting that:

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

6.2.2. **Chromium bioaccumulation**. Eisler (1986) reported that algae and higher plants accumulate chromium from seawater by factors of up to 8,600 and from solutions containing 50 ppm chromium by a factor of 18 in 48 hours. Although chromium is abundant in primary producers, there is little evidence of biomagnification through marine food chains. Baptist and Lewis (1969; cited in Eisler, 1986) followed the transfer of chromium through an experimental food chain and observed a decline in the concentration of chromium through each of four trophic levels. Comparison of the results of this food chain study with measurements of direct chromium uptake from seawater suggest that direct uptake is a far more important pathway than assimilation through the food chain. Bioconcentration factors (BCF) for numerous aquatic

species are given in U.S. EPA (1983). The reported BCF for chromium (VI) in fish muscle is less than 1.0. Values of 125 and 192 were obtained by EPA for chromium (VI) in oysters and blue mussels. The EPA document also gives values for chromium (III) and concludes that they are similar to those given above for chromium (VI). The EPA conclusion was that mean BCF values of 0.5 and 130 are appropriate for fish muscle and bivalve mollusks respectively. These are both relatively low BCFs. It appears that chromium does not biomagnify in food chains and that chromium concentrations at all trophic levels are primarily a function of ambient concentrations.

6.3. Benchmarks for assessing the potential effects of dissolved copper, chromium and arsenic released from CCA treated wood into aquatic environments. There is a large and diverse literature addressing the toxicity of copper, chromium and arsenic to aquatic species. Much of this was developed in support of EPA's Water Quality Criteria (WQC), which are protective of aquatic life and have been incorporated into state statutes designed to protect aquatic resources from Florida to Alaska. The reasonable benchmarks for assessing the toxicity of these three metals in the United States are US EPA Water Quality Criteria. Current EPA WQC, as adopted by Washington State in WAC 173-204, are summarized in Table (2). Note that these values are significantly lower than the  $LC_{50}$  values reviewed in the draft chapters. Recall also, that under worst case conditions, a single 30 cm diameter piling is expected to increase the water column concentration of copper by  $0.296 \,\mu$ g/L; of chromium by  $0.008 \,\mu$ g Cr/L; and of arsenic by 0.05 µg As/L. These increases are 0.036 times the chronic standard for copper; 0.0007 of the chromium six chronic standard and 0.003 of the arsenic standard. Obviously chromium and arsenic are far less important than copper in terms of aquatic biota and the increase in copper concentration is likely within the natural variability of dissolved copper in surface waters. Please note that these data were generated using surface water current speeds representative of the slowest likely to be found – except in a bucket of water or in a small aquarium.

Contaminant	Fresh Acute	Fresh Chronic	Marine Acute	Marine Chronic
Arsenic	360	190	69	36
Chromium (VI)	16.0	11.0	1,100.0	50.0
Copper	8.17	6.12	3.1	4.8
Zinc	62.8	56.8	84.6	76.6

Table 2. Water Quality Standards for Surface Waters. Values are expressed as **ng**/L or parts per billion (ppb). A hardness of 55 ppm as CaCO<sub>3</sub> was used for values requiring computation. See WAC 173-201A-040 for details.

The predictions made in Equations (1), (2) and (3) can also be used to assess risk using the risk quotient methodologies commonly used by EPA in assessing pesticide risk. Table (3) provides the lowest  $LC_{50}$  listed for each of the aquatic biota discussed in the RED. It must be emphasized that Table (3) was produced using worst case assumptions and in the real world, the increases in metal concentrations next to a single piling would be lower. One might argue that few projects are constructed of a single piling. However, the increases from multiple piling are

additive and even 100 CCA treated piling placed in a row in a very slow moving body of water would not increase the ratios in Table (3) to greater than 1.0. The metals lost from CCA treated wood must be added to background concentrations. The models allow an assessment of these cumulative effects. It is possible that very large CCA treated wood projects, proposed for construction in water bodies where elevated metal concentrations already exist, could result in adverse affects. It is also possible that large bulkhead projects in poorly flushed residential canals could result in short term adverse affects associated with copper. It is extremely unlikely that either arsenic or chromium losses from treated wood will have any adverse affect on aquatic resources.

Table 3. Comparison of the predicted concentrations of dissolved arsenic or chromium within a few centimeters of a CCA treated piling with commonly accepted  $LC_{50}$  values. The predicted concentrations have been multiplied by 100 to be consistent with a safety factor of 0.01. It is assumed that the chromic acid and arsenic acid have dissociated in the bioassay results. All values are in **m** metal/L

### a. Chromium

Biological compartment	Lowest LC <sub>50</sub> or LOAEC	Predicted concentration	Ratio
	(µg/L)	(µg/L)	Pred/Effect
Acute Fish	28,000	0.008	0.0000003
Chronic Fish	8,200	0.008	0.0000010
Freshwater Invertebrates Acute	760	0.008	0.0000105
Freshwater Invertebrates Life Cycle	8.6	0.008	0.0009302

### b. Arsenic

Biological compartment	Lowest LC <sub>50</sub> or LOAEC	Predicted concentration	Ratio
	(µg/L)	(µg/L)	
Acute Fish	50,000	0.050	0.0000010
Early Life Stage Fish	1,900	0.050	0.0000263
Freshwater Invertebrates Acute	15,000	0.050	0.0000033
Freshwater Invertebrates Life Cycle	38	0.050	0.0013158

**6.4.** Sediment quality criteria. There is a diverse and abundant literature important to understanding the biological response to sedimented metals. As will be seen in a subsequent section of this response, this information is particularly important in reading the papers of Weis et al. In addition, free sulfides are commonly found in natural sediments and they play an important part in mediating the biological effects associated with sedimented copper. Di Toro et al. (1992) described the relationship between acid volatile sulfides (AVS) and simultaneouslyextracted-metals (SEM). They have documented no toxicity in sediments where the ratios of the molar concentration ratios of SEM/AVS were less than one. This hypothesis has been validated for a number of metals including copper. Based on a growing literature, there is an increasing understanding of the critical role that free sulfides play in mediating metal toxicity in aquatic environments. There are numerous benchmarks describing various levels of risk associated with sedimented copper, chromium and arsenic. To the best of the author's knowledge, only Washington State has formally adopted sediment quality criteria and those are only for marine environments. Some of the available sediment quality benchmarks are summarized in Table (4). It is important to note that all of these benchmarks, and the literature supporting them, are in terms of bulk sediment. None of the benchmarks from anywhere in the world refers to the

concentration of metals as a function only of the proportion silt and clay in sediment. This issue will be addressed more fully in a following discussion of the Weis papers.

Brooks (2000b) provided a discussion of the factors affecting sediment quality benchmarks, reviewed additional benchmarks from the literature, and proposed benchmarks for assessing environmental risks associated with sedimented copper lost from pressure-treated wood. It should be emphasized that the recommendations, summarized in Table (5), were based on the analysis presented in that paper. However, the results were peer reviewed, including peer review by at least one EPA scientist who did not find fault with either the analysis or the recommendations. A summary of sediment quality criteria and guidelines gathered from around the world is available at <a href="http://bordeaux.uwaterloo.ca/biol447/waterquality//sedaquat3.html">http://bordeaux.uwaterloo.ca/biol447/waterquality//sedaquat3.html</a>.

# Table 4. Summary of benchmarks useful for assessing the biological response to sedimented copper chromium, arsenic and zinc. All values are in **mg**/g dry sediment from Jones *et al.* (1997).

	$\operatorname{AET}^1$	TEC or $\text{TEL}^2$	PEC or $PEL^2$	$(\text{TEC} + \text{PEC})/2^3$
Freshwater Copper		28	77.7	52.8
Freshwater Chromium		56	159	107.5
Freshwater Arsenic		12.1	57	34.6
Freshwater Zinc		159	1532	845.5
Saltwater Copper	390	18.7	108	63.4
Saltwater Chromium	260	52.3	160	106.2
Saltwater Arsenic	57	7.24	41.6	24.4
Saltwater Zinc	410	124	271	197.5

<sup>1</sup>Apparent Effects Threshold (AET) based marine sediment quality criteria are defined by Washington State in WAC 173-204. This is a marine standard above which adverse effects are observed as metal concentrations increase.

