

EFFECTS OF CCA WOOD ON NON-TARGET AQUATIC BIOTA

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Abstract;

Studies are reviewed that demonstrate the leaching of Cu, Cr, and As from pressure-treated wood in aquatic environments. The metals leached out accumulate in sediments near the wood (particularly bulkheads, which have more surface area for leaching than dock pilings). The metals also accumulate in organisms, including epibiota that live directly on the wood and benthic organisms, which live in sediments near the wood. Those inhabiting sediments closer to the wood accumulate higher levels of the contaminants. Other animals can acquire elevated levels of these metals indirectly as a result of consuming contaminated prey (trophic transfer). Once organisms have accumulated metals, they may exhibit toxic effects. Effects of CCA leachates in aquatic biota have been noted at the cellular level (e.g. micronuclei, indicating DNA damage), tissue level (e.g. pathology), individual organism level (e.g. reduced growth, altered behavior, and mortality), and community level (reduced number of individuals, reduced species richness, and reduced diversity). Effects are more severe in poorly flushed areas and in areas where the wood is relatively new. Residential canals lined with CCA wood are particularly toxic. The severity of effects is reduced after the wood has leached for a few months. Deleterious effects in the aquatic environment appear to be due largely to copper. Thus, alternative formulations that lack Cr and As due to concerns about their toxicity to humans, but contain greater amounts of Cu and leach more Cu will be more deleterious than CCA to the aquatic environment.

Keywords: leaching, uptake, accumulation, toxic, pathology

INTRODUCTION:

As shorelines are developed, many wooden structures such as bulkheads and pilings have been placed in marshes and estuaries. Many of these structures have been made of chromated copper arsenate (CCA) treated wood, which contains high quantities (<2.5 lbs/cubic foot) of the toxic metals Cu, Cr, and As, to prevent rotting and boring by invertebrates. The wood is impregnated under pressure with a mixture of these metal salts, and the components can react with lignocellulose in the wood to form insoluble compounds, a process known as fixation. Even when wood has been properly preserved, some quantities of these toxic metals leach out into the ecosystem, especially when the wood is new. Increased drying time has been found to reduce the leaching of metals from the wood [1](Hingston et al. 2002). Many studies have focused on leaching and factors that can affect the rate of leaching [2](Hingston et al., 2001). Factors of importance during the treatment process were the fixation time and formulation (ratio of preservative components), wood anatomy (softwood species high in lignin perform better than hardwoods), preservative treatment including temperature, and loading (concentration of treatment solution). Factors in the environment into which the wood leaches include salinity (higher salinity causes greater leaching), pH (high leaching at low pH), and temperature (higher leaching at higher temperature). The rate of leaching can be affected by the amount of time the wood has been leaching. Breslin and Adler-Ivanbrook [3] found that after 90 days of leaching, the rate of release decreased between 0.5 and 2 orders of magnitude. Archer and Preston [4] found that CCA-treated pine leached up to 25% of total active ingredients within six months, with total losses of 52% after 85 months.

A series of studies in the 1990s demonstrated that both in the lab and in the natural environment, the metals leached out from the wood accumulated in nearby sediments and biota. Of the three metals, Cu leaches most [5] (Warner and Solomon, 1990) and is the most toxic to marine and freshwater organisms [6] (Weis et al., 1991). Metals accumulated in nearby sediments and benthos, and adverse effects in the benthic organisms (such as polychaete worms and bivalves) adjacent to treated wood bulkheads have been noted. Accumulation and effects were especially severe in areas that were not well flushed by tidal action [7,8] (Weis and Weis, 1994, Weis et al., 1998).

In this paper we review information about uptake and accumulation of the metals leached from CCA wood in sediments and organisms, and the toxic effects that have been examined at different levels of biological organization.

UPTAKE:

In order to have a biological effect contaminants generally must be taken up into organisms, a process known as bioaccumulation. Once inside an organism, the contaminants may concentrate in particular organs and thus exert their effects. Measurements of bioaccumulation are standard parts of field assessments of environmental contamination. Uptake of Cu, Cr, and As has been studied in sediments and organisms living in the vicinity of CCA treated wood.

