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Ecological Impact of Chromated Copper Arsenate (CCA) Treated Wood for Marine Applications: A Review

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Wood when used in the aquatic environment has always been susceptible to deterioration by various biotic and abiotic agents. The biodegradability of wood is the major impediment restricting its use in the aquatic environment. Environmental risks associated with chromated copper arsenate (CCA) treated wood have been studied in detail by many researchers. The conflicting conclusions made by the researchers on the impact of CCA - the most commonly used wood preservative - on the aquatic biota highlight the relevance of the topic and suggest the need for further studies on quantifying the effect of leachate from the treated wood on different aquatic organisms. In the present communication, the effect of CCA on target and non-target marine organisms and the movement of the CCA components along the trophic chain and their bioaccumulation in organisms have been reviewed in detail. The toxicity of CCA constituents in the tissues and shells of organisms and the impact on the biodiversity are also discussed. The review on the data available, suggests a need of further studies to prove the exact mode of transfer of the constituents leached and speciation of leachate.

Key words: CCA, ecological impact, marine biota, toxicity, biodiversity

The versatility of wood as a construction material for boat building is well established. The biodegradability of wood is the major impediment restricting its use in the aquatic environment. Wood in the aquatic environment is always susceptible to deterioration by various biotic and abiotic agents. The risk of biotic decay is highest in wood permanently wetted by seawater. The microorganisms and invertebrates are responsible for the deterioration of marine timbers. The invertebrates of mainly two phyla, *viz.*, mollusca and arthropoda, belonging to four different families, *viz.*, sphaeromidae, limnoriidae, pholadidae and teredinidae degrade wood by boring (Eaton, 1985; Shanthakumaran & Krishnan, 1991; Rao *et al.*, 1991; Shanthakumaran & Srinivasan, 1993; Albuquerque & Cragg, 1995). The ever-increasing demand for conventional timber and dwindling supply have led to the increased use of less durable timber after chemical preservation. Use of preservatives certainly increases the life of wood for over 10 to 20 years.

Indigenous plant and animal extracts are used as preservatives for protecting wood from decay especially in the fisheries sector (Nair *et al.*, 1985). Commercial water borne preservative, CCA (copper-chrome-arsenate) protects wood against the attack of fungi, insects and marine borers. CCA has been in use world over for the last sixty years. In countries like United Kingdom, U.S.A., New Zealand, and Japan it has been a major preservative for wood used for above ground applications. In India, from 1940 onwards CCA was mainly in use for preserving wood for railway sleepers and electric posts but the use of treated wood for aquatic purposes is rather a new approach. Rough estimates available show that about 400 metric tonnes of CCA preservative is

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used per annum world over (Baldwin *et al.*, 1996). Timber used in fresh water pilings and columns should have 9.6 kg m^{-3} to 12.8 kg m^{-3} retention of CCA, while pilings and columns for salt-water immersion use 40 kg m^{-3} retention (Adler-Ivanbrook & Breslin, 1999).

Environmental risks associated with CCA treated wood have been studied in detail by Albuquerque & Cragg, (1995b), Baldwin *et al.* (1996) and Cookson *et al.* (1996). Many have reported that the use of CCA treated wood causes no hazard to the marine environment and has no adverse effect on non-target aquatic biota (Weis & Weis, 1992a, 1999; Cookson *et al.*, 1996; Brown *et al.*, 2001, 2003). Some researchers suggest that the metal leachates do accumulate in the aquatic biota and cause deleterious effects if exposed for several days (Fahlstrom, 1967; Brooks, 1997; Lebow *et al.*, 2000). The studies on the total number of individuals, biomass and growth characteristics of the non-target epibiota showed that there is an impact on the biodiversity, as the preservative treated panels showed reduction in species diversity and abundance of certain species (Fahlstrom, 1967; Weis & Weis, 1992; Lebow *et al.*, 2000). The conflicting conclusions made by the researchers on the impact of CCA on the aquatic biota highlight the relevance of the topic and suggest the need for further studies on quantifying the effect of leachate from the treated wood on different aquatic organisms. In the present communication the effect of CCA on target and non-target marine organisms, the movement of the CCA components along the trophic chain and its bioaccumulation in organisms have been reviewed in detail.