<sup>2</sup>The Threshold Effects Concentration or Level (TEC or TEL) is a sediment benchmark below which adverse effects associated with the element or compound are never expected. Adverse effects are often, but not always, found at concentrations above the Probable Effects Concentration or Level (PEC or PEL). See Jones *et al.* (1997)

<sup>3</sup>Some jurisdictions, such as the Ministry of Water, Land, Air and Parks (MWLAP) in British Columbia have used the mean of the TEL and PEL as a regulatory benchmark defining acceptable concentrations of metals such as zinc and copper.

## Table 5. Recommended benchmarks for assessing environmental risks associated with sedimented copper lost from pressure-treated wood. From Brooks (2000b).

Acceptable levels of sedimented copper
30 µg Cu/g dry sediment
55 µg Cu/g dry sediment
100 μg Cu/g dry sediment

Additional reviews of freshwater sediment quality benchmarks are available from Smith *et al.* (1996) and Ingersoll *et al.* (1996), Suter and Tsao (1996), Long *et al.* (1995, 1998) Jones *et al.* (1997). Understanding this issue is critical to evaluating the benchic response to metals lost from CCA and ACZA treated wood.

**6.5. Freshwater field studies.** Brooks (2000a, 2000b) and Lebow *et al.* (2000) are peerreviewed and published references available at most libraries. Both of these long-term Before-After-Treatment-Control designed studies provide invertebrate community inventories, sediment and water column concentrations of copper, arsenic and chromium or zinc and bioassay results for large CCA-C and ACZA treated structures located in worst case marine and freshwater environments.

6.5.1. The Timber Bridge Study (Brooks, 2000a). This study examined an eight-year old bridge crossing a freshwater swamp in Sandestin, Florida. Dissolved concentrations of copper and arsenic were not significantly higher under and immediately adjacent to the bridge when compared with reference conditions. In fact, both metals were found in lower concentrations under the bridge when compared with the reference. A statistically significant increase in dissolved chromium was observed with increasing distance from the bridge – the opposite of what would be expected if the CCA treated wood was contributing significant quantities of metal to the water. Consistent with the age of the bridge, sediment concentrations of copper, chromium and arsenic were slightly increased from 0.63 + 0.46 mg Cu/kg dry sediment; 1.00 + 0.48 mg Cr/kg; and 0.57 + 0.17 mg As/kg at the reference station to mean values of 2.10 + 1.08 mg Cu/kg; 3.23 + 1.22 mg Cr/kg; and 1.50 + 0.74 mg As/kg under the bridge. The highest sedimented arsenic concentration measured during this study was 4.30 + 5.12 mg As/kg at a distance of 0.45 meters from the bridge's dripline. All of these concentrations are well below any biological effects benchmarks and all of them are in fact, much less than average background concentrations found in pristine areas of North America where the average background concentration of arsenic is 7  $\mu$ g As/g. No adverse effects were

seen in either the invertebrate community inventories or in the bioassays conducted during the study.

6.5.2. Wildwood Study (Brooks 2000b and Lebow et al. 2000). This study examined the physicochemical and biological response to a large boardwalk constructed in wetlands located on the western slope of Mount Hood in Oregon. The study provided an opportunity to examine the environmental risks associated with the use of wood treated with preservatives such as CCA-C and ACZA in structures constructed in a very pristine and expansive freshwater wetland. The study included two levels of control. An untreated wood structure was constructed in a remote portion of the wetland to assess the response to the presence of the physical structure and each treatment included an upstream control. Water hardness in this abandoned channel of the Salmon River was very low (18.5 mg CaCO<sub>3</sub>/L) resulting in a low chronic dissolved copper standard (2.68 µg Cu/L). The large CCA structure, placed over an inundated area of the wetland with slow moving water, resulted in increases in dissolved copper concentration from a background of 0.2 µg Cu/L observed before constructions to values that with one exception were consistently less than  $1.0 \,\mu$ g/L. The single exception was observed on Day 162 when a dissolved copper concentration of 1.55 µg Cu/L was observed at a distance of 1.0 meters downstream from the structures dripline during rain. The maximum value recorded represented 58% of the EPA chronic water quality criteria at the observed hardness. Sediment concentrations of chromium were just over 10 mg Cr/kg dry sediment during the baseline survey and they actually declined following construction. The reasons for the decline, which was small and not statistically significant, were not investigated. At the end of the one year study, sediment concentrations of arsenic were stable at 7 to 8 µg As/g dry sediment from the upstream control to a distance of ca. 0.5 meters downstream from the structure's dripline. From that point downstream, they increased to a maximum of ca. 20 µg As/g dry sediment at 10 meters. All of the arsenic concentrations were less than the no effects concentration (NEC).

Based on the small increases in sediment and water column concentrations of metal at the CCA treated boardwalk, no adverse effects were anticipated in the aquatic invertebrate community on vegetation, colonizing artificial substrates or infauna resident in sediments. This community was abundant and diverse everywhere and no adverse effects were observed. The author emphasized that the neutral to slightly acidic pH and very low levels of hardness, alkalinity, and organic carbon observed in the Wildwood wetland environment would have exacerbated the effects of metals lost from treated wood. The very slow water currents allowed the small amounts of copper, chromium and copper lost from the structure to be retained in its immediate vicinity, further exacerbating the risks. It is emphasized that the aquatic invertebrate community appeared to be totally unaffected by the structure during this year long study.

**6.6.** Marine field studies by Weis *et al*. Lay persons have sometimes assumed that publication in a peer-reviewed journal insures scientific credibility. This is neither a correct nor standard interpretation of what it means to subject data to the peer -review process. Publication in a peer-reviewed journal means that two or three of the authors' colleagues feel that the material is worthy of publication and **further review by the broader scientific community.** While peer-reviewed data is held to a higher standard than non-peer reviewed data, it is not a guarantee of the accuracy of the conclusions. If peer-reviewed publication insured accuracy, then there would be no controversy in the peer-reviewed literature and we would all be basking in the

warm glow of cold fusion. In this section, several of the Weis *et al.* publications are subjected to more rigorous review than is commonly provided by journals.

6.6.1. Trophic transfer of metals. Weis and Weis (1992) asserted that the cause of snail mortality (*Nassarius obsoletus*) placed in 0.51 liters of seawater at 29 parts per thousand (0/00) and 24 to 26 °C was caused by consumption of algae collected from CCA treated structures. The water was changed in the "shallow polystyrene containers" every two weeks. The authors did not measure copper, chromium or arsenic concentrations in the water. This failure would immediately cause EPA to reject this bioassay data if it had been submitted by NPDES permittees in compliance with permit requirements. Because CCA contains copper, which is known to be bioconcentrated, one would expect that algae growing on CCA treated wood to have elevated copper concentrations. Because of the authors' failure to measure dissolved oxygen, sulfides, metal concentrations in the water and other parameters, it is not possible to determine whether the effects seen in the snails were due to consumption of the algae; due to increased concentrations of dissolved copper migrating from the algae into the water; or due to a combination of factors associated with the very limited water volume. To be truly meaningful, this study should have been conducted in flow through chambers with a constant supply of seawater. In addition, metal concentrations in the water and dissolved oxygen plus other physicochemical parameters should have been quantified and reported to determine the cause of the observed effects.