Sediments:

A mass balance in a freshwater lake in Virginia indicated that leaching of CCA-treated lumber was responsible for a large percentage of the overall levels of As in lake sediments [9] (Rice et al., 2002). Sediments have been studied that are adjacent to and at varying distances from CCA-treated wood bulkheads in estuaries. Metals leached from the wood accumulated in the fine particle fraction of the sediments, and were highest right at the wood and gradually declined further away [10]. Sediments adjacent to bulkheads in the northeast US generally had very low percentages of fine particles (silt and clay) but very high concentrations of the metals on these particles. Bulk sediment analysis would show low contamination because of the small percent of fine particles, however. Sediments further away from the bulkheads, and thus in deeper water, had higher percentages of fine particles but lower concentrations of the contaminants on them. Levels of copper were generally higher than the other two metals. Higher metal concentrations were seen in sediments in poorly flushed areas than in more open water environments. The degree of elevation of metals in the sediments was affected by the amount of water movements, the nature of the sediments (how much was fine particles) and the age of the wood [8]. Sediments in the Gulf Coast remained 99% sand, even 10 m out, so that while bulk sediment analysis would indicate low contamination, the fine particles were highly contaminated, showing the highest levels right by the CCA bulkhead (Figure 1). Similar analyses by dock pilings in moderately flushed environments did not show accumulation of the metals in the immediate vicinity of the pilings, presumably because they have less surface area for leaching.

Sediment contamination was also seen under and adjacent to CCA boardwalks (walkways) over salt marshes, and again the age of the wood was a major factor affecting the degree of contamination [11]. Metal concentrations were highly elevated under the walkways and up to 10 m away. This study is similar to that of Stillwell and Gorny [12] who studied contamination of soil under decks, with the difference that in tidal marshes leaching during rainfall sometimes occurs when the walkway is over water (at high tide), which will cause greater dispersion of the leachates. Dispersal of contaminants near an old walkway was greatest in the low marsh, less in the middle, and least in the high marsh, corresponding to the relative periods of tidal inundation. Accumulation under the walkway was generally greatest in the low marsh. Contamination was much higher in sediments under a new walkway than an old one, but metals had not dispersed as far.

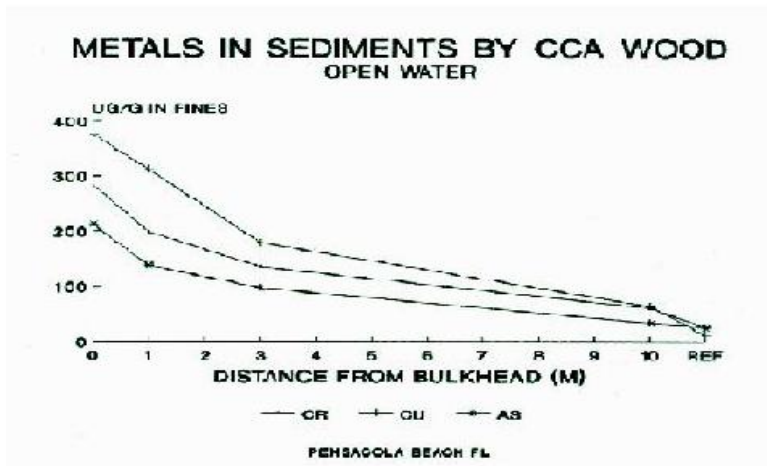


Figure 1: Concentrations of Cr, Cu, and As in Sediments by a CCA Bulkhead

Organisms:

Epibiota:

