Leaching of CCA-PEG and CuNap Wood Preservatives From Pressure Treated Utility Poles, and its Associated Toxicity to the Zooplankton, *Daphnia magna.*

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Abstract

The effect of simulated acid rain (pH 4.2) on leaching preservative components from pressure treated utility poles and the associated toxicity of leachates to *Daphnia magna* was studied. Leaching loss of preservative components from chromated-copper-arsenic and copper naphthenate pressure treated utility poles appears relatively constant between preservatives, poles and leaching events. Total copper loss over 10 leaching events was approximately 7.5 and 4.7 g Cu/m^3 (resp), based on total pole volume. Static acute toxicity tests indicate LC50 values for CCA and CuNap at 2.14% and 9.50% of original leachate copper concentrations. These values are equivalent to 0.036 and 0.044 mg Cu/L (resp). Chromium and arsenic concentrations in CCA leachate were deemed sufficiently low as to have little or no effect on LC50 determinations.

Literature Review

Neither chromated-copper-arsenic (CCA) nor copper naphthenate (CuNap) are new additions to the field of wood preservation, both pesticides have been in commercial use in this country for over 50 years. Both preservatives display effective and long lasting service performance, however CCA has received much more attention and wider use in utility pole treatment. Copper naphthenate, on the other hand has traditionally been employed as a fabric protection agent.

Chromated Copper Arsenate

CCA was first patented for use in 1933 (Arsenault, 1975). At that time CCA was mainly used for treatment of dimension lumber. The Canadian Institute of Treated Wood (CITW, 1989), indicated that CCA products have been used for treatment of utility poles for over 40 years. Commercial literature developed over years of research experience and performance trials, provide detailed information on the longevity, permanence and effectiveness of the product. Many of these studies have shown that CCA pressure treatment tends to harden the wood, especially in red pine, resulting in increased checking problems and decreased climbability of the poles. In an attempt to reduce these problems, the addition of 4% polyethylene glycol (PEG) to the treating solution is becoming more common.

Each element in the preservative plays an important role in imparting its overall effectiveness. Copper is an effective fungicide and inorganic pentavalent arsenic is toxic to wood destroying insects (CITW, 1989). Because CCA is an acidic system the chromium serves to prevent corrosion in the treating plant (Preston, 1988), and also plays an important role in the fixation of both copper and arsenic in wood (CITW, 1989). Furthermore, the copper component of the preservative deters the formation of moss on the treated wood surface (CITW, 1989). Generally speaking, copper is the primary fungicide, while arsenic is present for the control of copper tolerant fungi (Preston, 1989). Both arsenic and chromium are heavy metal poisons. Both have chronic and acute human health risks associated with them. Copper, on the other hand, is much less toxic and generally not a human health concern (Morgan, 1988). Recently the leachability of CCA components from treated wood and the consequential release of Cu, Cr, and As into the environment have become the topic of much discussion. It is clear that a wide variety of factors associated with the wood being treated, preservative used, and environmental factors will all affect the leaching tendencies of treated wood in service. Our previous studies have indicated that pH of the leach water can have a dramatic effect on rate and amount of CCA components leached from treated wood. More recent, unpublished studies have shown that the source of acidity in the leaching water can have an even more profound effect on leachability of CCA components.

There are many conflicting reports on the leachability of CCA and the ratio in which components are removed. This results largely from widely varying leaching parameters. Many studies report using extremely small specimens, shavings or even sawdust to maximize leaching and accelerate results (Arsenault, 1975; Irvine and Dahlgren, 1976), other reports (Evans, 1978) conclude that such results cannot be correlated with leaching from CCA impregnated wood in service. To more closely relate laboratory results to expected field performance one must use specimens which have similar surface area/volume ratios. It is widely known that the rate of leaching decreases with increases in specimen size and when the ratio of end grain exposed per unit surface area leached is reduced (Spodaryk, 1977; Arsenault, 1975).

In terms of amounts and ratios of CCA components leached, Webb and Gjovik (1988), report that loss of arsenic tends to fall behind that of copper and chromium, and is related to chromium concentrations and the preservative formulation. Leaching of copper is said to be more pronounced than chromium due to its increased mobility in wood, (Peek and Willeitner, 1988).

Copper Naphthenate

Copper naphthenate has been an accepted wood preservative treatment in North America for over 50 years. It has been employed mainly in nonpressure treatment of wood and fabric, and has not traditionally received much regard in the utility pole industry. In the past limited supplies and higher costs of naphthenic acid made it impractical for copper naphthenate to compete with the major preservatives, namely pentachlorophenol, creosote and the arsenical.