6.6.2. Bioconcentration of copper, chromium and arsenic in oyster tissues. Weis *et al.* have published the results of their assessment of metal in oyster tissues growing on or near CCA-C treated structures numerous times in different journals. Weis et al. (1993) detected significant increases in the concentration of copper in oyster tissues grown in residential canals bulkheaded with CCA treated wood. This should not be a surprise for two reasons. First, because these canals contain large surface areas of treated wood coupled with generally poor flushing and long water residence times; and second because there are many sources of copper in these waterways. For instance, copper based antifouling paints are used to protect boat hulls in nearly all marine environments. These paints are designed to release copper at a constant rate of ca. 25 to 200  $\mu$ g/cm<sup>2</sup>-day. Those loss rates are 50 to 400 times greater than the long-term copper loss rates from CCA treated wood. This is because CCA preservatives were engineered to remain in the wood, whereas antifouling paints are designed to slowly leach copper, thereby inhibiting the settlement of organisms on boat bottoms. Weis et al. (1993) did not inventory potential sources of copper in the residential canal they surveyed and absent such an inventory it is not possible to determine the sources of the copper bioconcentrated in the oyster tissues. Having said that, it is reasonable to assume that copper released from CCA treated wood will be bioconcentrated by oysters growing on that wood. The wood was not placed in the canals as habitat for oysters. The more important question is whether or not the metal bioconcentrated by the oysters represented a human or environmental health hazard.

Another factor not considered in Weis *et al.* (1993) is the presence of other contaminants in residential canals influencing the oysters' physiology and health. Dr. Fred Kutz of U.S. EPA Region III provided a report authored by Chaillou and Weisberg (1995). Table (6) summarizes data from that report. The exceedances of the ER-L for copper and arsenic in these canals was smaller by factors of ten to 293 than the exceedances of these same benchmarks by other pesticides. These data demonstrate that residential canals contain numerous contaminants that

can have adverse effects on aquatic life and suggest that copper, chromium and arsenic contribute little or nothing to the potential for adverse effects. Having said that, the information presented in Table (6) is not sufficient to establish a cause and effect relationship between the health of the biota in these canals and any of the listed contaminants. None of the contaminants were found above the ER-M where adverse effects are usually observed. It is always a mistake to infer cause and effect relationships based on correlation analysis as has been attempted by Weis *et al.* (1993). Absent an understanding of the potential contribution from the many contaminants found in residential canals, one cannot assume that observed effects were caused by one possible contaminant. The fact that oysters and other biota colonize CCA treated wood in and of itself suggests that the wood is not particularly toxic. Otherwise the larval stages of these organisms, which are most vulnerable, would be killed upon settlement. There is a peer reviewed publication (in-press) that substantiates these assertions and that will be discussed in a following section of this response.

Table 6.	Comparison of residential	canal sediment	concentrations of	various contami	nants
with biol	ogical effects criteria.				

Contaminant	Concentration in Residential Canal Sediments	Effects Range Low (ER-L)	Effects Range Moderate (ER-M)	Percent above the Effects Range Low
CCA Metals (µg/g	g)			
copper	40.6	34.0	270.0	19%
arsenic	10.6	8.2	70.0	29%
chromium	56.1	81.0	370.0	below ER-L
Other pesticides (	(μg/L)			
Chlordane	1.8	0.5	6.0	360%
Total DDT	3.1	1.58	46.1	196%
Endrin	0.5	0.02	45.0	2,500%
Dieldrin	1.7	0.02	8.0	8,500%

The second question that arises from these papers is whether or not the observed tissue concentrations of copper in C. virginica were unusual. Shuster and Pringle (1969) reviewed trace metal concentrations in C. virginica documented in five studies conducted between 1932 and 1968 from Maine through North Carolina. This period predates that in which CCA was used extensively in east-coast estuaries. The results of their survey are summarized in Table (7). The reader is referred to the parent document for sources of the data. The oyster tissues examined by Weis *et al.* (1993) from reference sites contained copper at ca. 6 to 17 µg Cu/g wet tissue, which is less than ten percent of the average concentration reported in any of the studies summarized by Shuster and Pringle (1969). Copper concentrations in oyster tissues from the Weis's canal site varied between ca. 60 and 210  $\mu$ g Cu/g wet tissue, with an average of ca. 180 to 190  $\mu$ g Cu/g. These values are all well within the range of averages reported in Table (7). Based on this historical data, there is nothing unusual about the tissue copper concentrations reported by Weis et al. (1993). Their assertion of adverse effects in the oysters digestive diverticula is based on correlation analysis and it did not consider the numerous sources of copper in these residential areas, nor did it consider effects caused by the numerous other pesticides found in similar areas at concentrations that are much closer to probable effect benchmarks than for copper, arsenic or chromium.

# Table 7. Comparison of copper concentrations in *Crassostrea virginica* from Atlantic coast waters, Maine through North Carolina. All values are in **ng** Cu/g wet tissue weight.

Area and Survey Year	Range of concentrations	Average concentration
Main to North Carolina (1965 – 1967)	6.8-517.4	133.4
New Hampshire through North Carolina (1960)	8.8 - 520.0	137.5
Long Island Sound (1964)	84.0 - 600.0	230.0
Rhode Island through New Jersey (1933)	34.4 - 137.2	78.5

**4.6.3. Sediment and macrobenthic effects.** Weis *et al.* (1993, 1998) reported sediment concentrations of copper, chromium and arsenic near CCA treated bulkheads and at reference locations. Based on macrobenthic community inventories, the authors asserted adverse effects associated with copper. These conclusions bear closer scrutiny.

Weis *et al.* (1993) examined sediment concentrations of copper, chromium and arsenic in proximity to CCA treated wood bulkheads. They related copper content as a proportion of the percent fines in sediments and concluded that copper was being lost from the bulkhead and contaminating nearby sediments to levels as high as 550  $\mu$ g Cu/g dry silt and clay (<64  $\mu$ m particle size). The authors did not provide data describing the sediment grain size distribution. However, they did note that, "In all the environments sampled, the sediments immediately adjacent to the bulkheads were comprised primarily of sand with a very low percentage of silts and clays, often less than 1%." This statement appears innocuous. However, reporting metal concentrations as a proportion of only the fines in sandy sediments introduces significant bias into the results. The National Oceanographic and Atmospheric Administration (NOAA, 1988) cautioned against this practice stating:

"To avoid concluding that a sediment composite has an unusually high or low level of contamination when, in fact, it is simply a sandy sample, no contaminant data were used if they were derived from sediments containing less than 20% fine-grained material."

Based on NOAA's reasoning, Weis *et al.* (1993) ran the risk of concluding an "unusually high level of contamination when, in fact, it was simply a sandy sample." Realizing the inappropriateness of basing metal content solely on percent fines in sandy sediments, it is reasonable to ask if their error resulted in inappropriate conclusions.

To the best of the author's knowledge, metal sediment quality benchmarks and criteria from every jurisdiction in the world are based on whole sediment weight – not on the weight of just the fines. In Washington State (WAC 173-204) the marine sediment copper standard is 390  $\mu$ g Cu/g dry sediment weight. This standard is based on an Apparent Effects Threshold (AET), which is the sediment concentration of a contaminant above which statistically significant ( $\alpha = 0.05$ ) adverse effects for a particular biological endpoint are expected. In developing sediment copper AET values, the Puget Sound Estuary Program (1988) developed organic carbon based apparent effects thresholds (AETs) for a number of marine organisms. The oyster AET was 49,000 mg Cu/kg organic carbon. This data was developed for the Pacific oyster (*Crassostrea gigas*). However, it is likely applicable to *C. virginica*. The Weis *et al.* (1993) study incorrectly measured sediment total organic carbon by determining the weight loss in a dry sediment sample before and after ashing at 400 °C. This method does not measure organic carbon. Ashing at 550  $\pm$  50 °C is a standard protocol for measuring Total Volatile Solids. Organic carbon on the other

hand is determined with an elemental analyzer or by measuring the accumulation of combusted  $CO_2$  in an ascarite tube. It is possible to correct the Weis error and estimate TOC based on TVS using an algorithm developed by Brooks (2003) in which same sample TVS and TOC analyses revealed that TOC = 0.45\*TVS - 0.004 ( $R^2 = 0.9027$ ). In this case, the estimated TOC from the Weis data is 0.56% and the AET would be 274.4 µg Cu/g dry sediment. In other words, increasing adverse effects on oysters should be anticipated at Fire Island in the Weis study when sediment copper concentrations exceed 274.4 µg Cu/g whole dry sediment.

