Environmental Fate

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Executive Summary

The major exposure from the use of chromated and non-chromated arsenical wood preservatives is to three environmental compartments: soil /sediments, surface and ground water contamination and bioaccumulation in the aquatic and benthic organisms. This chapter will address the environmental fate of arsenic and chromium from wood treated with chromated and non-chromated arsenical wood preservatives. The environmental fate of zinc, which leaches from wood treated with ACZA, was previously addressed in the Zinc Salts RED (Case 4099, August, 1992). Although copper is included in the discussion of some of the individual studies used in this assessment, below, the overall environmental fate of copper will be addressed in the forthcoming Copper RED.

The leaching of arsenic and chromium into water from pressure-treated wood has been widely investigated and both the laboratory and field studies. These studies generally indicate that leaching of the metals is a function of pH, salinity (fresh water, sea water, estuaries, natural and synthetic, sterile buffered water), temperature, moisture content of the treated wood, wood type, and wood texture. It has been observed that most of the leaching takes place in the first few days after the application. Most of these studies have shown that the extent and rate of leaching is: As> Cr. Available studies were conducted under different conditions and the exact concentrations of preseravtive solution absorbed by wood (e.g. utility poles) are not known. Sorption constants of these metals are high for various soils. Leaching of the metals into soils also depends on the pH of the soil, type and texture of the soils, organic content of the soils; however, studies on sorption into soils from utility poles have shown that the release of metals into soils/sediments from the base of treated wood, decks or utility poles or from the pressure treatment facilities, does not show a high degree of downward or ground level migration. In most cases, after migration of the metals a few meters down into soil, these metals attain the background level concentration of soil. Chromium is released into water and soil as Cr(III), but the concentration of Cr(III) is lower than arsernic, partly due to the fixation process in the wood structure. Arsenic is leached into soil and water as As(V).

In general, the metals in water exist as hydrated species (coordinated with water), or hydroxy species or the metal is bound to inorganic anions like FeF_6^{-3} , or bonded to organic ligands to form metal complexes or as organometallics (contains C-Metal bonds). Fate and transport processes, and interaction with aquatic and benthic organisms by these chemical species will vary from one of type of organism to another. The metals from CCA when released into water systems usually attain background concentrations. In view of the fact that the metals attain background level concentrations in soil and water, and the tendency of the metals to speciate, it is hard to ascertain the source of contamination in water and soil. Considering absence of comprehensive ground water monitoring relative to the leaching of metals from CCA into soils and water, it appears no significant possibility exists for ground water contamination in areas where utility poles have been placed and where decks have been built.

Environmental Fate Assessment

Chromium and arsenic as oxides are two of the active ingredients of the water-borne wood preservative <u>chromated copper arsenate</u> (CCA). As a wood preservative it is unique in more than one way. First, it is a mixture of inorganics metal species. Second, its efficacy as a wood preservative improves if, and when, it goes through the 'fixation' process during wood pressure treatment.

The physical properties and the chemistry of the three metals (arsenic, chromium and copper) of the water-borne wood preservative CCA are very well understood in aqueous and soil compartments. Most of the Agency's environmental fate guideline studies (hydrolysis, photolysis, soil aquatic metabolism, etc.) cannot be conducted on the individual, or a mixture of these, metallic actives due to their complex interactions with soil and water.

Chromium is a transition metals and has a tendency to exist in variable oxidation states in water and soils. Common oxidation states of chromium are Cr(III) and Cr(VI). Arsenic is a metalloid (shows the characteristics of both a metal and a non-metal) and also has a tendency to exist in variable oxidation states. Common oxidation states of arsenic are As(III) and As(V). In addition, the pH of aqueous media or soil, nature of soil (texture of soil, percent of organic carbon of the soil, etc.), salinity of water, temperature of water, and soil are some of the factors that give rise to the phenomenon of chemical speciation (formation of different metal species) which is a common phenomenon in these environmental compartments. Because of these parameters, the metal ions can form soluble or insoluble substance which can be cationic or anionic species or full simple molecules or complex compounds. In general, these metal ions exist in water and soil as:

- A. A free metal ion, which in aqueous medium is aquated (solvated or complexed with water molecules);
- B. Simple inorganic species like oxides, hydroxides, halides, carbonates etc.; or
- C. Complexed with organic and inorganic ligands.

Chromium:

Cr(II) is unstable in water. Cr(III) goes through hydrolysis and forms various species. The important species of Cr(III) found in aqueous systems are: $CrOH^{+2}$, $Cr(OH)_2^+$, $Cr(OH)_4^-$, $Cr(OH)_3(s)$. In addition, polymeric species like: $Cr_2(OH)_2$ and $Cr_3(OH)_4^{+5}$ are also formed in water. All these species are present in aqueous systems in the absence of any complexing agents. Similarly, Cr(VI) also hydrolyzes in water and forms CrO_4^{-2} , (at pH > 6.5), and $HCrO_4^-$ and $Cr_2O_7^{-2}$ in acidic medium. In fresh water at pH 6 species detected are: $HCrO_4^-$, $Cr(OH)^{+2}$, $Cr(OH)_2^+$, CrO_4^{-2} , Cr^{+3} and $Cr(OH)_3(s)$. On the other hand, the species detected in sea water at pH 8 are: CrO_4^{-2} , $Cr(OH)_{-2}^+$, $Cr(OH)_{-3}^+$, $Cr(OH)_{-4}^+$, $Cr(OH)_{-4}^+$, $HCrO_4^-$. Cr(III) is kinetically stable and Cr(VI) is thermodynamically stable in aqueous medium. Cr(VI) is more water soluble, and more mobile and can easily move through wet soils into ground water and may become more bioavailable. (Lebow, S. 1996). The half life of Cr(III) in water has been estimated from being

one month to 20 months and this shows persistency of the metal (Pettine, M. and F.J. Millero, 1990)

Chromium goes through oxidation-reduction reactions when sorbed in soils. Organic matter in soils, which has a high sorption capacity for chromium, reduces Cr(VI) to Cr(III) spontaneously. Manganese oxides in the soils, on the other hand, oxidize Cr(III) to Cr(VI). Chromate and dichromate ions form soluble salts and increase the mobility of toxic Cr(VI) in soils. Chromium as Cr(VI) reduces to Cr(III) under anoxic conditions. In water at neutral conditions (pH 7), formation of dichromate ions (chromium as Cr(VI)) is minimized. Cr(VI) is adsorbed less and less by hydrous metal oxides and soils as the alkalinity of the medium increases. The presence of anions like sulfate and phosphate decrease the sorption phenomenon. At low pH and low concentrations of chromium, however, adsorption of Cr(III) on iron and manganese oxides increases.