Effect of CCA on marine biota

Studies conducted during the last decade (Lee *et al.*, 1993; Cooper *et al.*, 1997; Lebow *et al.*, 2000) have shown that the metals leached from the CCA treated wood pollute the marine eco-system. It is difficult to measure the impact of heavy metals on marine ecosystem because many marine organisms are mobile and hence exposure to polluted waters always varies (Rao *et al.*, 1991; Cooper *et al.*, 1997; Cragg *et al.*, 1999; Kuppuswamy *et al.*, 2004). In the marine ecosystem, pollution monitoring and sampling are practically very difficult and the metals leach out in various chemical forms some of which are toxic and bioavailable while others are not.

Although the above factors restrict the studies on aquatic biota, a number of attempts made show that there are a number of ways by which aquatic organisms come in contact with the toxic effects of CCA. The metals leaching out from the CCA treated wood before getting diluted with water, come in contact with the epibiotic community that include the fouling and wood boring organisms living attached to the treated wood and may cause direct toxic effects. In the case of organisms swimming in the water column, leached metals are directly imbibed into the body. The leachate deposited in the sediments becomes the source of metals for burrowing forms. Besides, metals may indirectly enter into the body of an organism through food chain and food web.

Effect on target organisms

Although the research efforts in the area of efficacy of CCA as a preservative against wood deteriorating fungi, crustaceans and molluscs proved to be successful (Edwin *et al.*, 1993, 2000). In aquatic conditions, the treated wood was found to be destroyed after prolonged service in the field (Purushotham & Rao, 1971; Cookson, 1987; Santhakumaran & Krishnan, 1991). A study conducted by Kumar *et al.* (2000) in India, showed that CCA was more effective than any of the oil type preservative like creosote in preventing wood borers particularly, *Martesia* spp. which is a major cause for destruction of wood in tropical waters. The damage caused to wood treated with CCA after an exposure period of 35 months in the field was below 25% (Srinivasan & Vallabhan, 1982). In a study conducted by Cookson & Barnacle (1987), CCA treated wood was found attacked by *Limnoria* sp. The same retention of CCA preservative imparts differential toxicity to different organisms (Brooks, 2003; Edwin & Pillai, 2004). According to Brooks (2003) low retention of CCA does not inhibit the growth of teredo. The variable performance of this preservative leads to a new approach of multiple preservative treatments involving the use of CCA and creosote together (dual treatment). It is found that a dual preservative treatment incorporating a water borne preservative followed by an oil borne preservative does not affect the mechanical properties of treated wood than CCA alone (Edwin *et al.*, 1999, 2005; Edwin & Thomas, 2000). Dual preservative treated wood performed better than CCA treated wood on exposure to marine conditions (Edwin *et al.*, 1993; Edwin & Pillai, 2004).

Effect on non-target fouling organisms

CCA uptake and toxicity responses would be expected to be highest in epibiotic or fouling organisms that live attached to the hard structures like wood in the aquatic environment. They are generally considered as non-target to CCA. In CCA treated wood used for marine construction, there is no need to inhibit growth of the fouling organisms since they do not degrade the wood. Sub tidal exposure trials conducted using CCA treated wood of different retentions showed no significant toxic effects to fouling organisms. But the number of individuals reduced considerably in treated panels while no change occurred in the community structure (Cookson *et al.*, 1996).