How much copper did the Weis *et al.* (1993) study actually document? If we assume that the sediments contained 1% fines (silt and clay) as suggested by Weis *et al.* (1993), then the weight of the whole dry sediment would have been approximately 100 times the weight of just the fines. Therefore, the Weis *et al.* (1993) study at Fire Island actually measured only 550/100 =  $5.5 \mu g$  Cu/g in whole dry sediments associated with CCA treated bulkheads. That is about  $1/10^{\text{th}}$  of the average concentration of copper in the earth's crust (EBI, 2002) and well below any documented biological effects level. The same approach leads one to conclude that copper, chromium and/or arsenic were actually at sediment concentrations where no biological effects could possibly be inferred.

Weis *et. al* (1998) examined five bulkheads with similar results. Their data is more appropriately interpreted in Table (8) based on metal concentrations as a function of total sediment weight. Sediment concentrations of copper did not exceed Washington States SQC at any station and copper exceeded the mean of the TEL and PEL only at the 10 meter and reference stations at Old Fort Pond.

Table 8. Sediment copper and (arsenic) concentrations reported by Weis *et al.* (1998) near five CCA treated bulkhead sites on the Atlantic coast of the United States. The data, originally reported as a function of only the fine sediment fraction have been converted to a whole sediment basis for comparison with sediment quality benchmarks and criteria. Arsenic concentrations are provided in parentheses. All values are in **m**g metal/g dry sediment. Sediment metal concentrations exceeding the mean of the TEL and PEL are bolded. Those values are 64 **m**g Cu/g and 30 **m**g As/g.

Site	0.0	1.0	3.0	10.0 m	Reference <sup>1</sup>
Middle Pond	8.70 (3.62)	1.20 (0.58)	1.00 (0.31)	15.91 (6.21)	0.91 (0.38)
Old Fort Pond	11.4 (3.83)	10.83 (3.28)	59.9 (7.63)	<b>71.07</b> (9.24)	<b>65.68</b> (6.70)
North Inlet	35.85 (24.23)	7.32 (5.46)	1.84 (2.29)		3.62 (2.15)
Osborne Cove	0.88 (0.43)	1.50 (0.17)	0.10 (0.03)	1.55 (0.40)	0.92 (0.30)
Drum Point	0.13 (0.05)	0.09 (0.04)	0.15 (0.07)	0.48 (0.15)	0.36 (0.22)

<sup>1</sup>For those sites where the reference was an aluminum bulkhead or a shoreline across the bay, values for the deepest and therefore most protected sediments were entered in the reference column.

Having shown that there is no basis for assuming that sediment copper or arsenic would affect the macrobenthos, why did Weis *et al.* (1993) assert adverse effects caused by CCA bulkheads? First, one should be surprised by the low macrobenthic diversity reported by the authors. Brooks (2000a) reported between 10 and 23 taxa in each of 18 samples collected from sandy sediments under and adjacent to a new CCA treated bridge in Horseshoe Bayou, Sandestin, Florida. The sampler used had a footprint of 0.0309 m<sup>2</sup>. At North Inlet, Weis *et al.* (1998) observed only 2.5 to 4.0 taxa at the reference bulkhead and only 5.8 to 8.2 species were observed near the aluminum bulkhead used as a reference at Bullhead Bay. Species diversity

was not as low at Osborn Cove (18.3 to 26.3 taxa). Numerous errors are evident in the protocols and analyses used by Weis *et al.* (1998), including the following:

- They failed to understand the inappropriateness of assessing metal concentrations on just the fine fraction of sediments containing less than 20% fines. The authors should have been aware of the commonly acknowledged caution provided by NOAA (1988);
- The authors failed to compare the bulk sediment concentrations of copper, chromium and arsenic with any of the numerous sediment benchmarks describing the potential for biological effects. Had they done so, they would have realized that the observed metal concentrations were below those concentrations at which adverse effects are anticipated;
- The authors assumed that the observed copper in these residential canals was solely associated with the CCA-C treated bulkheads. A more rigorous approach would have been to inventory other sources particularly boats with copper based antifouling paints that may have been moored at or near the bulkheads;
- The authors relied on correlation analysis to assert that higher concentrations of copper adjacent to CCA-C treated bulkheads caused a reduction in the number of taxa observed in the macrobenthos. They failed to assess the effects caused by mechanical disturbances associated with the transfer of horizontal energy in waves at the vertical bulkhead surface into random energy that remobilizes the nearfield sediments, metals in those sediments, organic carbon that many infaunal organisms rely on for food, and the animals themselves. Correlation analysis is never an appropriate sole basis for establishing cause and effect relationships. The author's presented no inferential statistical analysis adequately assessing the significance of the differences in sediment physicochemistry that were observed;
- The authors conducted their studies in sandy environments containing few organisms. An appropriate experimental design would have included consideration of the numerous factors that can influence macrobenthic communities and a site selection process that would minimize those extraneous influences, like other sources of metal and mechanical disturbances, and focus on the question being asked.

The main point here is that there is no basis in the literature for describing sediment concentrations of metals as a proportion of the fines in sediments containing less than 20 percent fines. To examine the biological response from a more traditional point, the variables, TAXA, DISTANCE, COPPER, TVS and FINES were entered into a Statistica<sup>TM</sup> database for analysis. The proportion of fines was transformed using an  $\arcsin(\operatorname{sqrt}(\operatorname{fines}))$  transformation and count data was transformed to  $\operatorname{Ln}(N + 1)$  to meet the need for normally and continuously distributed variables and homoscedasticity applicable to most inferential techniques.

Pearson correlation coefficients were analyzed for all of the pairwise combinations of variables. The number of taxa was significantly ( $\alpha = 0.05$ ) correlated only with distance from the bulkheads (r = 0.49) and with sediment arsenic concentrations. Copper and arsenic were significantly and positively correlated with each other suggesting that the small increases in each metal were perhaps associated with the same source (the CCA treated bulkhead). As one would expect, copper and arsenic were positively and significantly correlated with the transformed

proportion fines (r = 0.93 for copper and 0.61 for arsenic) and with transformed Total Volatile Solids (r = 0.78 for copper and 0.49 for arsenic). The transformed number of taxa was not significantly negatively correlated with copper (r = -0.14). Interestingly, sediment concentrations of copper were as high in sediments collected along the undisturbed shoreline as they were within 1.0 meters of the CCA-C treated bulkheads. This is graphically described in Figure (7). Note that all of the observed concentrations and their upper 95% confidence limits are less than commonly accepted sediment quality benchmarks. Sediment along the undisturbed shoreline held as much copper as sediment immediately adjacent to the CCA bulkheads. Sediments adjacent to the concrete and aluminum bulkheads contained unusually low copper concentrations, most likely because of resuspension and re-deposition into deeper water of clay particles to which the naturally occurring metals adsorb.



# Figure 7. Box and whisker plot comparing sediment copper concentrations (**m**g Cu/g dry sediment) at distances $\leq$ 1.0 meters from bulkheads constructed of CCA treated wood, aluminum and concrete with an unarmored shoreline.