The organisms that live attached to the wood are the organisms in which the greatest uptake would be expected. These are referred to as epibiota or the “fouling community.” Green algae growing on treated wood in Long Island NY had about four times as much copper, twice as much Cr and five times as much As as algae from nearby rocks [13]. Red algae growing on a bulkhead in open water in the Gulf Coast of Florida had three times as much Cu, and two times as much As as those from nearby rocks, while those living inside a canal lined with CCA wood had much higher concentrations. The same phenomenon was seen with barnacles: those on rocks had about 1 ug g^{-1} Cu, while those on the open water CCA dock had 3 ug g^{-1} , those in the canal had about 10 ug g^{-1} and those attached to new wood inside that canal had about 80 ug g^{-1} [14]. This again indicates greater leaching and accumulation from new wood and in areas with less water movement. Oysters (*Crassostrea virginica*) inside the canal had highly elevated copper levels (over 150 ug g^{-1}), a 12-fold increase over controls, and were frequently greenish in color. Other metals did not accumulate in oysters to such a degree: arsenic concentration was about 2x that of controls. There was a negative correlation of copper level with oyster weight, indicating the concentrations are diluted as the animals grow [15]. This may have negative implications for predators that preferentially eat smaller more vulnerable oysters, since these are the ones with the highest metal concentrations. Green oysters have been previously noted in Taiwan, where they had accumulated copper from industrial sources [16] and were considered a public health risk because they had acquired copper levels far exceeding international limits for human consumption.

The marine isopods *Limnoria* spp. (gribbles) bore through wood, including CCA treated wood, for protection and as a source of food. This is ironic, since one of the reasons for the use of wood preservatives is to prevent damage by marine borers. They can tolerate the high

concentrations of metals by storing copper in granules in their digestive caecae. An increased number of copper-containing granules was seen in isopods from CCA treated wood compared to those from untreated wood. The ability to store copper in granular form which is inert may explain why this organism can bore through and consume CCA wood without suffering toxic effects [17]. Arsenic and chromium were not elevated in these granules or in digestive caecal cells, however.

Benthic organisms:

Bioavailability of sediment-associated metals depends on a large number of factors including metal speciation, the degree of binding to the sediments, the degree of oxidation or reduction of the sediments, and the pH. Metals tightly bound to fine particles in the reduced state are believed to play a minor role in toxicity, while those in pore waters are considered more responsible for uptake and toxic effects. Benthic organisms living in sediments contaminated by CCA wood bulkheads have been found to have elevated levels of metals. Fiddler crabs (*Uca pugilator*) from intertidal burrows near CCA bulkheads had metal levels about double that of controls [13]. Metals in subtidal benthic worms living adjacent to a bulkhead in the Gulf Coast of Florida were also elevated, and the levels decreased with distance from the bulkhead [7]. The levels in the benthic organisms generally paralleled the levels in the sediments in which they lived [8].

Saltmarsh plants (*Spartina alterniflora*, *S. patens*, and *Phragmites australis*) living under and near CCA walkways in Delaware were analyzed for metals together with the afore-mentioned sediments. Accumulation patterns in plants were similar to those in the marsh sediments, but the elevation of metal concentrations did not disperse as far and was not greater under the new vs the old walkway, despite the great differences in sediment concentrations [11]. In ribbed mussels (*Geukensia demissa*) collected from these locations, bioaccumulation was seldom statistically significant, due largely to small sample sizes. Additional work is needed to further investigate detritus feeding invertebrates in salt marshes under walkways.

Trophic Transfer:

Animals need not be directly exposed to the source of contamination (i.e. CCA wood) to accumulate contaminants from it. They may be exposed indirectly, via their food. Trophic transfer is considered the major mechanism for contaminant accumulation in larger organisms higher up in the food web. A number of motile animals such as grass shrimp, amphipods, gobies etc. are frequently found associated with wood in the field, probably feeding on the epibiota. This provides a mechanism for contaminants to pass into the food web. Experiments were done in which algae (*Ulva lactuca* and *Enteromorpha intestinalis*) collected from CCA wood or from rocks were fed to mud snails (*Ilyanassa obsoleta*). The snails took up contaminants (largely Cu) from the algae and suffered harmful effects [13]. Chromium in *Enteromorpha* was transferred to the herbivorous rabbitfish, *Siganus canaliculatus*, through feeding [18].