Arsenic:

The common and important arsenic ores are: tenantite, cobaltite, arsenopyrite, niccolite and enargite. Arsenic has a great tendency to sorb to soils and sediments. Its sorption capacity (μ g total As/g soil) with silty fine sand with little clay ranges from 1.0 to 252. For brown clay sand it is between 1.0 to 80.0 and with fine sand the sorption capacity varies from 1.1 to 7.9. Arsenic sorption is dependent on pH, redox conditions, competing anions, salinity and clay content and hydrous oxide content (aluminum or iron). Arsenic mobility in clay soils is low to moderate. As(V) under proper conditions can reduce to As(III). In aerobic and anaerobic sediments, arsenate is more strongly sorbed than methylarsenic acid (Holm, R.T. 1979; Wauchope, R.D. 1975).

As the sorption of arsenic decreases with rising pH, the mobility of arsenic increases. Organoarsenates decrease the sorption of arsenic and increase the arsenic mobility Organoarsenates are more mobile than arsenic. Arsenic mobility in clay soils is low to moderate. However, in loamy and sandy soils, mobility increases (6-10 cm/day for loamy sand). Between pH 2 and 11, the common species of arsenic present in aqueous medium are: $H_2AsO_4^{-1}$ and $HAsO_4^{-2}$. Beyond pH 12, it is mostly $HAsO_3^{-2}$ and AsO_3^{-3} .

Fixation:

Fixation is a chemical process which consists of a series of chemical reactions that ensue after the wood has been pressure treated with CCA. Fixation precedes the actual 'action' of CCA to act as a wood preservative. It depends on a number of parameters: temperature, humidity (moisture content of the wood), pH and drying period for the wood after the pressure treatment has been completed. Under laboratory conditions, increasing concentration of the wood preservative will lower the pH of the solution mixture and will accelerate the rate of fixation (Anderson, A.G. 1990).

The process of fixation consists of a series of chemical reactions:

First, 'an initial reaction' of absorption of the preservative to the cellulosic and lignin components of the wood. Second, a primary precipitation reaction which converts Cr(VI) to Cr(III) and this process continues for the duration of fixation period. Lastly, the conversion of copper arsenate into basic copper arsenate (Anderson, A.G. 1990).

Earlier research on the temperature effect on the fixation process on scot pine and beech showed that increased fixation occurs when the temperature was raised to 30 °C and that the maximum fixation was attained in 42 hours (Wilson, A. 1971). In another study on fixation (Cooper, et al. 1992), it was shown that for western red cedar the fixation process was best achieved at 70 °C and 93% relative humidity within 14.3 hours. For douglas fir, red pine, lodge pole pine, southern pine and jack pine the fixation at the same temperature and humidity conditions was best achieved between 5.9 to 8.3 hours. In a study on red pine it was shown a freshly treated wood when freezed dried and reequilibrated with moisture, reduction of Cr(VI) to Cr(III) took place even at low moisture contents or even at over dried conditions (Kaldas, M. and P.A. Cooper, 1996).

Another series of studies on hemlock, grand fir, white fir, noble fir, pacific silver fir and douglas fir showed when the wood samples were removed as the drying process was on, and systemically treated with CCA by a full-cell process, the treatability and penetration of CCA into the wood depended on the drying rate (Lebow et al., 1996). In a related study, it was shown that the fixation process is temperature dependent (McNamara W., 1989).

In another study, the fixation rate of commercially available CCA on sawdust, measured by arsenic leaching, showed that at about 20 ° C, 98-99% CCA was fixated by day five. The same study also showed that as the fixation process proceeds, the pH of the preservative rises (Dalhgren S.E., 1972). Another study showed that rate of fixation also depended on the type of wood (Wilson A., 1971).

The process of fixation has been traditionally looked upon as the fixation of Cr(VI) changing into Cr(III) in the wood tissues. A recent work on southern pine, jack pine, and red pine has indicated that copper and arsenic components are stabilized (fixated) earlier than chromium (Cooper et al., 1996).

Special Leaching or Aqueous Availability:

The leaching of CCA metals and subsequent entrance of these metal ions into environmental compartments (water, soil, plants, and animals) is an important process for environmental fate and transport assessment. A very earlier work on leaching of CCA was done on the wood used in residential houses to build foundations and this study showed no significant leaching of CCA components and the conclusion drawn at that time was that there was no environmental hazard to the ground water, soil, plants or animals (Arsenault, R.D., 1975). Later studies have not only contradicted this observation but have elucidated the mechanisms of leaching and also estimate the amounts of leaching of CCA metals from the treated wood.

To elucidate the leaching mechanism of arsenic from CCA-treated wood, an extensive study was carried out in the presence and absence of electrolytes. This leaching study was conducted with a simulated rainfall (rain intensity: 1±0.15 inch/hour). Southern pine, kiln-dried plywood specimen (29.2 cm x 29.2 cm x 1.9 cm) were selected and treated with 4% CCA solutions (CCA-A, B and C) in the presence and absence of electrolytes. The mean absorption of the preservation solution was 17.12 pounds per cubic feet (pcf). Initially water runoff and soil leachate samples were collected after 15, 30, 45 and 60 minutes of simulated rainfall and then after 3, 9 and 27 hours of rainfall.

After the simulated rainfall, it was determined that plywood samples showed a significant decline of arsenic on one face of the plywood from 3.23 mg/g to 1.441 mg/g and on the other face from 3.23 mg/g to 1.22 mg/g. Analysis of the soils (sand and loam) revealed that the amounts of arsenic were not different for the soil in contact with the treated plywood sample than the soils in contact with untreated (blank) plywood. The amounts of arsenic in the surface water runoff was depended on the texture of the soil and the time of exposure to the rainfall. Runoff samples collected after one hour of simulated rainfall did not show the presence of arsenic. The samples of CCA-C in the presence of the electrolyte (sodium dichromate and copper sulfate) indicated the highest arsenic absorption to the wood but also the highest leaching. The surface water runoff collected from the loam soil had a higher concentration of arsenic (44.5 µg/L) but in the sand the amount of arsenic was only 7.3µg/L. The concentration of arsenic increased dramatically for the first three hours of rainfall and then slowly decreased thereafter. The soil leachates from the sand after the first hour of rainfall with the CCA-B (non-electrolytic) showed the higher concentration of arsenic (98.6 μ g/L) but with CCA-C (electrolytic) the amount was 61.3 μ g/l. Loam soil leachates for CCA-B (non-electrolytic) showed the presence of 11.9 µg/L arsenic and for CCA-C (electrolytic) the arsenic amount was 22.2 µg/L. (Chen and Walters, 1979).