Is there any way to determine whether or not the changes in the number of taxa adjacent to these structures were associated with the copper or with mechanical disturbance? As previously noted, the number of taxa was not significantly correlated with sediment copper concentrations. Table (9) describes appropriate physicochemical and biological data. These data were submitted to Analysis of Variance, which indicated that the number of taxa were significantly different between shoreline and bulkhead treatments (F = 3.71, P = 0.03). The proportion TVS was also significantly different (F = 3.70, p = 0.03). Differences in sediment concentrations of arsenic and copper or in the proportion of fines at distances < 1.0 m were not

significant between treatments. Post hoc testing using the LSD test with  $\alpha = 0.05$  indicated that there were significantly more taxa along the undisturbed shoreline than were observed at the CCA bulkhead (p = 0.007) or at the aluminum bulkhead (p = 0.02). The differences between the concrete bulkhead and the undisturbed shoreline were not different – nor were differences between the three types of bulkheads significantly different. The few taxa observed in these environments makes a determination of statistically significant effects difficult. The studies would have been far more meaningful if they had been conducted in deepwater water, with sediments containing higher concentrations of fines, TVS and most important with abundant and diverse macrobenthic communities. However, the evidence presented here suggests that there were no significant differences in the number of taxa observed at distances  $\leq 1.0$  meters from the three bulkhead types and that the number of taxa were significantly reduced at two of the three bulkhead types when compared with an unarmored shoreline.

# Table 9. Breakdown of sediment concentrations of copper and the number of taxa observed in the macrobenthic community sampled at distances $\leq$ 1.0 meters from different types of bulkheads. Data reported in Weis *et al.* (1993).

Breakdown Table of Descriptive Statistics (Weis 1998 Data) N=20 (No missing data in dep. var. list)								
Treatment	Copper	Confidence	Confidence	Copper	Таха	Confidence	Confidence	Taxa
	Means	-95.000%	+95.000%	N	Means	-95.000%	+95.000%	Ν
CCA	7.790000	0.02878	15.55122	10	5.01500	1.61114	8.41886	10
Aluminum	1.059400	0.52127	1.59753	4	3.71250	0.68473	6.74027	4
Shore	4.581500	-3.76788	12.93088	4	15.75000	6.99538	24.50462	4
Concrete	0.169000	-1.64163	1.97963	2	8.00000	-7.88276	23.88276	2
All Grps	5.040080	1.12487	8,95529	20	7,20000	4,36200	10.03800	20

Based on the fact that metal concentrations observed by Weis *et al.* (1993) were less than biological effects benchmarks, this analysis suggests that the observed effects were more associated with mechanical disturbance created by the bulkheads rather than being associated with the construction material.

**6.7.Other studies describing the biological response to CCA treated wood in marine environments.** Several studies describing the physicochemical and biological response to CCA preserved wood are available in the literature. These are briefly reviewed in the following paragraphs.

6.7.1.**Brooks (2000a)** assessed the environmental response to a 332' long 20 ton bridge constructed across Horseshoe Bayou in Sandestin, Florida. The bridge was constructed entirely of CCA-C preserved wood including the piling, support beams, wooden deck and guardrails. The bridge was in the final stages of constructed and was chosen for this U.S. Forest Service sponsored study because it was thought that water column concentrations of copper, chromium and arsenic associated with losses from the CCA preserved bridge would be maximum at this time. The water in Horseshoe Bayou had a salinity of 25.5 o/oo, temperature of 15.8 °C during the survey and a pH of 8.1. Currents were less than 1.0 cm/s during slack tide and they increased to 2.5 cm/sec three hours following slack. Water depths varied between 30 and 40 cm at low slack tide.

The U.S. EPA chronic marine water quality criteria are 3.11 µg Cu/L; 36 µg As/L and 50 µg Cr(VI)/L. Concentrations of dissolved copper varied between  $1.55 \pm 0.10$  under the bridge to  $2.03 \pm 0.35$  µg Cu/L at the reference station. Arsenic was measured at  $6.19 \pm 0.43$  µg As/L under the bridge. These values slowly increased away from the bridge to a maximum of  $8.27 \pm 2.10$  at the reference station. Total chromium concentrations were  $1.72 \mu$ g Cr/L under the bridge and  $1.80 \pm 0.25 \mu$ g/L at the reference station. No indication of increased concentrations of dissolved copper, chromium or arsenic were found in association with this large structure.

Sediment concentrations of arsenic and TVS were found to be elevated and within 0.9 meters of the bridge's dripline. However, the maximum sediment concentration of copper (11.87  $\pm$  13.01 µg Cu/g dry sediment) did not exceed the Threshold Effects Level (TEL = 18.7 µg/g) for this metal. The maximum concentrations of chromium (23.57  $\pm$  30.16 µg Cr/g) and arsenic (17.9  $\pm$  20.96 µg As/g) did exceed their respective TELs, but they were both less than the mean of the TEL and PEL frequently used as a benchmark for assessing biological effects (106.15 µg Cr/g and 24.42 µg As/g). No adverse effects were anticipated in the macrobenthic community and none were observed. In fact, all biological endpoints were as high or higher directly under the bridge as they were at the reference station. Survival in all laboratory bioassays using *Menidia beryline* was excellent and statistically significant differences in survival were not observed between laboratory controls, the local reference station or treatment stations.

The elevated concentrations of CCA-C metals found in sediments were of concern, even though they did not exceed biological effects benchmarks and no adverse effects were seen in the macrobenthic community or in the bioassays. As noted earlier, construction was being completed on this bridge during the survey. Within the preceding few days, workers had drilled 1,568 holes for attaching the bridge's railing. Each hole was ca. <sup>3</sup>/<sub>4</sub> inches in diameter and 13 inches long. All of the drill shavings had blown into the estuary and were lying in mats around the bridge. No effort was made to avoid this material during the sampling, which was carried out in strict compliance with written protocols. The result was that background TVS of 0.43 to 1.43% was increased to 2.95 to 5.12% within a meter of the bridge's dripline. The author noted that the metals remained bound in these shavings and no adverse effects were generated. However, their presence in the estuary represented unnecessary risk and he cautioned that permits and contracts for similar construction should be conditioned to require that all construction debris, including sawdust and shavings be cleaned up and properly disposed.

6.7.2. **Brown** *et al.* (in press). This author recently peer-reviewed a publication that is relevant to this discussion. Although it is not yet in press, it will be soon and the information is illuminating. The following review is provided with the permission of both the senior author of the paper and the editor of the journal. These authors completed a study in which test panels of Scots pine sapwood, measuring 20 cm long x 10 cm wide by 2.5 cm thick were preserved to retentions of 12, 24 and 48 kg/m<sup>3</sup> with CCA. Panels were attached to rectangular exposure frames constructed of plastic. Each frame carried eight panels in a randomized array; two control panels (untreated wood) and two panels at each of the three CCA retentions. Twelve frames were submerged at each of the exposure sites located in the United Kingdom, France (two sites), Portugal (two sites), Sweden and Greece. Seawater temperatures at these sites ranged from 5 °C to 28 °C. Salinity was reported to vary by as much as 26 parts per thousand. Epibiotic communities were surveyed six months, 12 months and 18 months following immersion.

As might be expected, fouling communities varied greatly across the wide range of

environmental conditions surveyed in this study. Between 12 and 28 taxa were identified at different sites. All of the fouling communities were reasonably diverse. The author's found no evidence of significant differences in community structure between panels treated to different CCA retentions. However, the paper did report significant **decreases** in both the diversity and abundance **of biota on the control panels** when compared with the treated panels. They hypothesized that at least in part this was likely due to deterioration of the untreated wood panels resulting in the sloughing of some portion of the fouling community. The authors concluded that, "In view of the diverse nature of the fauna examined, the wide range of site characteristics used and the community-level approach, this study provides findings from which quite generalized conclusions can be drawn. It would appear from these findings that leaching rates from CCA-treated wood are insufficient to disturb fouling community development living at sites with normal tidal water circulation."