METALS IN SNAILS, *THAIS HAEMASTOMA* EXPERIMENTAL AND FIELD-COLLECTED

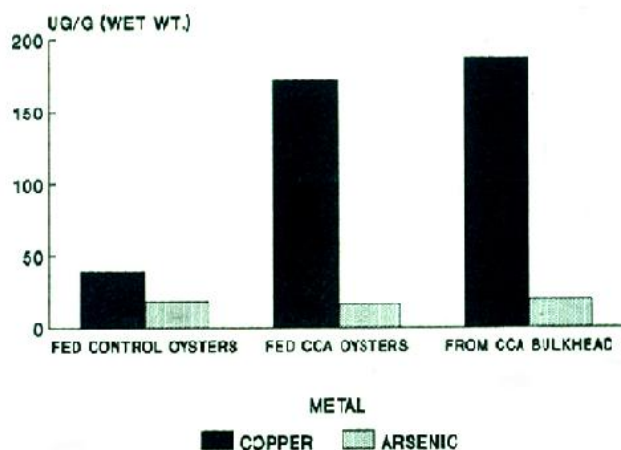


Figure 2. Metal accumulation in snails fed oysters from CCA bulkhead and a reference site, and in snails collected from a CCA bulkhead.

Another lab study fed oysters (*Crassostrea virginica*) collected from CCA wood to *Thais haemastoma*, a carnivorous snail. Control snails were fed oysters collected from rocks at a reference site. The experimental snails increased their body burden of copper about four-fold over an eight week experiment (Figure 2), and attained Cu levels comparable to that of snails collected in the field from a CCA bulkhead ($>150 \text{ ug g}^{-1}$). Juvenile fish (spot *Leiostomus xanthurus* and pinfish, *Lagodon rhomboides*) were collected from inside and outside a CCA-lined canal. Those inside the canal had about 5 times as much Cu and 7 times as much As as reference fish. It is likely that these body burdens were obtained at least partly from their food [19]. A field experiment was performed in which organisms were caged along with CCA and untreated wood with epibiota for three months. The epibiota on treated panels had elevated Cu and As compared to epibiota on untreated wood, and amphipods caged with the treated wood developed elevated Cu. However, caged grass shrimp (*Palaemonetes pugio*), naked gobies (*Gobiosoma boscii*) and mummichogs (*Fundulus heteroclitus*) did not accumulate elevated levels of the metals. Thus, trophic transfer was seen only for the amphipods. Fish may have a more efficient mechanism for regulating metal levels in their tissues [20].

TOXICANT EFFECTS:

Toxicant effects can be studied at many levels of biological organization. Initially, toxic chemicals interact with molecules inside cells of organisms. Effects can move from biochemical to cellular to tissue, to organ to individual organism to population to community to ecosystem. Understanding effects at one level of organization may provide insights into effects at higher levels of organization. Research into impacts of leachates from pressure-treated wood in the aquatic environment has examined effects on cellular level, to individuals, populations, and communities.

Cell Level:

Oysters (*Crassostrea virginica*) living inside a canal in the Gulf Coast of Florida lined with CCA wood bulkheads were found to have twice as many micronuclei in gill cells as reference oysters [21], indicating that there are DNA-damaging contaminants at the site (Figure 3). When control oysters were transplanted into the canal for three months, the number of micronuclei increased significantly [21]. Both chromium and arsenic are known to be genotoxic [22, 23]. The form of Cr used in wood treatment is Cr (VI), which is highly genotoxic.

Bacteria that normally degrade pentachlorophenol (*Flavobacterium* sp. strain ATCC 53874) play an important role in degrading and waste removal of this other chemical used as a wood preservative. When these bacteria were exposed to CCA, which often occurs in the same places as pentachlorophenol (i.e., wood treatment facilities) their ability to degrade the PCP was inhibited. Inhibitory effects were seen in this laboratory study at concentrations thousands of times less than those used commercially [24]. Both a commercially available and a laboratory prepared CCA solution inhibited the growth of these environmentally beneficial and important bacteria, even at low concentrations [25].