More recently copper naphthenate has gained renewed interest in the wood treating industry due to government restrictions and, more importantly, environmental considerations of the use and disposal of the major wood preservatives. Copper naphthenate is described as a broad spectrum, ground contact wood preservative, effective at concentrations 1/8th of that required for equal performance with pentachlorophenol. Of the available alternatives, copper naphthenate (CuNap), appears to have provided the most complete performance data, although the published literature available is limited.

Copper naphthenate is well known for its fungicidal activity of which both the copper and naphthenic acids play important roles in its overall effectiveness. It has been used as a general purpose fungicide for wood and fibre products for close to a century. CuNap has been shown to provide long term protection against fungus, mould, mildew, and marine parasites.

Copper naphthenate has a relatively low acute toxicity and is not considered to be carcinogenic. It is not listed as a hazardous waste or a restricted-use pesticide, and treated wood is not specifically regulated for handling and disposal. CuNap treated wood has not been shown harmful to humans, livestock, plants or bees. However, the Dangerous Properties of Industrial Materials (7th ed., 1984) describes copper naphthenate as harmful to aquatic life in very low concentrations and it is listed as extremely phytotoxic by The Pesticide Manual (6th ed., 1979).

Minich and Goll (1942), indicate the water solubility of solid copper naphthenate to be approximately 1.5 mg/L (1.5 ppm) solution. It is well known that many acids react with copper naphthenate to produce copper salts and free naphthenic acids. Studies by Marsh et al. (1944), indicate that fabric treated with copper naphthenate was leached free of all copper with a 0.00316 N nitric acid bath. This presents the obvious question of rainfall acidity on leaching tendencies of CuNap treated wood.

Aquatic Toxicity of CCA and CuNap Preservative Components

Symptoms of copper toxicity have been described by many, however the exact mode of action is unknown. Copper is essential to the function of enzymes such as peroxidase and cytochrome oxidises, and thus may disrupt processes involving these enzymes when levels become elevated above essential concentrations (Goyer, 1986; Rand and Petrocelli, 1985). Toxicity of copper to aquatic organisms is generally caused by the Cu^{2+} ion and some copper hydroxide species (Hardy et al., 1988).

Acute toxicity of chromium, while having been observed in several aquatic species, has not been completely understood. Both Cr^{6+} and Cr^{3+} cause toxic effects however Cr^{6+} is somewhat more toxic due to its ability to penetrate biological membranes (Goyer, 1986; NRCC, 1976). High levels of chromium have been found in RNA proteins, but its function is unknown. Chronic effects of Cr^{6+} in man include respiratory cancer (Goyer, 1986), however mutagenic effects have not been reported in aquatic organisms.

Arsenic has been well characterized in its toxic actions, with the primary toxic effects occurring through activity on metabolic systems (Hall, 1989). Arsenic has been noted to uncouple oxidative phosphorylation through the alteration of enzymes such as ATPase. Arsenic has also been shown to increase mitochondrial membrane permeability. Both As^{3+} and As^{5+} show similar toxic effects (NRCC, 1978).

In general, all metal components contained in CCA and CuNap have been shown to be acutely toxic to aquatic organisms, with 48 hr LC50 values for *Daphnia* spp. reported to be as low as 0.023-0.041 mg/L and 0.01-2.5 mg/L for copper and chromium respectively (Blaise et al, 1986; Muller, 1980). Arsenic, on the other hand, is comparatively much less toxic, having a 48 hr LC50 value of 7.4 mg/L (Biesinger and Christensen, 1972).

Preliminary bioassay experiments have shown that CCA leachate can potentially be much more toxic than any single constituent metal. These studies indicated that interactive toxicity can occur with metal components of CCA and dictated further work to characterize the toxic effects of all three metal components as found in actual leachate from CCA-PEG type C treated utility poles.

The intention of this study was two fold; first, to quantitatively determine the effects of simulated acid rain on the leachability of CCA-PEG and copper naphthenate treated utility poles and secondly to establish the toxicity of the leachate to the aquatic organism *Daphnia magna*.

2 Methods and Materials

One of the most important requirements of a wood preservative is that it remain in the wood matrix under service conditions. It is widely accepted the only sure way to determine the permanence of a wood preservative is to conduct actual service tests. These tests however usually take from ten to forty years depending on a number of factors. Greaves (1933), nicely summed up the value of laboratory efficacy testing of wood preservatives in stating that it is desirable to make use of laboratory tests that can be accomplished in a short period of time and that will enable some opinion to be formed on the permanence of the preservative under study.