6.7.3. Weis and Weis (undated). The American Wood Preservers Institute was able to procure a copy of an unpublished report by Weis and Weis (undated) to the New Jersey Department of Environmental Protection. The study involved the seasonal (Spring, Summer and Fall) collection of sediments and bivalves at four sites between 1995 and 1996. The four sites represented areas with low dock density and low water flow; low dock density and high water flow; high dock density and high water flow; and a worst case environment with high dock density and low water flow. At each site, four stations located between 0.0 and 10 m from the structures were sampled together with a remote reference station. Sediments and clam tissues were analyzed for copper, chromium, arsenic and polycyclic aromatic hydrocarbons using reverse-phase, high-pressure, liquid chromatography. The particle size distribution and organic content of sediments was also determined. In this study Total Organic Carbon was assayed using a Carlo Erba elemental analyzer. Significant seasonal trends were not apparent in the data. The author's noted that sediment concentrations of copper, chromium and arsenic were as high, or higher at reference sites as they were near the treated wood structures. Total organic carbon was very high at some sites containing few fines (2.10 to 2.94 percent TOC at Shrewbury Site (1) where the proportion silt and clay was only 7.88 to 9.93%). In general, sediment metal concentrations were below sediment quality benchmarks - except at poorly flushed and depositional Site (4) where the proportion of silt and clay varied between 47.2 and 96.9 percent. In the Fall 1995 samples, sediment concentrations of copper at this site varied between 94.3 µg Cu/g at the reference station and 125.8  $\mu$ g/g at treatment station 4B. None of the values exceeded Washington State's copper SQC of 390 µg Cu/g dry sediment. Chromium and arsenic concentrations were similarly elevated at Site (4). The reference station at Site (1) had moderately high concentrations of all three metals in the Summer of 1996 and high chromium in the Spring of 1996. All metal concentrations were low at all other stations (treatment and reference) at all other times. The concentration of metals in clam tissues were low at all times in all seasons – including clam tissues from Site (4) where metal concentrations were high in the sediments. This is simply a response to the binding of these metals by clay. Arsenic concentrations in clams were most frequently higher in clam tissues from reference stations than from clams close to the CCA-C treated structures.

The author's concluded that, "Thus, it appears that leachates from piling, in reasonably well flushed areas have negligible ecological effects in the immediate vicinity, while those from bulkheads, particularly new ones and ones in poorly flushed regions, have demonstrated, clearcut, ecological effects in the adjacent benthic environment." The first part of this conclusion is consistent with reports by Wendt *et al.* (1995), Brooks (2000a), Breslin and Adler-Ivanbrook (1998) and Brown *et al.* (in-press). While this author agrees with Weis and Weis that the environmental risks are higher when large surface areas of CCA preserved wood are used to bulkhead poorly flushed residential canals, this author does not believe that the evidence provided by Weis *et al.* (1993, 1998) or in their other papers describing that work is nearly as "clear-cut" as they purport (see Section 4.6 of this report). Those "clear-cut" effects were more likely created by an inappropriate analysis than as a result of the use of CCA-C treated wood. The bottom line is that Weis and Weis (unpublished) did not observe increased concentrations of copper, chromium or arsenic in sediments or clams near docks constructed of CCA-C treated wood – even when they examined a poorly flushed area containing a high density of docks.

6.7.4. Adler-Ivanbrook and Breslin (1999). This study examined the uptake by blue mussels (*Mytilus edulis*) of copper, chromium and arsenic lost from CCA-C treated wood in both laboratory and *in-situ* studies. Mussels were grown either downcurrent of CCA-C preserved wood treated to a nominal retention of 40 kg/m<sup>3</sup> in laboratory studies and mussels held in pearl nets with a floor of similarly preserved wood. The mussels in pearl nets were placed in open marine environments. Their study found little evidence of significant uptake of any of the three metals in either the laboratory or field studies. Metal levels in the mussel tissues were within the range of values reported for this species in Long Island Sound and around the United States. The author's found that the metal loss rates from CCA-C treated wood resulted in water concentrations of copper, chromium and arsenic that were too low to be measurably bioconcentrated by mussels – even though the animals were held in close association with the wood.

6.7.5. Wendt et al. (1995). In response to assertions made in a series of Weis papers in the early 1990's, and a subsequent critique of those papers by Breteler (1992), the South Carolina Department of Natural Resources undertook a study to describe the accumulation of metals and PAH associated with high densities of residential docks in South Carolina macrotidal creeks. The results from treatment sites were compared with reference creeks where there were no docks. These creeks were poorly flushed depositional environments with silt and clay comprising 37 to 98% of the sediment matrix. Their study included physicochemical assessments of sediments and oyster tissues and biological evaluations using oyster growth and mortality, *Microtox* **ä** and rotifer (*Brachionus plicatilis*) bioassays. Additional *in-situ* bioassays were undertaken using fish (*Funculus heteroclitus* and *Sciaenops ocellatus*), mud snails (*Ilyanassa obsoleta*) and juvenile white shrimp (*Penaeus setiferus*). The reader should note the broad array of biological endpoints assessed in this study in an effort to verify the various reports by Weis *et al.* 

Average copper concentrations in sediments ranged from 19 to 58  $\mu$ g Cu/g dry sediment. With the exception of one exceptionally high sample collected near a CCA treated dock, sediment copper concentrations averaged 38  $\mu$ g Cu/g dry sediment, which was well below Long and Morgan's ER-L and ER-M values used as biological benchmarks by the authors. Similarly, chromium concentrations ranged fro 21 to 64  $\mu$ g Cr/g. After correcting the data for aluminum, there were no significant differences in mean chromium concentrations among sites. Arsenic was found in these fine-grained sediments at between 6 and 26  $\mu$ g As/g. Aluminum corrected concentrations of arsenic were also not significantly different near docks when compared with reference areas.

Tissue concentrations of copper were however, significantly increased in oysters growing directly on CCA treated piling when compared with oysters from nearby surfaces or with reference conditions. However, the concentration of copper in all of the oysters examined in this study varied between 8 and 108  $\mu$ g Cu/g wet tissue – well within the normal range reported by Schuster and Pringle (1969) or by several authors cited by Wendt *et al.* for undisturbed conditions in South Carolina. No obvious patterns in mean tissue concentrations of chromium or arsenic were observed in relationship to proximity to CCA treated docks.

The condition of field-collected oysters did not differ significantly among sites. No significant correlations were observed between either condition index or shell thickness and copper concentrations in oyster tissue. Significant differences in these two endpoints were observed as a function of tissue arsenic concentrations. However, oysters growing on or near CCA-C treated docks did not have significantly elevated tissue concentrations of arsenic. None of the bioassays or biological endpoints found significant adverse effects associated with proximity to the CCA treated docks. No significant differences were observed in mean percent survival of mud snails, mud minnows, juvenile red drum or juvenile white shrimp between sites near to or distant from newly constructed docks. In addition, there were no significant differences between dock and reference sites with respect to mean concentrations of copper, chromium, or arsenic in composite sediment or tissue samples.

The results of the six week oyster growth and bioaccumulation studies showed slightly reduced increases in shell height, width and total oyster weight at dock sites when compared with reference sites. However, none of the differences were significantly different at  $\alpha = 0.05$ . In this study, there was no evidence of metal accumulation in caged oysters after six weeks of exposure to newly constructed docks, nor were there any significant difference in the mean percent survival or growth of the oysters compared with reference sites. In summary, the authors noted that:

"In summary, our findings suggest that, in natural estuarine environments subject to normal tidal exchange, wood preservative leachates from dock pilings have no acutely toxic effects on four common estuarine species, nor do they affect the survival or growth of oysters over a six-week period. In some cases, metal leachates may accumulate in sediments and oysters immediately adjacent to pilings, but do not appear to become concentrated in sediments or oysters elsewhere in the same creeks."