In another study, it was shown that from the southern pine wood the metals from CCA leached much more from the high-temperature pressure treated kiln-dried wood than the air-dried pressure treated wood.(Less et al., 1993).

A leaching study conducted on southern pine, pressure treated with CCA-C wood preservative, was submitted by the registrants to the Agency. The study was carried out at three pHs: 5, 7 and 9, in 0.10M HCl and in simulated sea water which was prepared according to the ASTM Method D1141-90. The southern pine blocks (3.8 cm x 3.8 cm x 29 cm) were pressure treated upto 0.80 pounds per cubic feet (pcf) for the studies in pHs 5,7 and in 0.10 M HCl while the for simulated sea water, the blocks were pressure treated upto 2.5 pounds per cubic feet (pcf). The pressure treatment was carried out according to the AWPA Standards. The study was conducted for 60 days altogether. The amounts of the metal ions leaching was found highest with 0.10 M HCl solutions: total arsenic leaching in 0.10M HCl on day 1 was 170 μ g/cm²/day and it declined to 27 μ g (day 30). However, when arsenic was examined in its two common oxidation

states, As(III) leached at a rate of $10\mu g/cm^2/day$ (day 21) and it increased to 38 $\mu g/cm^2/day$ on day 30 while for As(V), the rate was $10\mu g/cm^2/day$ on day 21 and it increased to 22 $\mu g/cm^2/day$ on day 30. The rate of leaching for Cu(II) in 0.10M HCl was 149 $\mu g/cm^2/day$ on day 1 and declined to 22 $\mu g/cm^2/day$ on day 30. The rate of leaching for total Cr in the in presence of 0.10M HCl was 46 $\mu g/cm^2/day$ for day 5 and declined to 30 $\mu g/cm^2/day$ on day 30. When analyzed for Cr(VI), the leaching rate in 0.10M HCl was 1.5 $\mu g/cm^2/day$ for day 21 and reduced to 1.0 $\mu g/cm^2/day$ for day 30 (Stanley, J.S., 1994).

In a 40-day study conducted in Canada on the pressure-treated jack-pine with CCA at various pHs of 3.5, 4.5, 5.5, 7.0 and 8.5 and also in a solution containing dilute sulfuric acid (0.10N). The pressure treated blocks were separated into two sets: One set was kept in open air for one year to simulate 'weathering'. The second set of blocks were kept in-house to simulate 'new conditions'. All blocks were of uniform dimensions of 5 cm². The preservation retention of the blocks was close to but not exactly like CCA-C (the recommended level by AWPA Standards is 0.40 pcf (6.4 kg/m^3) .

'Weathered' blocks leached copper significantly more at pH 3.5, 4.5 and 5.5 than the 'fresh' blocks. Release of chromium was less at pH 3.5 and 4.5. Arsenic showed a higher release rate at pH 5. Generally, the leaching order was Cu > As>Cr. It is recognized that fixation of chromium (conversion of Cr(VI) to Cr(III)) prevents the leaching of chromium from the wood. The pHs in this study were maintained using citric acid/NaOH mixture solutions, and in distilled water a pH of 7 was maintained. The borax/HCl solution resulted in pH 8.5. A similar trend was observed when the leaching was conducted in dilute sulfuric acid solution at pHs 2.5, 3.5 and 4.5 (preservation retention was 0.13 pcf (1.99 kg/m³) (Warner, J.E. & K.R. Solomon, 1990).

A 13-day study on leaching from douglas-fir, redpine, lodgepole fir and western red cedar, pressure treated with 2.3% CCA showed and confirmed that the presence of citric acid/NaOH buffer increases the rate of leaching from the wood at a high pHs like pH 7. (Cooper, P.A., 1991).

A twelve month study was conducted on leaching of CCA-C metals from pressure treated jack pine wood with 1.8% CCA-C treatment solution and a preservative retention of 0.40 pcf (6.4 kg/m³). In this study, the CCA metals from these pressure treated wood blocks were leached into four different compartments: leaching into distilled water, leaching into natural weathering conditions, leaching into soil burial and leaching into compost (made by vegetable matter). It was observed that leaching into compost was higher than into other compartments: 13% leaching was observed in the compost, in soil burial it was 1.3%, weathering sample showed about a 1.5% leaching and leaching into distilled water was about 5%. Leaching order, however, was the same as with other studies: Cu> As> Cr. (Cooper et al., 1992).

A similar 21-day leaching study with southern pine sapwood, pressure treated with 1.03% CCA-C with preservative retention of 0.3 pcf (4.8 kg/m³) showed a leaching rate of 1 μ g/cm²/day for Cu and As and 0.01 μ g/cm²/day for Cr which is the same trend (copper \approx arsenic

> chromium) as other leaching studies have shown (Merkle, et al., 1993).

In an Australian Study, Tasmanian Parks and Wildlife Service (M. Comfort, Scientific Rep. 93/1, 1993), conducted a leaching study on Southern Tasmanian boardwalks (ages 1 to 14 years) which were the pressure treated with CCA. Soil samples collected about 6 inches and a few meters away form the boardwalks showed that the chromium (88 ppm) and copper levels (49 ppm) in the close proximity samples were high compared to the distant ones which were not different from the blank samples. The blank samples showed chromium at 20 ppm and copper between 1-3 ppm. The ages of the boardwalks did appear to contribute in the high levels of the metals.