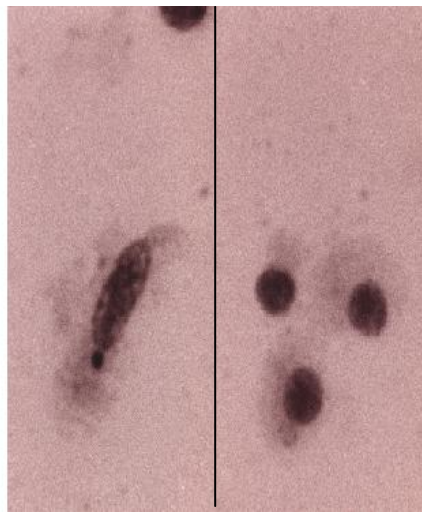


Figure 3. Micronucleus in cells of oysters from a CCA lined canal, on left.

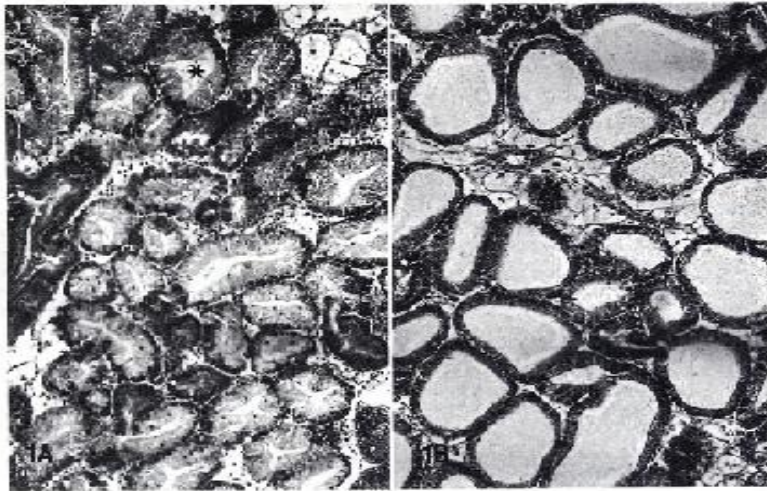


Figure 4. Pathology of digestive gland in oysters on CCA wood. On left is normal oyster digestive gland diverticula, and on right severe change in CCA oysters with dilation of lumina and loss of cell height.

Tissue Level:

The oysters living inside the CCA-lined canal in Florida also had an elevated incidence of a pathological atrophic condition of the digestive diverticula (Fig. 4) [15] P. Weis et al., 1993c). This pathology had previously been noted in oysters exposed to a variety of stressors including copper [26]. The condition did not appear, however, in control oysters transplanted into the canal site for 3 months, during which time they attained about two-thirds of the copper level of the canal oysters.

Individual Organisms:

Effects on individual organisms have been studied both in laboratory toxicity tests and in organisms in the field. There have been numerous lab tests on effects of each of the three metals individually, but there has been relatively little work on effects of treated wood leachates. In fresh water subject to simulated acid rain, the copper leached was far in excess of the lethal level for *Daphnia magna* [27]. The LC50 for this species is about 0.036 mg Cu l⁻¹ which is only about 2% of the leachate concentration. Leachates from treated wood from different tree species all failed LC50 tests using fish [28].

The toxicity of leachates depends on the volume of water in which they are leaching, and the length of time the wood has been leaching. New wood leaches the fastest and is therefore the most toxic. Wood leachates were toxic to fiddler crabs (*Uca pugilator*), green algae (*Ulva lactuca*), fish (*Fundulus heteroclitus*) embryos, and sea urchin (*Arbacia punctulata*) sperm and embryos [6, 29]. The toxic effects of wood that had already leached for several weeks were much less severe. Sublethal effects observed included bleaching of the green algae, reduced fertilization and inhibition of larval development in sea urchins, and retardation of regeneration and molting in the fiddler crabs. One of the most sensitive organisms was the mud snail, *Ilyanassa obsoleta*, which upon exposure to leachate retracted into their shells and became inactive on the bottom of the tank. If they were placed back in clean water, they recovered, but if they remained in water with CCA leachates, they died after several days. Studies using individual metals or combinations of metals indicated that the algae bleaching and the snail mortality was due to copper. This