Uptake of CCA: The uptake of the CCA leachate by fouling organisms and other forms inhabiting water column and sediments is the first step to trophic transfer. All the constituent metals of CCA are found to be the natural parts of earth's lithosphere. According to Brooks (2003) the average crustal concentrations are: 50 $\mu g\ g^{-1}$ for copper, 125 $\mu g\ g^{-1}$ for chromium and 7 $\mu g\ g^{-1}$ for arsenic. Plants absorb inorganic soluble fraction of the metals, while the degree of absorbency varies from plant to plant and depends on the concentration of chemical in the water as well as its bioavailability (Walthert, 2003). The uptake and metabolism of chromium and copper, which are essential micronutrients for plants and animals, is a normal biological process. Pentavalent form of the arsenic which is chemically similar to phosphate is readily taken up by plants and animals for normal cellular respiration and metabolism. All these metal forms are found to be bioconcentrating in the aquatic organisms and in some forms they get biomagnified. Since, copper tends to leach out most and bioaccumulate, it was hypothesized that copper would be accumulated in higher concentrations in consumers (Warner & Solomon, 1990). Copper is highly toxic to those aquatic organisms, which have permeable gill surfaces that permit easier uptake of copper. According to Brooks (2003), high level of arsenic in the tissues of an organism, is mainly due to the incidental uptake of arsenic from sediment while feeding. Uptake of chromium is rather direct from seawater than assimilation through the food chain (Baldwin *et al.*, 1996; Brooks, 1997, 2000, 2003).

Bioconcentration and biomagnification of CCA constituents: When Cu, Cr and As of CCA leachate get access to the fouling organisms they get either stored in their body or may get entry into the food web. In such cases it should be studied whether the bioaccumulations of the metals and consequent adverse effects occur in higher organisms except those living attached to the treated wood (Adler-Ivanbrook & Breslin 1999). Studies have been conducted on the mechanism of bio concentration and biomagnification of CCA constituents. When the test organism *Lumbriculus variegatus* was exposed to the CCA leachate near a sawmill area, for about 28 days, arsenic was found to be bioaccumulating in the tissue of the organism. Oligochaetes near the site showed very high concentration of arsenic in their tissues (Lyytikainen, 2001).

The chemical nature of the contaminant in an organism can also affect uptake by a consumer. The studies by Reinfelder & Fisher (1991) showed that only the soluble form of the metal that was stored in diatoms was transferred to copepods. In gastropods, metals are stored in granules. In such cases the metals are not assimilated from the granules but pass directly through the gut to the predator (Nott & Nicolidon, 1990). In a field study conducted with CCA treated panels kept in a cage where various consumer organisms were reared, it was found that in three months, the epibiotic organisms have taken up the metals from CCA, which get trophically transferred to grazing organisms like amphipods. In their body the metals get bioaccumulated. But the metal concentration in glass shrimp, *Palaemonetes pugio* and two fish species, naked goby, *Gobiosoma bosci* and mummichog, *Fundulus heteroclitus* was unaffected by CCA treated wood. None of the above consumers showed bioaccumulation of metals except amphipods (Weis & Weis, 1999).

Algae, *Ulva lactuca* and *Enteromorpha intestinalis*, collected from CCA treated wood and from rocks nearby when fed to mud snails, *Ilyanassa obseleta*, the snails took up the metals mainly copper, from the algae and suffered adverse effect (Weis *et al.*, 1992). But later, the study was found unrealistic by Brooks (2003) as the epibiota analyzed was scraped from CCA treated wood in such a way that the possibility of contamination cannot be omitted. The studies were conducted on the assumption that the copper in CCA is bioconcentrated and algae growing on CCA treated wood have elevated concentrations of copper. However, in this experiment, the levels of copper, chromium and arsenic in the water in which snails were grown, were not determined (Weis *et al.*, 1992). So it was found impossible to determine the relevance of trophic transfer of CCA leachate from algae to snails. Brooks (1997, 2000, and 2003) is of the opinion that mortality may also be due to a combination of the factors including very limited water volume.

In the laboratory studies, Weis & Weis (1993) made an attempt to define trophic transfer of CCA leachate, where predatory snails, *Thais* fed with oysters collected from residential canals bulkheaded with CCA treated wood, were adversely affected. Analysis of snail tissue showed significant increase in copper concentration. Brooks (2003) suggests that there are many other sources of Cu in these waterways. Another factor not considered in the experiment was the presence of other contaminants in the residential canals. A report by Environmental Protection Agency, demonstrated that residential canals contained numerous contaminants that can have adverse effects on aquatic life and suggested that the adverse effects due to the presence of copper, chromium and arsenic can be negligible (Chaillou & Weisberg, 1995). Brooks (2003) concluded that without understanding the potential contribution of each contaminant found in the canals, it is impossible, to assume that adverse effects are caused by copper, chromium or arsenic.