In a European study (Italy), on CCA leaching from treated wood, rain water was used for extraction. CCA treated wood samples from a post were meshed through a 5 mesh, 25 springs/cm² sieve. The coarse powder so obtained was digested in 96% sulfuric acid and 3% hydrogen peroxide in a 5:1 ratio and the analyses showed the presence of As (1.602 mg/g), Cr(1.345 mg/g) and Cu(0.813 mg/g). Before the extraction, rainwater which was collected in Turin in 1994, was analyzed for the presence of anions and cations including As, Cr and Cu and the amounts of these respectively were: 0.068, 0.029 and 0.021(all in mg/L). This rainwater was then used to extract the coarse powder and the leachates were collected at different times, the last one was 78-hour leachate. The 78 hour extraction sample contained As and Cr ($50 \mu g/g$) and Cu($150 \mu g/g$). The same study also conducted the extractions at pHs 6 down to 3. Maximum amounts of metal ions were released at pH 3. A similar trend was observed in another study. The CCA solution used in the study was purchased commercially and in the stock solution each metal ion was about 1000mg/L from which running samples were prepared (Aceto, M. and A. Fedele, 1994).

In a study in simulated sea water, it was observed that copper leached into water from pressure treated full-sized pilings at 529 mg level and arsenic level was measured at 60 mg and little or no chromium was measurable (Baldwin et al., 1994).

In a freshwater study on the old lockgates and freshly constructed lockgates of pressure treated wood with CCA the copper concentrations (200 ppb) were high at the newly constructed lockgates, 40 meters downstream, while the concentrations of copper were low at the old lockgates (40 ppb). Chromium concentrations were the same (90 ppb) at both locations while arsenic was 90 ppb level at the new lockgate and at 60 ppb level 40 meters downstream (Cooper, P.A., 1991).

In another study, the leaching of the metals from CCA was investigated as the fixation process was in progress. It was carried out on the pole sections (8" x 2' diameter) of red pine poles which were pressure treated with CCA-C of 1.7% and 3.5% concentrations as well as with pressure treated (1.5% CCA-C) the jack pine boards (2" x 6"). The study was conducted at 95% humidity and 60 ° C. As the fixation process proceeds, the metals from the CCA-C were extracted by 2-hour long spray of simulated rain (rainfall: 150 mm). The concentrations of the

metal ions in the leachates progressively declined as chromium fixation process progressed. Arsenic stabilized (fixed) faster than copper fixation which in turn was faster than chromium fixation. For red pine, pressure treated with 1.7% CCA-C at 95% humidity and 60 ° C, the preservation retention was 0.48 pcf (7.7 kg/m³) and 1.02 pcf (16.4 kg/m³) when the CCA-C solution was 3.5%. The retention for jack pine, under the same humidity and temperature conditions, the preservation retention was 0.24 (3.9 kg/m³) when the wood was pressure treated with 2 % CCA-C solution.

For the red pine pole at both the preservation retentions of 0.48 and 1.02 pcf and 99.9% chromium fixation level, the leaching losses from the wood were: $4 \mu g/cm^2$ for Cr, $9 \mu g/cm^2$ for Cu and $3 \mu g/cm^2$ for As. For the jack pine wood, on the other hand, at 99.9% chromium fixation level, the leaching losses of the metal ions from the wood were: 0.28 $\mu g/cm^2$ for Cr, 0.88 $\mu g/cm^2$ for Cu and 0.62 $\mu g/cm^2$ for As. The leaching losses continued to decline as the Cr(VI) fixation progressed from 60-70% to 99.9% level (Cooper et. al, 1995).

A recent estuarine study on the southern yellow pine, pressure treated with CCA-C, reaffirmed the results from previous studies that the leaching of the metal ions from the wood was highest for Cu and lowest for Cr. This study measured the laboratory leaching rates for copper, arsenic and chromium from the freshly pressure treated southern yellow pine as well as the actual loss of these metal ions from a weathered CCA-C treated lumber which had been service for 14 years as a bulkhead in Sayville, New York, south shore estuarine canal. The retention level of the CCA-C in this weathered bulkhead was between 0.61 pcf to 1.0 pcf (9.6 to 16.0 kg/m³) as communicated by S. Roller Lumber Corp. This lumber from the canal was chosen as it had experienced 4 types of weathering: the wood surface at the water level (air exposure), the wood surface exposed to tidal water off and on (air/water exposure), the wood surface continuously submerged in water (water exposure) and last, the wood surface buried deep in the sediment below the canal. (soil exposure). The CCA-C retention level for the weathered lumber was 0.20 pcf (3.1 kg/m^3) for surface exposed to air, 0.30 pcf (5.0 kg/m^3) for the wood surface exposed to tidal water off and on, 0.068 pcf (1.1 kg/m³) for the wood surface submerged under water and 0.60 pcf (9.9 kg/m^3) for the wood surface buried in the sediment. The leaching losses of the metal ions from these weathered surfaces were in the order of: subtidal (wood surface exposed to air and water) > tidal (wood surface submerged in water) > air >sediment. The extent of metal ions leaching was in the same order as the laboratory leaching studies: Cu > As > Cr.

The laboratory leaching study by the same group showed that the freshly pressure treated southern yellow pine (CCA-C), the leaching rates for the metal ions were: $5.71-17.78 \ \mu g/cm^2/day$ for Cu, $0.20-0.98 \ \mu g/cm^2/day$ for Cr and $0.15-0.90 \ \mu g/cm^2/day$ for As, for the initial 12-hour. This laboratory leaching study was conducted under saline conditions (3,13, and 26 ppt) which generally mimic the estuary conditions. The preservation retention level for CCA-C in the southern yellow pine was between 0.29 pcf to 4.0 pcf (4.6-64.0 kg/m³) when measured all over the wood. Overall, the preservation retention level, however, was 2.5 pcf (40.7 kg/m³). The analysis of the metal ions in the leachates, expressed as the oxide ratio yielded: 48.8:36:15.4

 $(CrO_3:As_2O_5:CuO)$ which was very close to the actual ratio of 47.5:34:18.5 which is the recommended ratio by AWPA Standards. The Agency has noted that the retention level of CCA-C under marine water, as recommended by AWPA, should be at least 2.5 pcf (40.7 kg/m³). However, AWPA recommends that retention level southern yellow pine wood in some areas of the USA like north of New Jersey and north of San Francisco can be about 1.5 pcf (24 kg/m³) (. Breslin and Adler-Ivanbrook, 1998).

Some laboratory and field studies have shown that the leaching process is aided by slow or drizzling rain than by heavy showers (Evans, F.G., 1987; and Cockroft and Laidlaw, 1978).