6.7.6. **Office of the Hearing Examiner for City of Olympia File 96-0451.** In 1997, Mr. Mark Silversten appealed a denial, by the City of Olympia Planning Department, to use ACZA treated piling in Budd Inlet Washington for expansion of a restaurant. The Hearings examiner overruled the City and approved the use of ACZA, but conditioned the permit to require the use of piling produced using WWPI (1996) *Best Management Practices* and he required that, "The applicant shall monitor the chemical release into the water and sediment from the pilings installed by the applicant. The applicant shall follow a protocol developed by Dr. Brooks. The protocol shall be reviewed and approved by the Washington Department of Fish and Wildlife or Ecology if either is willing and able. The applicant shall make the results of the monitoring available to the City of Olympia Environmental Review Officer and the State Departments of Ecology and Fish and Wildlife, if requested. The applicant shall allow independent monitoring if requested by any angency or department of the city or the State." Brooks (1998) reported completion of the required monitoring. Dissolved metals were not

detected within 15 cm of the pilings surface on the day they were being driven. Detection limits were 4  $\mu$ g Cu/L, 5  $\mu$ g As/L and 8  $\mu$ g Zn/L. Pre-construction mean sediment copper concentrations actually declined from 40.7  $\pm$  10.6  $\mu$ g Cu/g dry sediment to 22.7  $\mu$ g Cu/g four months following construction. Similarly, arsenic declined from 5.7 + 0.7  $\mu$ g As/g preconstruction to non-detectable levels post construction and zinc declined from 68.6 + 15.1  $\mu$ g Zn/g to 54.0  $\mu$ g Zn/g. Thus, while the model of Brooks (1997b) predicted an increase of 0.113  $\mu$ g Cu/L within a few centimeters of the piling on the day of installation and small increases (0.56  $\mu$ g Cu/g) in sediments, these environmental concentrations actually declined following introduction of the treated wood. While it would be foolish to assert that installation of the treated wood caused the decline, the evidence suggests that the very small amounts of metal lost from the treated piling were within the natural variability at this site. These results are consistent with other model verification studies in that less preservative was observed in the environment than was predicted by the models. The bottom line is that this 19 piling structure had no apparent affect on water or sediment chemistry.

**7.0.Risk Characterization.** Hopefully, the detail provided herein demonstrates the benefits of a rigorous and critical analysis of all of the literature – whether peer reviewed or not. There is a common thread binding the literature reviewed above. That thread is that despite a longer than 40 year history of extensive use of CCA and ACZA treated wood in aquatic environments in North America, there is little and no convincing evidence of adverse effects. Excepting the work of Judith and Pedrick Weis, all of the authors that have examined this issue have found no evidence of adverse effects. Even the Weis' failed to find adverse effects in their unpublished report to the New Jersey Department of Environmental Protection. The following conclusions follow from this response:

• We can accurately answer the question "What are the metal loss rates from CCA or ACZA treated wood structures used in aquatic environments." Data contained in the literature provides consistent answers to this question.

• Worst case models do exist for predicting environmental concentrations of the metals lost from CCA and ACZA treated wood. The worst case assumptions made in developing those models result in a significant degree of environmental conservatism. One of the models (Brooks, 1996) has been peer reviewed and published.

• Any assertion that peer reviewed publications can be accepted at face value are not consistent with accepted scientific principals, which require the critical review of every document, whether published in journals or not. ,

• Current understanding of metal loss rates from CCA treated commodities, coupled with available models enables one to predict environmental concentrations of copper, arsenic and chromium or zinc in sediments and dissolved in water near CCA or ACZA treated structures. Observed concentrations of metals around treated structures are very consistent with the model predictions. It is only when researchers start inappropriately magnifying bulk sediment metal concentrations by factors of 50 or 100 or even 400 that questions are raised.

• The numerous environmental risk assessments reviewed herein that have been conducted by researchers from all over the world have found little or no environmental risk

associated with the use of CCA or ACZA treated wood in aquatic environments. Even the Weis' work, when analyzed in a manner consistent with practices widely held in the ecotoxicological literature, does not suggest significant adverse biological effects.

• Having drawn these conclusions, it is the author's opinion that there are instances where the use of CCA treated wood in aquatic environments deserves careful management. Certainly long lengths of CCA or ACZA treated bulkheading in poorly flushed residential canals are one such application. That was the original purpose of the models – to identify and manage those projects to insure the continued safe use of all forms of preserved wood.

**6.0.** *Best Management Practices.* Brooks (2000a) documented the un-necessary environmental risk associated with CCA preserved wood shavings that were allowed to blow into Horseshoe Bayou at a bridge under construction. In response to these types of issues, Lebow and Tippie (2001) published a *Guide for Minimizing the Effect of Preservative-Treated Wood on Sensitive Environments.* Best Management Practices have also been developed by WWPI/CITW (1996) for the production of all types of pressure treated wood intended for use in aquatic and other sensitive environments. For CCA treated products, these *BMPs* suggest Air Seasoning, Kiln Drying, Steaming or a Hot Water Bath to insure an appropriate level of fixation. The document notes that the best available technology for confirming fixation in CCA treated material is use of the Chromotropic Acid Test (AWPA Standard A3-11 [1995]). The CCA *BMP* concludes with a requirement for visual inspection to insure that no excessive residual materials or preservative deposits exist. Similar *BMPs* are provided in WWPI/CITW (1996) for ACZA preserved wood products.

The question naturally arises, "Do these *BMPs* improve the environmental performance of CCA treated wood products?" Brooks (2002) reported the results of dynamic leaching studies on 60 cm long piling sections, treated by Wood Preservers Incorporated in Warsaw, Virginia to a retention of 40 kg CCA-C/m<sup>3</sup>, the AWPA (2001) standard for marine use. The preserved pilings were produced using procedures specified in AWPA. Following treatment, the pilings were subjected to a vacuum and then "fixed" with live steam in a specially designed fixation cylinder. Several such fixation cylinders have been designed using steam and/or hot water. Unique to the Wood Preserver's system is an array of nozzles that spray clean fresh water onto the piling as they are pulled from the fixation cylinder. The wash down water is recycled as a portion of the make-up water for the next charge. This wash down system is intended to remove remaining surface CCA residues resulting in a clean product. For the reported study, 3.4 meter long piling averaging 20 cm in diameter were treated to 40 kg CCA-C/ $m^3$ . Following treatment, 30 cm was cut from each end of the piling to reduce end effects. As previously noted, piling ends are either imbedded in sediments or above water. The ends are not normally exposed to open water. The remainder of each piece was then cut into three equal sections. One randomly chosen section from each of three piling was set under cover (no rain falling on the piling) and allowed to fix at ambient temperature and humidity. The remaining two sections from each piling were steam fixed. When fixation was complete, one of the two sections was removed and the last section was sprayed down with the remainder of the charge. This provided three sections at each treatment (fixed at ambient conditions; fixed but not washed; and briefly washed with a freshwater spray). Fixation was assured in each piece of piling using the chromotropic acid test. The pilings were then shipped to Aquatic Environmental Sciences where the cut ends were sealed with fiberglass resin. The sections were then leached in 40 liter tanks. A constant flow of

water was maintained using Masterflex<sup>™</sup> peristaltic pumps. Water inside the tanks was constantly mixed. Diluent from each tank was sampled on days 0.5, 1.5, 2.5, 4.5, 7.5, 10.5, 15.5, 22.5, 30.5 and 45. Metal concentrations in the systems water supply and in the diluent from triplicate treated replicates and single untreated controls of southern yellow pine piling from the same were determined at the Battelle Marine Sciences Laboratory using ICP-AES. The results for copper are provided in Figure (8). The calculated loss rates in Figure (8) are based on leaching data from a previous study on non-BMP products. As can be seen, piling fixed at ambient conditions to pass the chromotropic acid test had an initial loss rate of ca. 2.6 µg Cu/cm<sup>2</sup>. Copper losses declined quickly and reached low, long-term, loss rates  $< 0.50 \,\mu$ g/cm<sup>2</sup>day in about two weeks. Initial copper loss rates from piling sections undergoing steam fixation, but without benefit of a final wash were about 25% of the non-BMP data. The rates declined quickly to long-term loss rates in about 1.5 days. The initial "first flush" of copper was essentially eliminated by spraying the piling with freshwater following fixation. Similar results were seen with respect to arsenic losses. Chromium losses were low for every treatment in which fixation was assured using the chromotropic acid test. Brooks (2002) demonstrated the benefits to aquatic environments possible through the use of *Best Management Practices*. Many federal and state agencies now condition permits requiring BMPS for treated wood used in sensitive environments.