During the same time when polychaete worms collected from the sediments adjacent to the CCA treated bulkheads were given as food to juvenile pin fish, *Lagodon rhomboides* and spot, *Leiostomus xanthurus* for one month, no significant elevation in metal concentration was found (Weis & Weis, 1993). To verify the results, mummichogs were caged for three months and examined, even, after which no noticeable results were obtained. Fishes usually inhabiting the polluted areas exhibit elevated amounts of organic and inorganic contaminants. Since protective mechanisms are more effective it is necessary to have longer exposure period to have a noticeable deleterious effect (Weis & Weis, 1999). Mummichogs were found to have low trophic transfer coefficient (TTC), a measure of the potential of the contaminant to biomagnify in a species. Low TTC value explains the organism's ability to survive in contaminated environments (Suedel *et al.*, 1994).

In summary it could be narrated that those organisms living in close proximity of the CCA treated wood can accumulate leached metals from CCA. However, accumulation and transfer possibility in higher organism is very less, since a longer exposure time is required for metals to get accumulated.

Toxicity studies

Decay control attributed to the wood preservatives is mainly due to their direct toxicity. All the constituents of CCA are considered to be the priority pollutants by US Environment Protection Agency. Arsenic and chromium are tolerated at moderately high levels by aquatic species. Chromium and arsenic concentrations in CCA leachate were sufficiently low as to have little or no effect on Lethal Concentration (LC_{50}) determinations (Buchanan & Solomon, 1990). With respect to CCA treated wood, copper is the most toxic metal to aquatic organisms, particularly in marine environments as uncomplexed cupric ion, is most detrimental to the early life stages of marine invertebrates. As these stages are not readily visible, its toxicity is not necessarily apparent to casual observation.

A number of laboratory toxicity tests and field exposure tests were conducted to explain the possible deleterious effects of CCA leachate on aquatic biota. According to Cragg *et al.* (1996) the toxicity of the leachate depend on the nature and volume of the water in which leaching occurs and the nature of wood sample. Information on the acute and chronic toxicity studies of pollutants on various aquatic organisms has been compiled by U.S. Environmental Protection Agency and Pesticide Action Network, North America. But toxicity studies in aquaria are found to be very rare since there is a possibility of overestimation of toxicity effects in static aquaria. These studies may not be much relevant since studies do not represent a natural estuarine environment (Brown & Eaton, 2001). In fresh water, due to changes in physico-chemical properties, the amount of metal leaching and its absorption varies significantly. Studies conducted in *Daphnia magna* in fresh water subjected to simulated acid rain, the leaching rate of Cu was in excess. Even 2% of the leachate was found to be lethal, since LC_{50} value was about 0.036 mg Cu l^{-1} (Buchanan & Solomon, 1990). Similar toxicity studies on fishes using treated wooden panels were also conducted where, when the volume of the water is very less, the effect on biota will be very high since dilution possibilities are less. In seawater, leaching rates are higher due to tidal action; but at the same time dilution makes it less available to the organisms. Wood just after treatment is more prone to leaching (Weis *et al.*, 1991). The toxicity and leaching effects gradually decline with increase in time of exposure. The fiddler crabs *Uca pugilator* showed suppression in limb regeneration, although it was not confirmed whether there were any sublethal adverse effects due to elevated metal levels (Weis *et al.*, 1991; Weis & Weis, 1992 a). Pollution and toxicity effects on fertilization phase of those organisms that release gametes directly into water are well documented. In sea urchin, *Arbacia punctulata* 90% of the sperms failed to fertilize the eggs, and further development of fertilized ones was totally inhibited and lower concentration of these metals did not have any effect either on fertilization or on larval development. The sublethal effects observed in the study included the bleaching of green algae *Ulva lactuca* (Weis *et al.*, 1991; Weis & Weis, 1992 b).