Most of the leaching from the treated wood in the field and laboratory tests take place in the first few days after the application of the wood preservative. Leaching rates depend on the size of the wood, type of wood, fixation process. I has been shown that the round posts show a higher rate of leaching than the saw dust of the lumber. Hardwood leach more than softwood. Pressure-treated red-pine leaches at a higher level than do the lodgepole, Douglas fir, and the red pine (Cooper, P.A., 1990).

No leaching study has addressed the issue of whether the metals leach as copper, or copper arsenate, or chromium arsenate or as complexes with inorganic or organic ligands or as derivative of wood-metal moieties or as water soluble wood extracts. If the metals get complexed with organic ligands and become more mobile in soils and these then will not be adsorbed to humic substances.

Mobility in water for these metal ions from the CCA depend on many factors which may give rise to a number of pathways: these metals can first diffuse through the soils as complexes, simple salts, or free ions, or percolate through the soils as insoluble substances and are then carried to the water systems. Porous soils help the wood preservative components to move through into water and this increases the mobility of the metals in water. As insoluble and having been deposited on the sediments, these metals can be of environmental concern (bioaccumulation) for the benthic organisms.

Migration into soils:

In an earlier work (DeGroot, et al., 1979) on CCA-A, CCA-B and ACA-treated southern pine wood stakes which were installed thirty years prior to the leaching study in acidic porch fine sandy soil in southern Mississippi, it was shown that the amount of leaching and mobility of the metal ions in the acidic soil is not significant. Background levels of As, Cr and Cu in this soil core depths were measured and are shown below:

Depth	As*	Cr*	Cu*
0-6 in.	1.3	3.8	4.0
6-12 in.	0.6	7.5	4.2
12-18 in.	1.0	6.9	6.6

* All values were reported in ppm and at 95% confidence interval

The preservation retention level for CCA-A was 0.70 pcf (10.6 kg/m 3) and for CCA-B it was 0.55 pcf ($8.8~kg/m^3$).

Table 1 summarizes the amounts of the metal ions that have leached into the soil from these stakes over a period of thirty years. The data includes the vertical transfer (downward migration from the stake) and vertical or lateral migration from the base of the stake of the metal ions.

Levels ⁴ of A	Levels ⁴ of As, Cr and Cu in soil core after vertical (downward) and lateral transfer from the stakes					
Soil core location ²	As CCA-I ¹	As CCA-II ¹	Cr CCA-I	Cr CCA-II	Cu CCA-I	Cu CCA-II
(beneath) 0-6	18.9 ³	108.1	25.1	22.9	56.6	48.3
6-12	1.6	21.4	8.2	7.4	6.9	8.2
12-18	1.2	1.1	9.2	6.2	5.7	6.4
(lateral transfer) 0-0	73.2	183.2	45.9	24.2	75.8	47.9
0-3	5.6	117.7	9.4	8.2	11.8	15.3

TABLE 1

Levels ⁴ of As, Cr and Cu in soil core after vertical (downward) and lateral transfer from the stakes						
6	1.3	7.0	4.7	6.4	5.6	4.9
9	1.5	4.9	6.2	5.3	12.3	7.2

Notes:

- 1. CCA-A and CCA-B in the present terminology
- 2. Distance reported in inches
- 3. All values in ppm
- 4. At 95% confidence interval.

The above data indicated that in acidic soil the leaching and migration of metal ions was not very high either beneath (downward migration) the soil or by lateral transfer (ground level migration) of the metal ions from the stakes.

In a Nigerian study, on soil and vegetable contamination in and around a CCA wood treatment factory, very high levels of the metal ions were detected and these levels progressively decline significantly as one moves away from the treatment and storage sites. High levels of the metal ions were also detected in the vegetables and crops grown within the premises of the factory. The concentrations of the metal ions were measured in the top 4 cm of soil at and around the treatment/storage facility. *Table 2* summarizes the concentrations of the metal ions at various location in and outside the factory. The study did not provide the information of the type of soil at the factory premises and also which type of CCA (A, B or C type) was used by the wood treatment factory.

Measure	Measured metal ion concentrations in top 4 cm soil in a wood treatment factory & background level concentrations (in µg/g, dry weight)					
Sampling Site	As(conc. range)	As (mean)	Cr(conc. range)	Cr(mean)	Cu(conc. range)	Cu(mean)
1	3456-7148	5312	2154-5810	3996	3817-7216	5424
2	956-4678	2552	868-3740	2046	1618-5478	3460
3	1092-3508	2211	788-3158	2005	2031-5180	3710
4	238-921	597	197-764	498	407-1062	763
5	8.4-21	16.1	38-78.6	59.3	67.4-103	82.9
6	0.1-40	6	5-1500	70	2-250	30

Table 2

Notes:	Sampling site # 1:	soil samples from the preparation and mixing sites in the
	factory.	
	Sampling site #2:	soil samples from the areas in the factory where freshly
	treated wooden poles	are stacked.
	Sampling site# 3:	soil samples from the areas where sludge is deposited
	inside the factory.	
	Sampling site#4:	soil samples from 12 randomly selected sites inside the
	factory.	
	Sampling site 5:	soil samples from 1 km distance from the factory site.
	Sampling site 6:	Background concentrations as reported in literature.
(Bowen, H.C.	. 1979)	

In a recent study, 85 samples of contaminated soil were obtained from under and around seven decks which were CCA pressure treated and the ages of these decks were from 4 years to 15 years. These soil samples were composites of the upper 5 cm soil layers and the soil type was sandy loam. The extraction of the metal ion from the soil samples was carried out by digesting into conc. nitric acid under a pressure of 120 psi in a microwave oven and then diluted with deionized water. The concentration of the metal ions were determined by using ICP-AES (inductively coupled plasma atomic emission spectrometry). In addition, arsenic also determined with graphite furnace atomic absorption spectrometer (GFAAS). The average amounts (in mg/kg) were: 75 for Cu, 43 for Cr and 76 for As. These amounts indicate the leaching of the CCA components into the soil is high. This study also showed that the amounts of the metal ions increased in the soil with the age of a deck.

The same study also indicated that soil samples taken 15 cm from the deck perimeter showed the average amounts (mg/kg) of the metals to be: 67 for Cu, 46 for Cr and 32 for As which indicates that the soil contamination decreases a short distance away from the deck perimeter.

Table 3 summarizes the average amounts of these metal ions along with the amounts from control samples as well as EPA's statutory limits on these metal ions.