phenomenon of retraction into the shell has been reported for other gastropods after copper exposure [30, 31]. When mud snails were fed green algae, *Ulva* or *Enteromorpha*, collected from CCA wood or from rocks, the snails consuming the algae from the treated wood retracted and died over a four week period. This indicates that trophic transfer of the contaminants can be responsible for this potentially lethal response to copper [13].

In the experiment described earlier in which carnivorous snails (*Thais haemastoma*) were fed oysters (*Crassostrea virginica*) from a CCA-lined canal, their consumption rate gradually decreased over an eight-week period compared to snails feeding on control oysters. These snails grew significantly less than the snails feeding on control oysters, and increased their body burden 4-fold over this period of time [19]).

Laboratory bioassays of leachate were performed on larval oysters (*Crassostrea gigas*) to investigate behavioral responses [32]. Early veliger stage larvae were observed to avoid concentrated leachate, and 3- and 7-day old larvae swam faster in leachate than in clean sea water and moved up and down more in the leachate. This altered behavior may retard settlement of the larvae to metamorphose into adults, and may be involved with reducing the numbers of organisms that settle on the CCA wood (see below).

Communities:

Epibiotic Community:

Epibiota are species that settle and attach themselves to hard structures in aquatic environments. When boards of CCA and untreated wood were placed into an estuary in Long Island NY and examined for settlement on a monthly basis, treated wood had a reduced number of species, lower diversity index, fewer barnacles and reduced growth of those barnacles that did settle. One species of bryozoan, *Bugula turrita*, was found to grow at greater density on the treated wood [33]. When the epibiota were removed and the same boards placed back in the estuary, the epibiota settling subsequently on the CCA wood had less of a difference from control community, indicating that the toxicity of the wood was reduced after having soaked for a period of time. The third time there were no statistically significant differences between the community on the CCA wood and the control panels [34]. However, differences in the growth of certain species including the green alga *Enteromorpha* and the bryozoan *Conopeum* were still observed.

Brown and Eaton [35] assessed the epibiotic community on panels of treated and control wood after 6, 12 and 18 months. They found similar species richness on the CCA and the control panels, although the number of individuals was higher on CCA wood due to higher numbers of certain dominant species (*Elminus modestus*, *Hydroides ezoensis* and *Electra pilosa*) on the CCA wood, which caused the diversity index to decrease. The relative lack of impact seen in this study compared to the previous ones is probably due to the effects being seen in relatively short one-month exposures coinciding with the higher leaching rates, contrasted with the six-month or longer exposure in this study, by which time leaching had probably decreased.

Benthic Community:

The benthic community in sediments adjacent to bulkheads was reduced in species richness, total numbers of organisms, and diversity compared to reference sediments with lower metal concentrations. The physical characteristics at the sites studied were very similar as was the water depth. The reduction was greater inside a CCA-lined canal compared with an open water CCA bulkhead, but both were significantly less than the number of species, number of organisms and

diversity at the reference site (Figure 5) [7]. Within the canal, only two species were found in sediments by the bulkheads, the polychaete worms *Neanthes succinea* and *Hobsonia florida*. A follow-up study was performed to see the spatial extent of the benthic impacts at different distances from the bulkheads. Sediments and organisms were collected at CCA bulkheads and at 1, 3, and 10 m out from them at five different sites in the Atlantic coast from New York to South Carolina. Reference areas were bulkheads made of other materials or unbulkheaded areas nearby. At most sites, effects (reduced community) were seen at 1 m but not at 3 or 10. At two of the sites, however, effects were seen at 3 or 10 m where the metal concentrations in the fine particles were less, but the percent of fine particles was greatly increased [8]. Differences in the spatial extent of impacts were attributed to the age of the bulkheads, the energy of the environment, and the nature of the sediments at the different sites. A number of sites with docks rather than bulkheads were examined, and these did not demonstrate accumulation of metals in sediments adjacent to pilings or any consistent differences in benthic communities. It appears that leachates from pilings in reasonably well-flushed areas do not have negative effects in the immediate vicinity. Wendt et al. [35] studying docks in the very well flushed ACE Basin also did not find effects of CCA dock pilings.