Weis *et al.* (1992) conducted studies, on mud snail, *Ilyanossa obseleta* exposed to the CCA leachate in aquaria. In the presence of leachate, mud snails became inactive and retracted into their shells and when placed back into clear water, they recovered. Retraction of the body into the shells was observed in molluscs as a common phenomenon to tide over the stressful conditions in a polluted environment (Weis *et al.*, 1992).

Accumulation in cells: Heavy metals when accumulated in the body of the organism affect the basic units of life, cells and genes. Cr (VI) and arsenic present in the wood preservative have potency to impart toxicity to the genes (Tkeshelashvili, 1980; Nakamuro & Sayato, 1981; Weis *et al.*, 1995). The oysters *Crassostrea virginica* inhabiting CCA lined canal showed an increased number of micronuclei in gill cells indicating that the constituent chemicals of CCA can cause damage to DNA (Weis *et al.*, 1995). There are certain bacteria like *Flavobacterium* sp. that degrade pentachlorophenol (PCP) and other chemicals used in wood treatments. The ability of these bacteria to degrade PCP is inhibited when exposed to CCA (Wall & Stratton, 1994). Laboratory prepared and commercially available CCA solutions inhibited the growth of environmentally beneficial bacteria even at low concentrations (Wall & Stratton, 1995).

Accumulation in tissues: The tissues in the liver and kidney are the major centres involved in the processing of various chemical contaminants. The pathological examination of the digestive diverticula of oysters living in the canals lined with CCA showed the presence of severe lesions compared to control oysters (Weis *et al.*, 1993). The studies confirmed that longer exposure is required for the onset of severe pathological changes (Tkeshelashvili *et al.*, 1980; Weis *et al.*, 1993; Wall & Stratton, 1994). During the months of reproductive onset, the same pathological condition was observed in control oysters also. This is supposed to be a non-specific response towards stressful conditions. In the laboratory when oysters were exposed to Cu concentrations 0.1 to 0.5 ppm, similar pathological condition was observed within two weeks (Weis *et al.*, 1993). Of the CCA constituents, Cu was found to be more toxic and 0.5 ppm of $CuSO_4$ was found to be lethal to 50% of *Villorita cyprinoides* and when 1 ppm CCA was used there was 50% mortality (Sreeja, 2008). The accumulation pattern of copper, chromium and arsenic in tissues of *Oreochromis mossambicus* grown in aquarium tanks where CCA treated wood panels were exposed has shown that maximum accumulation was in liver tissues (Sreeja *et al.*, 2006, 2008).

Accumulation in shells: The reliability of the barnacle shell as an indicator of various trace elements in the aquatic environment has been established (Bourget *et al.*, 1974; Watson *et al.*, 1995). The studies revealed that barnacles, which are living in environments of high metal loadings, had higher concentration of the concerned metals. There are large number of variables that influence metal concentration in shells such as seasonal change, shell size, growth rate, type of treatment procedure and type of wood species used. The mean levels of Cu and Cr detected in the shells showed that only those forms living in close proximity of the leachate show these elevated levels (Scown & Cookson, 1999).

Physiological responses: One of the easily detectable measures of the CCA toxicity is reduction in growth rate in algae. Green algae especially *Ulva lactuca, Enteromorpha intestinalis* and *Cladophora* are considered as good bioindicators of contamination by nutrients as well as heavy metals. The growth of algae and amount of primary production are directly related. Inhibition in the photosynthesis may substantially reduce primary production (Sheehan, 1984). When exposed to CCA, chlorophyll content of *Ulva lactuca* was found to decrease and the reduction is mainly due to Cu (Weis *et al.*, 1991; Weis & Weis, 1992a). Ulva collected from CCA treated wood showed elevated levels of all the three metals but no decrease in chlorophyll content (Weis & Weis, 1992a). Algae in the first experiment may have been exposed to unrealistically high concentration of leachate, leading to blanching or algae collected from the dock may have some mechanism to deal with high concentration of the leachate (Reed & Moffat, 1983).