2.1 *CCA-PEG and CuNap Leaching Study*

2.1.1 Utility Poles

Copper naphthenate and CCA-PEG treated utility poles were used in this study to determine the leachability of copper containing wood preservatives under simulated acid rain conditions.

Six CCA-PEG, Type C , Red Pine (Pinus *resinosa*) and six CuNap, Lodgepole Pine (Pinus *contorta*), pressure treated utility poles were provided by Ontario Hydro for testing. Forty-five cm pole sections were removed from each pole at approximately the same location to provide comparatively uniform specimens for study.

It is recognized that wood poles vary greatly between species, even between or within individual poles of the same species. Thus differences in retention capacity and leaching tendencies of wood preservatives from the above mentioned poles are both expected and deemed inherent between poles.

Treatment records of the CuNap and CCA treated poles used in this study indicated their respective mean retention levels to be approximately 2.14 kg/m^3 Cu and 8.75 kg/m^3 CCA oxides (based on sapwood volume).

2.1.2 Leaching Apparatus

The leaching apparatus as shown in Figure 1, delivered a simulated acid rain solution (SAR), at approximately 150 ml/min, to an annular ring encircling the top circumference of each pole section. Identical SAR delivery rates between pole sections was provided through the use of a positive displacement multichannel peristaltic pump. Observations of poles in service, have shown SAR solution movement down the pole surfaces to be very similar to that of an actual rainfall event. A sealed, stainless steel skirting prevented unrealistic leaching of pole section bases.

The entire apparatus was covered with a polyethylene plastic enclosure during leaching events to prevent excessive evaporation of the leaching solution. Upon completion of each leaching cycle, the enclosure was removed to allow surface drying, enabling some wicking action on the preservative components.