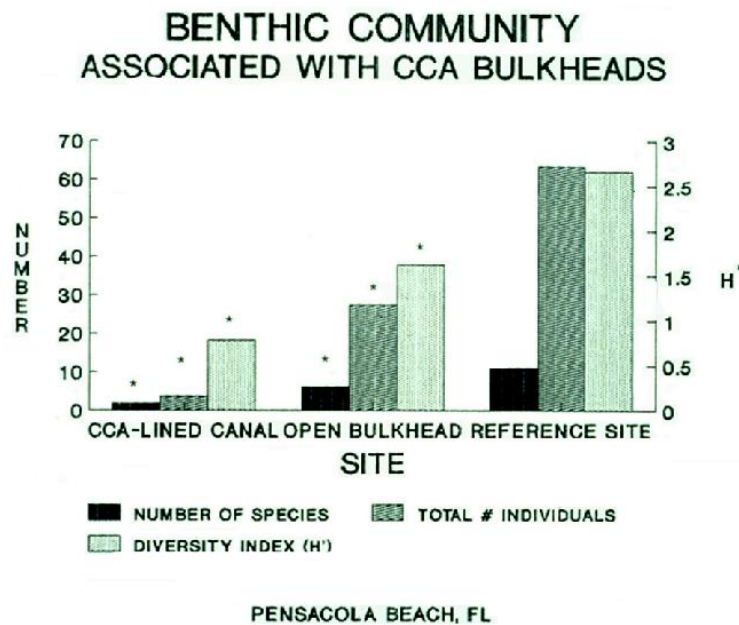


Figure 5. Species richness, number of individuals, and diversity index in sediments from a CCA-lined canal, open water bulkhead, and reference site.

Ecosystem:

To our knowledge there have not yet been any studies on ecosystem level impacts in aquatic environments. However, a few studies on terrestrial soil ecosystems have been reported. Microbes in CCA-contaminated soils in the field have been shown to be negatively affected [37]. Microbial biomass carbon and nitrogen were lower in contaminated soils. Bacterial respiration, biomass P, and denitrification all declined with increasing CCA contamination. Soil biological activity including respiration, nitrification and sulphatase was found to be reduced in pasture soils contaminated by CCA timbers [38].

CONCLUSIONS:

The recent attention devoted to CCA wood and the recent restrictions posed by the EPA are because of potential risks to humans from playground equipment and decks. Nevertheless, there have been many documented (rather than potential) deleterious effects seen in many types of aquatic organisms, not just in the laboratory where concentrations may be greater than field situations, but in the field at many sites. The effects are greater in poorly flushed areas and when the wood is new. The environmental impact of CCA wood could be reduced considerably if it could be soaked out for a few months before being put on the market. The water into which it leached could then be recycled by being pressure-treated into new pieces of wood.

Most of the harmful effects of CCA wood in the aquatic environment seem to be due largely to the copper, rather than the arsenic, which is the main concern in the human health field. There will continue to be pressure to reduce the use of Cr and As in treated wood preservative formulations. Substitute formulations of treated wood are being developed that do not contain arsenic, but contain greater amounts of copper than traditional CCA does and leach more copper than CCA wood [39]. Many well-meaning people are likely to want to use these products instead of CCA for structures in or near the water, as well as for decks and playgrounds, on the assumption that they are safer than CCA. While these new formulations are preferable for such terrestrial uses, they will be a much greater environmental risk for aquatic environments than CCA is, and they should come with warnings that they should not be used in or near the water.

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