The major physiological activities like feeding and respiration can be taken as an index to determine the degree of metallic pollution. Carnivorous snail *Thais sp.* when given a diet of oysters collected from CCA treated canals, the growth rate was highly reduced (Weis *et al.*, 1992). Barnacles growing on CCA treated piles showed reduction in over all growth rates when compared to that on the untreated ones.

Impact on biodiversity

The alterations in a biological community can be considered as an important index to deal with biodiversity changes in that population. The most sensitive organisms are easily eliminated from the polluted environment while the most tolerant ones become established due to decreased interspecific competition, resulting in a more simplified ecosystem. To measure the community changes, diversity indices are commonly employed. Many studies conducted showed that the metal leachate from the CCA treated wood has adverse effects on early fouling community. It was found that the species diversity, abundance of certain species and biomass levels were significantly reduced on CCA treated panels (Weis & Weis, 1996, 1999).

The number of individuals of certain species was found to be higher on CCA treated panels than on untreated ones and serpulid forms like *Ficopomatus enigmaticus* abundance of individuals increased with increase in CCA preservative loadings (Weis & Weis, 1996).

There was dominance of certain species like *Eluminius modestus, Hydroides ezoensis* and *Electra pilosa* on CCA treated panels while total number of species remained same (Brown & Eaton, 2001). The actual cause of the dominance of some organisms on CCA treated panels is not yet defined. The reasons cited were that treatment procedures may change the surface properties of the wood like texture, colour, etc that may in turn affect the attachment of the organisms. It was concluded that the leaching of CCA from treated wood is insufficient to disturb the fouling community development at sites with normal tidal water circulation (Brown & Eaton, 2001). However, the organisms were found to be adversely affected by the close proximity of the leachate (Weis & Weis, 1996).

According to some studies, the CCA leachate has no adverse effects on non-target aquatic biota (Cookson, 1996; Cragg *et al.*, 1996). Studies conducted to examine the effect of CCA and other preservatives on aquatic organisms at Krishnapatnam on the east coast of India indicated that the impact of CCA preservative on epibiotic community in the sea was negligible (Tarakanadha & Rao, 2002). The total number of individuals, biomass and growth were actually higher on CCA treated panels compared to control ones. Heavy settlement of barnacles, bryozoans, oysters and moderate settlement of serpulids on CCA treated panel indicate that these preservatives may have less impact on fouling organisms or the organisms may be tolerating the toxicants. CCA treatment gives wood a dark green colour and changes the physical properties of timber, giving it a different texture that may enhance barnacle settlement (Weis & Weis, 1996).

The application of finishes like FRP sheathing and painting of CCA treated rubber wood was found effective in reducing leaching of the constituents as they retained more than 85% of the preservatives after 18 months of estuarine exposure (Sreeja *et al.*, 2006; Peter, 2008).

Even after sixty years history of the use of CCA treated and other chemically treated wood in aquatic environments there is little or no convincing evidence of its adverse effects. But only limited information is available about the ultimate fate of the CCA treated wood in the aquatic environment. The lack of information coupled with the concerns over potential environmental hazards has prompted a number of experts to put forward various management practices. The review on the data available suggests a need for further studies to prove the exact rate of leaching and speciation of the leachate. The studies clearly confirm that Cu is of most concern in association with CCA treated wood in aquatic environments.

From a purely biological point of view Cu level in aquatic environment should be kept below 6 $\mu g\ l^{-1}$, so that the adverse effects are minimized. But it is not possible to study and characterize the effects of CCA on aquatic environment merely from its effects of copper, chromium and arsenic. Without knowing the exact nature of the leachate, it will be difficult to study its effects on the marine biota. Further, there is a lack of latest knowledge on the realistic concentration of the leachate in aquatic environments, the toxicant effects on a single organism and on biodiversity of non-target organisms. In tropical countries like India where chemically treated timbers are used, the studies on the impact of these preservatives on the aquatic environments assume great relevance. The need for more eco-friendly chemicals for marine purposes has emerged as a need of the day.

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