Average amounts of metal ions (mg/kg) in the soil samples beneath decks and statutory limits				
Location/ Statutory Limits	Chromium (total)	Chromium(VI)	Arsenic	
Beneath decks	43	nd	76	
Control soils	20	nd	4	
EPA 503(1993)	1200	-	41	
State of CT (1996)	3900	100	10	

Table	3
1 4010	-

This study, did not point out which type of wood was used for the decks (southern pine or red pine etc.) and which type of CCA was used for pressure treatment of the lumber (Stilwell, D.E. and K.D. Gorny, 1997).

Biotic Transformations & Bioaccumulations:

An earlier study (Chou, et al., 1973) showed that between 3-4% of the metal ions were taken up by the Poria Monicola Fungal Hyphae on the pressure treated southern pine veneers with CCA which contained potassium dichromate, copper sulfate pentahydrate and arsenic pentoxide dihydrate in the ratio of 9:7:4.

Another comprehensive study (Irvine and Dahlgren 1976), the growth of number of marine and non-marine fungi and bacteria were affected when exposed to copper -chrome-arsenate put in an agar media. Table 4 summarizes the Minimum Inhibition Concentration (MIC) of the CCA components needed to affect the growth of the these organisms.

Table 4

Type of Fungi	$CuSO_4(mg/L)$	$Na_2Cr_2O_7 (mg/L)$	$As_2O_5(mg/L)$	CCA %
Marine:				
Corollospora cristata	137	482	244	0.2
Lulworthia sp.	274	482	488	0.1
Ceriosporopsis halima	546	1,928	976	0.2
Asteromyces cruciatus	546	2410	>1220	0.4
Cladosporium herbarum	>1,370	482	>1,220	0.2
Dendryphiella salina	1,096	964	1,220	0.4
Monodictys pelagica	274	482	244	0.1
Diplodia oraemaris	274	964	122	0.1
Zalerion maritimum	137	241	122	0.05
Cirrenalia macrocephala	68.5	482	244	0.05
Non-Marine:				
Chaetomium globosum (P117)	546	241	488	0.05
Chaetomium globosum(R24)	274	482	244	0.025
Leptosphaeria sp.	546	120.5	488	0.025
Melogramma sp.	1,096	241	61	0.0125
Botryosporium sp.	1,370	120.5	244	0.4
Phoma sp.	546	964	976	0.1
Fusarium sp.	546	482	976	0.025
Doratomyces sp.	137	120.5	488	0.025
Stachybotrys atra	274	120.5	488	0.025
Graphium sp <u>.</u>	274	60.3	244	0.0125

Minimum Inhibition Concentration Values for Marine & Non-Marine Fungi

Note: * means that growth of the fungi were stimulated at low concentrations.

For most of the microorganisms the M.I.C. values for chromium ranges from 120.5 to 964 mg/L except for *Ceriosporopsis halima* (1928 mg/L) and *Asteromyces cruciatus* (2410 mg/L). In case of arsenic tolerance, most of the organisms had M.I.C. values between 244 to 976 mg/L except for *Asteromyces cruciatus* (1220 mg/L), *Cladosporium herbarum* (1220 mg/L) and Dendryphiella salina (1220 mg/L). The majority of the organisms showed M.I.C. values between 274 to 546 mg/L vis-a-vis copper except for *Melogramma sp.* (1370 mg/L) and *Dendryphiella salina* (1370 mg/L). The range of tolerance for arsenic and chromium by these microorganisms were more than for copper.

It has been shown that in an estuary there are different pathways by which the CCA components leaching from the treated wood can impact the aquatic biota.. CCA components can dissolve in water forming aquated cations. These species can then be taken up by biota. Epibiotic organisms. Fouling organisms that live directly on the wood have the highest uptake of the contaminants. These metallic contaminants can be absorbed by sediments near the wood (e.g. docks). These can then are taken up by the benthic organisms. These could be biomagnified through the food chain. The uptake (bioaccumulation) of these metallic contaminants depend on the concentration of the metallic species which in turn depend on the amount of water flow in an estuary, amount and age of the CCA treated wood. Green algae *Ulla lactuca and Enteromorpha intestinalis*, collected from the CCA-treated bulkheads in Southhampton, NY showed a higher degree of bioaccumulation for all three metal ions whereas the species collected from the nearby rocks showed a lower degree of bioaccumulation. *Enteromorpha*, for example, collected from the dock showed a bioaccumulation of 55 μ g/g Cu, 6 μ g/g of Cr and 4.7 μ g/g of As; however, the same microogranism collected from the nearby rocks showed a bioaccumulation level of 14 μ g/g for Cu, 2.5 μ g/g of Cr and 1 μ g/g of As. (Weis and Weis, 1992a).

In another study, (Weis, et al., 1993a) it was shown that if the organisms are tested for bioacuumulation in a body water where the water flow rates are different, the contaminants are bioaacuumulated at different levels. For example, algae Cermium sp., oysters Crassostrea virginica, barnacles balanus eburneus, and mussles Brachydontis recurvis were collected from a CCA-treated dock in an open water environment and from bulkheads in a poorly flushes residential canal adjoining Santa Rosa Sound, Pensicola Beach, Florida as well as from the nearby rocks in open water. Open-water docks organisms had a significantly higher level of bioaccumulation. For example *Ceramium*, living in open water area, showed a copper concentration of $3 \mu g/g$, an increase of $2 \mu g/g$ from non exposed organisms, arsenic showed an increase from $3 \mu g/g$ (non-exposed organism) to 5.5 $\mu g/g$. The same study showed that organisms (e.g. barnacles) that grew on rocks nearby the dock, had a $1 \mu g/g$ of copper bioaccumulation, those on the open water dock had 3 µg/g of copper, those in the canal (poorly flushed areas) has about 10 μ g/g of Cu and those that grew on the new wood docks (1 year old) inside the canal had a bioaccumulation of 80 µg/g Cu. In a related study (Weis, et al., 1993 b), it was shown that the tissues of oysters living inside a canal showed the concentration of Cu to be $150 \,\mu g/g$, an increase of 12-fold over the controls. The same oysters did not show an increased bioaccumulation for the other two metals. Other studies have also shown the same trend, oysters have a tendency of bioacumulating copper more than other metals (Schuster & Pringle, 1969).