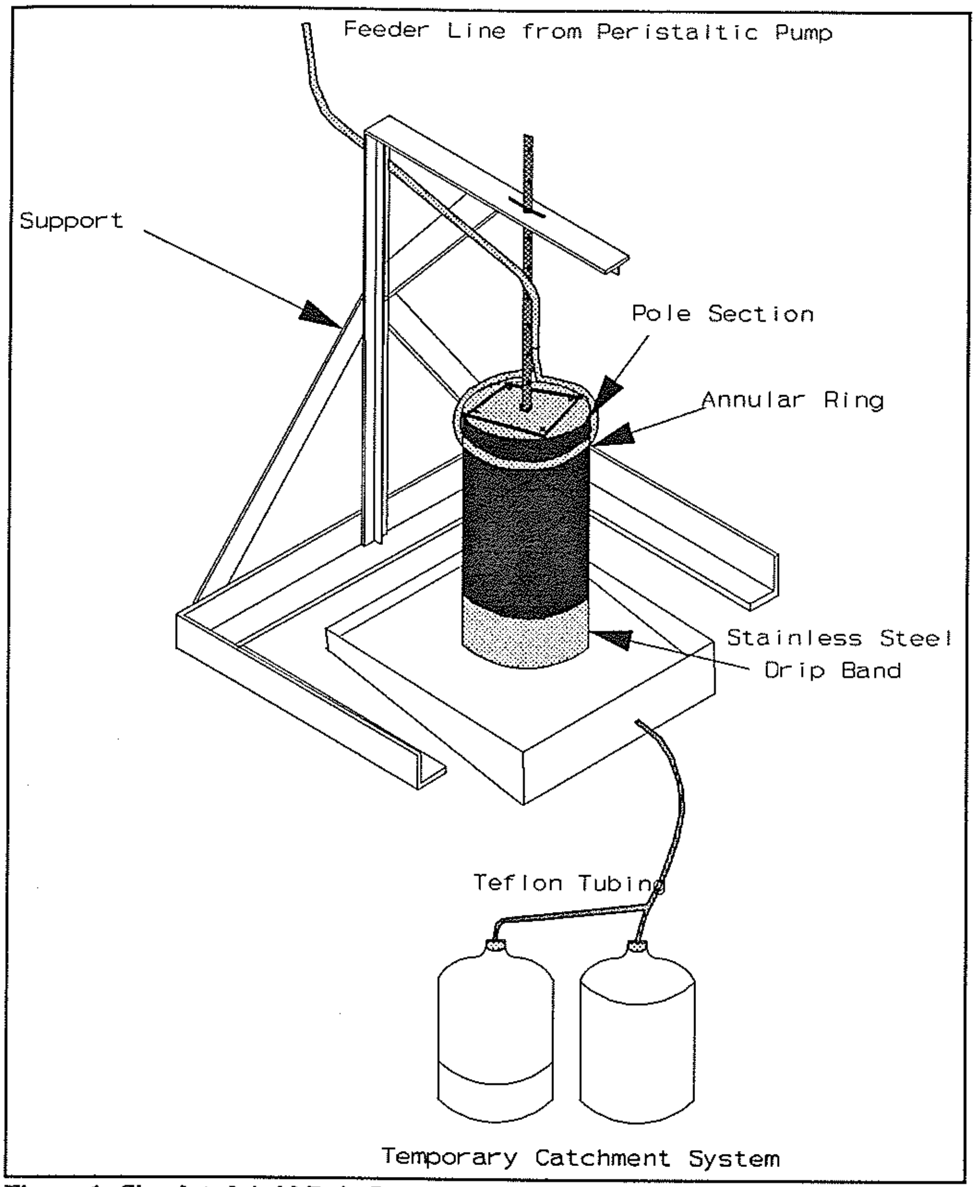

Figure 1 Simulated Acid Rain Leaching Apparatus

2.1.3 Simulated Acid Rain Solutions.

Simulated acid rain solutions containing mineral salts, and inorganic acids, as described by Kuja et al. (1986), were adapted for use in this study. Sulfuric and nitric acids were added to the stock solution to give a SO_4:NO_3 weight ratio of 2:1 and a pH of 4.2 in the final solution mixture.

Table 1 Simulated Acid Rain (SAR) Solutions

Chemical	Concentration (g/L)
Potassium Chloride (KCl)	0.035
Calcium Sulfate ($CaSO_4$)	1.239
Ammonium Sulfate ($(NH_4)_2SO_4$)	0.912
Ammonium Nitrate (NH_4NO_3)	1.304
Magnesium Sulfate ($MgSO_4.7H_2O$)	0.715
Sodium Sulfate (Na_2SO_4)	0.226
Potassium Bisulfate ($KHSO_4$)	0.053
Potassium Sulfate (K_2SO_4)	0.027
Sulfuric Acid	0.92 ml/L
Nitric Acid	0.81 ml/L

2.1.4 Leachate Analysis

Leachate samples collected from CCA treated poles were generally free of particulate matter and did not require cleanup prior to analysis. Initial leaching studies with copper naphthenate, however, displayed some leaching of petroleum compounds, and tests were conducted to establish levels of organic copper. Levels of organic copper proved to be inconsequential,and thus all further leachate samples were acidified with 0.02 ml of 10% HCl prior to analysis to ensure complete dissociation of copper naphthenate in solution.

Upon conclusion of the CuNap leaching study all catchment system glassware was rinsed with 10% HCl, followed by dichloromethane to remove any copper which may have been tied up in oily organic residues found. Results of analysis are shown in Table 2.

Analysis of leachate solutions was performed using flame (acetylene/air) Atomic Absorption (AA) Spectroscopy. The instrument used was an Instrumentations Laboratory Model 251 (AA), using hollow cathode lamps and deuterium background correction where necessary (ie. As). The detection limits for this unit were found to be; 0.035 mg/L Cu, 0.073 mg/L Cr, and 0.603 mg/L As.

2.1.5 Leaching Parameters

Preliminary investigation showed that to properly wet a pole surface similar to that expected with a natural rainfall, the leaching apparatus would have to deliver approximately 150 ml/min. Duration and frequency of rainfall events were a function of pole section dimensions, expected angle of incident rainfall and total annual precipitation for Southern Ontario (833mm/yr). Assuming a rainfall angle of incidence of approximately 70° to any pole surface, we derived the following:

1) Portion of annual rainfall expected to contact pole surface - Incident Rainfall (IR)
$IR = \tan 20^\circ \times 833.33$ mm
$IR = 30.0$ mm

2) Pole dimensions - Mean Pole Diameter (MPD) = 21.2 cm
- Mean Pole Length (MPL) = 42.0 cm

Total rainfall expected to contact one side of pole = (MPD) x (MPL) x IR = 26.98 L

To provide the study with a worst case scenario, the total amount of SAR to be used is doubled, simulating wetting of both sides of the pole. Therefore the total amount of simulated acid rain applied per pole section was approximately 54-56 L, over ten leaching events of approximately 35 minutes in duration.