Figure 8. Copper loss from southern yellow pine piling treated to 40 kg/m<sup>3</sup> and fixed at ambient conditions or in a steam fixation cylinder with and without a final freshwater washdown. The predictive algorithm presented in Brooks (1996) is provided for comparison.

**7.0.** Summary comments regarding the environmental response to arsenically treated wood products. A systematic and rigorous approach leads to the following conclusions:

- Metal loss rates from treated wood commodities into realistic aquatic conditions have been characterized and modeled. The variability in loss rates associated with preservative retention, ambient water temperature, pH and salinity are reasonably accounted for in the predictive algorithms.
- Environmentally conservative models do exist that predict concentrations of copper, chromium and arsenic in sediments and water near structures constructed of CCA and ACZA treated wood.
- The predicted environmental concentrations of copper, chromium and arsenic are far lower than biological effects benchmarks or criteria for all species.
- The lay perception that peer-reviewed literature can be taken at face value is inconsistent with a scientific understanding of the peer review process. Hopefully, this response has demonstrated the pitfalls and misinterpretations that can arise when published literature is not examined critically. In the case of Weis *et al.* (1993, 1998), the analysis in these papers strongly suggests that the observed macrobenthic effects were associated with mechanical disturbances at the bulkheads rather than as a result of what turned out to be low concentrations of copper, chromium and arsenic in sediments near those bulkheads. Like the peer reviewed and published reports of cold fusion, Weis *et al.* (1998) has not stood up to critical review and specific and contrary evidence has been provided by all of the authors reviewed in this paper.
- The bulk of the literature, including unpublished studies by Weis and Weis, clearly and repeatedly demonstrate an absence of adverse environmental effects associated with the use of CCA treated wood in open aquatic environments. The author agrees that treated wood is a product that should be managed and that there is elevated risk associated with large projects involving large CCA treated wood leaching surface areas in poorly circulated bodies of water. However, models exist to assist in identifying and managing projects constructed using inorganic arsenical preserved wood.
- Regulatory agencies and project proponents should be aware of and use available *Best Management Practices* for the production and use of treated wood products.

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## **Glossary and Acronyms**

**Gravimetric Units.** Many papers and reports use different units to express similar terms. The following table provides a guide to these different terms and units as they appear in this paper.

## Contaminant concentrations in tissue, water or sediment

$\mu g/L = ng/ml$	Micrograms per liter = nanograms per milliliter	= ppb $=$ parts per billion
mg/L	Milligrams per liter	= ppm = parts per million
g/L	Grams per liter = $o/oo$	= ppt = parts per thousand
$\mu g/g = mg/kg$	Micrograms per gram = milligrams per kilogram	= ppm $=$ parts per million
ng/g =	Nanograms per gram	= ppb $=$ parts per billion

## Wood preservative retention

Pcf =	Pounds per cubic foot
$Kg/m^3 =$	Kilograms per cubic meter

## **Glossary and acronyms**

Abundance	Number of a given taxonomic level of organization.
AET	Apparent Effects Threshold employed in Washington State to define
	enforceable Sediment Quality Standards. Increasing adverse
	biological effects are observed above the AET concentration.
Amphipod	Freshwater or marine benthic arthropod commonly referred to as a
	scud in freshwater.
Anthropogenic	Derived from human activity.
As	The element arsenic
AVS	Acid Volatile Sulfides – a measurement of sulfides in sediment
	released when a sediment sample is incubated in cold hydrochloric
	acid (see SEM)
Benchmark	A value assigned or proposed for a compound to indicate its relative
	hazard to an organism, community or ecosystem.
Bioaccumulation	The process by which an organism incorporates an element or
	compound into their tissues from water or food.
Bioconcentration	The process by which an organism incorporates a compound or
	element from all environmental routes (e.g., water, food, respiratory
	surfaces, etc.) into its tissues.
Biomagnification.	The accumulation of contaminants at increasing concentrations in
	higher trophic levels in the food chain.
BMP	Best Management Practice – as used herein the term implies specific
	procedures used during the production of treated wood to improve the
	products environmental performance.
Bulkhead	A structure installed to interrupt and/or reduce wave action along a
	shoreline.
Chironomid	A group of aquatic insects commonly referred to as midges.

Cumulative Impacts.	The sum of all impacts from a specific action(s) or event(s) in surrounding areas.
Depuration	Cleansing by elimination.
Diffusion	Process wherein a constituent passively moves out of a material
	(solid, liquid or gas) into the surrounding medium.
Diversity	The number of different species (or other taxonomic levels of
J	organization) present in a community.
Ectodermal	The outer layers of cells that differentiate an organisms from its
Elutriate	Liquid medium which receives additional material in leaching
	studies.
Epibenthic fauna	The community of organisms living on the surface of sediments or
•	some other structure.
Epibiota	Organisms on the surface of a substance
ER-L	Effects Range – Low = a contaminant concentration benchmark
	below which adverse effects are not expected.
ER-M	Effects Range – Moderate = a contaminant concentration benchmark
	above which adverse effects should be expected in sensitive taxa.
Exposure	The process defining the relationship between an organism and a
	contaminant bounded by concentration, duration, and mode of
	exposure (i.e. inhalation, ingestion, etc.)
Fines	That portion of the sediment grain size distribution $\leq 63 \ \mu m$ in
	diameter encompassing silts and clays.
Food chain	A series of predator – prey relationships defining the production and
	consumption of organic matter.
Guideline	A recommended value that should be followed but that does not
	carry a burden of enforcement.
In vitro	Within an artificial environment (test tube, culture dish, etc.)
In vivo	Within a living organism
Infaunal	Animals living in the sediments
LC <sub>xx</sub>	An expression denoting the lethal concentration of a compound of
	some specified period of exposure (e.g. 96 hrs) for a portion (e.g.
	50%) of a population. For instance a 96-hr $LC_{50}$ describes the
	concentration of a contaminant that will kill 50% of the animals in a
	96-hour exposure.
Mesocosm	An experimental environment created on an intermediate scale of
	perhaps a part of an acre or in several thousand gallons of water.
Microcosm	An experimental environment created in 5-gallon aquaria or other
	relatively small containers.
Microtox™	A toxicity testing system based on the inhibition of light output from
	marine photo-luminescent bacteria.
PEL	Probable Effects Level – a sediment benchmark above which
	increasing adverse biological effects should be anticipated.
pН	Measurement of the free hydrogen ion content on a logarithmic scale
	from 1 to 14 with a value of 7.0 being considered neutral.
Plankton	Small marine or freshwater plants and animals that drift with the
	surrounding water – includes animals with weak locomotory power.

Polychaete	Segmented annelids having hairy parapodia.
Retention	The pounds or kilograms of preservative retained in a cubic foot or cubic meter of treated wood. Pressure treated wood retention
	standards are specified by the American Wood Preservers Association
	(AWPA) in their annual book of standards. The retention refers only
	to the treated zone, which is typically the outer 1 to 2 inches of a piling or timber.
Richness	A measure of a community of organisms that depends on the number of taxa and their abundance.
Sediment	Inorganic and organic material underlying water bodies.
Standard	A promulgated value used to assess compliance with a law or regulation.
SQS	Sediment Quality Standards for contaminant levels that are enforceable by law.
Teleost	Vertebrate (bony) fishes.
TEC	Threshold effects concentration. A sediment benchmark below which adverse effects are not expected in aquatic communities.
TOC	Total organic carbon – the percent, by weight, of a sediment that is comprised or organic carbon.
TVS	Total Volatile Solids – the proportion, by weight, of a dry sediment that is lost during combustion at $550 ^{\circ}$ C.