A study on the sediments adjacent to and close by distances to CCA-treated bulkheads, on analyses showed a higher level of the three metal ions. Sediments adjacent to bullheads in New York and New Jersey estuaries consist of fine-grained particles (silt and clay often less than one percent). These sediments in these locations showed a very high concentration of the metals between 100-2000 μ g/g. Sediments which were ten meters away from the bulkheads, consisted of higher percentages of silt and clay (up to 60%) showed a lower concentrations of the metals. Sediments in poorly flushed areas showed a higher concentrations of the metals then the ones which are open water areas with regular water flows. Again the sediments around the newly built bulkheads showed the highest concentrations of the metals.

These sediments can possibly become a pathway of exposure to the benthic biota as shown in another study. Fiddler crabs *U. Pugilator* showed that the metal concentrations were double in the organisms than on the sediments (Weis and Weis, 1992 a).

In 1979, The Agency published a document Water-Related Environmental Fate of 129 Priority Pollutants (EPA-440/4-79-029a) which summarized the open literature searches the fate of these Priority Pollutants in aqueous medium. The fate and transport of arsenic, chromium and copper are discussed in the following paragraphs:

Arsenic:

Table 5 summarizes the bioconcentration factors for arsenic in various taxa:

Г					
Taxon	Bioconc. Factor	Reference			
Freshwater Plants	333	Chapman, et al., 1968			
	6000	Reay, 1973			
FreshWater fish	333	Chapman, et al., 1968			
Marine Plants	333	Chapman, et al., 1968			
Marine Invertebrates	333	Chapman, et al., 1968			
Marine Fish	333	Chapman, et al., 1968			

Note that the bioconcentration factors were reported as the ratio of the concentration of the element in the aquatic organism (in ppm, dry weight) to the concentration of the element in water (in ppm).

The data from the table indicate that arsenic does show a tendency to accumulate through water and biomagnification (food). The bioconcentration factors are not large, however, The EPA document also reported other bioaccumulation studies:

A. Isensee et al. (1973) conducted a microcosm study on the bioaccumulation of cacodylic acid derived arsenical and dimethyl arsine for 32 days. This simulated ecosystem contained algae, snails, daphnia and fish. Fish had minimum bioaccumulation in this selected group. Snails were next in line in bioaccumulating arsenic while the algae and daphnia showed the highest tendency to bioaccumulate arsenic. At the end of the study period (32 days), only 30% of arsenic was incorporated by the biota.

B. Green sunfish *Lepomis cyanellus* was exposed to various concentrations of sodium arsenate and the data indicated that the bioaccumulation of arsenic (presumbaly as As^{+5}) was a function of the sodium arsenate concentrations. The uptake of arsenic by liver, gut and muscle was also found to depend on the temperature.

C. A sixteen week exposure with sodium arsenate to young and adult bluegills *Leomis marchochirus* showed that the concentration of arsenic in the adult bluegill was the same as in the pond but the arsenic levels in the young bluegills were twice as high as in the adults.

D. A fish in a pond which was accidently contaminated with arsenical was analyzed and arsenic level was 2.5 mg As/L; fish accumulated 6.6 μ g As/g in muscle, one fifth of what is in water. Lake Michigan plankton and benthos showed a concentration factor of 6.0 and 6.6 μ g/As/g respectively. Analysis of biota in Lake Superior showed the plankton contained 30% less As than the Lake Michcigan Plankton.

The same EPA document reported bioaccumulation and bioconcentration information about chromium which is summarized in the following:

Chromium:

Table 6Bioconcentration Factors for Chromium

Taxon	Bioconcentration Factor	Reference
Freshwater fish	200	Chapman et al., 1968
Freshwater invertebra	ates 2,000	Chapman et al., 1968
Fresh water plants	4,000	Chapman et al., 1968
Marine fish	400	Chapman et al., 1968
Marine invertebrates	200	Chapaman et al., 1968
Marine plants	2,000	Chapman et al., 1968
Benthic algae	1,600	NAS*, 1974
Phytoplankton	2,300	NAS, 1974
Zooplankton	1,900	NAS, 1974
Mollusc viscera	440	NAS, 1974
Crustacean muscle	100	NAS, 1974
Fish muscle	70	NAS, 1974

NAS * means National Academy of Sciences.

An early study determined the chromium partitioning between water, sediment and chironomid larvae (a benthic invertebrate). Highest concentration of chromium was found in the sediment (7.64 μ g/g), followed by bioaccumulation of 2.96 μ g/g of Cr in the chironomid and 1.1 μ g/l in water (Namminga and Wilhm, 1977).

Another study showed a biomagnification of chromium when benthic worm (tubificid) when fed with chromium rich bacteria bioaccumulated (extracted) the metal from the bacteria (Patrick and Loutit, 1976).

Radiolabed Cr(III) was found to biomagnify through the food chain in an estuarine. The food chain consisted of phytoplankton, brine shrimp, post-larval fish and mummichog. The concentration of the radiolabeled chromium declined in the food chain through trophic levels (Baptist and Lewis, 1969).

Another study was conducted on the bioaccumulation of metals on the benthic (sediments and microorganisms) impacted by the CCA treated wood bullheads in a large Atlantic Coast Estuaries. Accumulation of metals around the bulkheads and bioaccumulation in microorganisms were investigated at distance zero to 1, 3 and 10 meters from the bulkheads. Five sites, with different bulkhead ages, were chosen:

A. Middle Pond in Southhampton, New York. The bulkhead was one year old. Additionally, two reference sites, one an unbulkheaded site in the same pond and the second a bulkhead made up of aluminum in the nearby estuary at Bullhead bay in Southampton, N.Y.

B. Old Fort Pond, also in Southampton. This was an eight year-old bulkhead in a poorly flushed location. A transect from the opposite shoreline was chosen as a reference.

C. Bulkheads along the Debardaue Canal, at the North Inlet Research Reserve in South Carolina. These were 2 year-old bulkheads with intertidal situation and the Canal itself was very well-flushed. An aluminum bulkhead in the same vicinity was chosen as a reference site.

D. A two-year old bulkhead in Osborn Cove off the Patuexent River in the Chesapeake Bay, Maryland. This was a poorly flushed location and the natural shoreline was used as a reference site, 30 m across the cove.

E. A pair of adjacent bullheads at the Drum Point in Solomon, Maryland. One bulkhead was a CCA-treated (approximately 6-8 year old) and the second was made up of concrete.

Generally, the impact of CCA-treated wood in an estuary depended on the surface area exposed to leaching, the leaching rate itself, metal speciation (type of metal species present under the conditions), rate of uptake (bioaccumulation) by epibiota,, tidal activity (well or poorly-flushed) locations, adsorption by sediment (a function of particle size of the soil), trophic transfer to grazers and predators.

In the following the data summary is presented:

Middle Pond:

Sediments around the bulkhead were variable and made up of coarse and fine mixture. Fine sediment fraction was more at 10 meter from the bulkhead and find fractions generally retained the metals more tightly than the coarse fraction of the sediment. However, the percent of the contaminants (the metals from the leaching from the wood) was highest at distance 0 meter from the bulkhead.

The concentration (bioaccumulation) was highest in the microrgansims at distance 0 meter from the bulkhead and progressively decreased to 1 to 3 to 10 meters away form the bulkhead. Comparatively, the metal contamination (bioaccumulation) of mcirorganisms at the reference site was much lower than at the experimental site. The organisms present at the experimental and references sites were: Marenzelleria virdis, Leitoscoloplos sp., Neanthes spp., Clymenella torquada, a Capetillid and the snail Ilyanassa obseleta. Of these Neanthes was the most predominant organism.

Old Fort Pond:

Chromium levels in the fine fractions of the sediment remained the same irrespective of the distance from the bulkhead, while the copper concentration was twice as high at zero distance from the bulkhead than at a distance away from it. Arsenic levels progressively declined moving away from the bulkhead. The change in the percent of total carbon in the sediment did not show any change in the accumulation numbers.

The dominant organisms at this site (both actual and reference) were: *Marenzelleria* virdis, *Leitoscoloplos sp.*, *Neanthes spp.*, *Clymenella torquada*, a *Capitellid* and *Hypaniola* gray as well as clams *Melaena lateralis*, the bubble snail *Haminoea* and *Cyathura polita*. The data analysis for the bioaccumulation in these species was difficult as it did not show any trend in the concentration levels of metals at various distances from the bulkhead.

North Inlet, Debardeau Canal:

The highest concentrations of the metals was at the site at zero meter distance from the bulkhead. Since this site consisted of the wood bulkhead and the reference site was aluminum, the analysis showed that there were no organisms at the wood bulkhead at distance of zero and one meter from the wood bulkhead while at 3 meter distance *Notomastus* was the main organism and other organisms were also present like *Neanthes*, a nemertean *Lineus socialis* At the Al bulkhead also the dominant organism was *Notomastus* and besides there were *Clymenella*, *Lineus*, *Neanthes*, *Melaena lateralis* and *Mercenaria*.

Osborne Cove:

The copper accumulations did not vary much from zero meter distance to the maximum (10 meters). However, arsenic did show some variations with distance.

The type of organisms existing at the zero meter actual site were: *Lanonereis culveri*, *Hargeria rapax*, *Marenzerellia virdis*, and *Hobsonia florida*. Reference sight consisted of, in addition to the ones mentioned, the follwoing: *Hypereteone heteropoda*, *Leitoscoloplos fragilis*, *Streblospio benedecti*, *Macoma balthica*, *M. Mitchelli*, *Lepidodactylus dyticus*, *Balanus improvsus* and *Cyathura polita*.

Drum Point

Both copper and chromium showed a declining accumulation moving away from the bulkhead.

The organisms present on this site were predominantly: *Leitoscoloplos fragilis*, *marenzelleria virdus*, *Leptocheirus plumulosus*, *Gemma gemmma*. No significant difference bioacummulation differences were observed at various locations on this site.

In summary, bioaccumulation in Middle Pond organisms were highest in the organism living closest to the wooden bulkheads. Bioaccumulation in tissues declined dramatically at a 3 meter distance from the bulkhead. In some cases, it rose again by 10 meters but primarily due to the increase in the fine sediment fraction which has a tendency to adsorb and retain the metals.

It appears at all bulkhead sites metals are retained (accumulated) by fine-grained sediments and a reduction ensues in the nearby biota. Unbulkheaded and aluminum bulkheads do not show this tendency. The biota at 10 meter out from the bulkhead at Middle Pond showed reduction because of percent increase of fine-grained sediments while for Old Fort Pond the same phenomenon was observed at 3 and 10 meters away from the bulkheads because of the same reason. At all sites, the impact on biota was highest between zero and 1 meter distance from the bulkheads. And in all cases, copper was observed to be responsible for the reduction in the biota around the bulkheads (Weis et al., 1998)

A recent study on bioaccumulation of CCA components in Blue Mussels *Mytilus Edulis* was conducted and the laboratory and field expsoure data were collected over a period of one year. The CCA-treated wood was of the Southern Yellow Pine type. CCA-C treated wood boards (4.4 cm x 22.8 cm x 3 m) were pressure-treated at a treatment retention of 2.5 pcf (40 kg/m³). Two sets of blue mussels, one 4-5 cm long and the other 3.5 to 4 cm long were collected from the east jetty at the Flax Pond inlet, Old field, New York. the laboratory sea tables were arrnged in such a way that one set of blue mussles were upstream to water flow and the other downstream to water flow. The mussles were sampled form each sea table at time 0, one week and one month. Similar arrangements, samples of blue mussles, submerges in water and were placed adjacent to the wood. After the experiment was terminated, freeze-dried mussles were digested in nitric/perchloric acid mixture and samples collected were anlayzed for copper, chromium and arsenic by flame (Cu) and graphite furnace (Cr and As) atomic absorption spectrophotometry. The laboratory and field exposure studies showed that no significant difference in the average dry tissue weight and length between CCA-C treated and control treatments.

Table 8 summarizes the concentrations of Cu, Cr and As in the tissues of blue mussel. Concentration of these metals obtained by Mussel Watch, organized by national Status & Trends sampling stations in Long Island Sound are also included in the table for comparison purposes.

Contaminant	Lab. Exposure	Field Exposure	Mussel Watch ²
Cu	7.88	8.54	8.91
Cr	0.86	0.72	1.61
As	8.82	7.14	6.24

TABLE 8	1

Notes: 1. All values in $\mu g/g$

2. Data from 1990 reports

Note that the measured metal contents of mussel tissues in both laboratory and field exposure studies are at or lower than the average values obtained from the national or regional monitoring studies. The species of these elements affect their bioaccumulation in mussel tissues.

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