2.2 *Daphnia magna Exposure Studies*

During the course of this study two series of experiments were performed. In the first, acute toxicity tests determining the 48hr LC50 value for CCA-PEG leachate were performed. The simulated acid rain solution used in pole leaching studies proved toxic to *Daphnia magna* due to its low pH. Thus, in evaluating the toxicity of CCA leachate, Cu, Cr, and As reagent grade chemicals were mixed with well water in exact ratio as that of the leachate. In the second bioassay series, an actual copper naphthenate leachate was used in toxicity testing. In order to quantify the overall effects of copper, naphthenic acids and petroleum carrier, in the ratios normally found in the leachate, several well water leaching events were conducted to collect leachate for testing. The water used in CuNap leaching was the same as the dilution water used in *Daphnia* bioassays. It has a typical pH of 7.9, total hardness of 374 mg/L, alkalinity of 223 mg/L ($CaCO_3$), and 7.1 mg/L dissolved oxygen.

2.2.1 Bioassay Test Solutions

CCA - metal solutions were prepared by dissolving reagent grade potassium dichromate, cuprous sulphate and sodium arsenate in glass distilled water to give 1000 mg/L stock solutions of Cu^{2+}, Cr^{6+} and As^{5+}, the theoretical species found in CCA leachate. As previously stated, Cr^{6+} is much more toxic than Cr^{3+} and Warner (1990) found a significant amount of Cr^{6+} deposited on CCA pole surfaces. In addition Cr^{6+} is also found in runoff from treatment facilities, thus it was decided to utilize the Cr^{6+} in the acute toxicity tests. CCA component concentrations were verified by atomic absorption spectroscopy. Toxicant dilutions used for bioassays were prepared by adding appropriate volumes of stock solution to fresh, aerated well water.

Copper Naphthenate - As indicated above, serial dilutions of well water leachate were used to provide the desired concentration of CuNap leachate for *Daphnia* exposure studies.

2.2.2 *Daphnia magna* Static Acute Toxicity Tests - Bioassays

Static 48-hr acute toxicity tests were performed using standard testing procedures as outlined by Ontario Ministry of the Environment, (1987).

Bioassays with wood preservative leachate toxicants consisted of six toxicant concentrations and a well water control, each with 5 replicates. Each replicate was represented by 5 *Daphnia magna* neonates (<24hr old) in 80 ml of toxicant solution contained in a 100 ml glass beaker.

Adequate test concentration ranges are defined as a set of concentrations which cause at least two partial kills, with at least one kill on either side of the 50% mortality level (ASTM, 1988). Choosing good concentration ranges results in more reliable LC50 estimates.

Each bioassay was contained in a clear, loosely-covered plastic container to prevent contamination and reduce evaporation. Containers were then placed in an environmental chamber under the same conditions as the breeding colonies. Breeding colonies providing neonates for testing (young Daphnids), were placed in an environmental chamber at 20 ± 2°C, with a 16:8 light dark photoperiod. The bioassays were monitored throughout each test for the presence of floaters (*Daphnia* caught in the solution surface tension). The appearance of floaters in test solutions is a recognized indication of the onset of a toxic effect, however floaters in controls negate the validity of a test (ASTM, 1988).

Upon conclusion of each test, the number of dead animals in each beaker were counted and tabulated. Animals were considered dead if no movement of any kind was seen when individuals had been drawn into a small glass pipette and observed through the magnification of its optical curve for 20-30 seconds.

The LC50 estimates, probit line slope, and 95% confidence intervals for Daphnia bioassays were determined by probit analysis using statistical analysis software developed at Guelph University. All LC50 determinations were performed using maximum likelihood probit analysis.

3 Results and Discussion

3.1 *CCA and CuNap Simulated Acid Rain Leaching Studies*

3.1.1 CCA Leaching

The total accumulated loss of metal components from CCA-PEG poles during the ten day leaching period are displayed in Figures 2-4. CCA loss values were relatively constant among and within pole sections from one leaching event to another. The only exception to this case being pole #1, whose arsenic loss was much higher and thus provides the larger portion of error. In any case, copper was preferentially removed followed by arsenic and chromium, with approximately 7.50, 0.77, and 0.06 g/m^3 (total pole volume) respectively, being leached over the course of the study. Chromium and arsenic concentrations in the leachate, were sufficiently low as to require an 18x concentration of the sample to provide adequate levels for detection. These results would tend to agree with the literature, indicating that CCA components in pressure treated utility poles appear to be relatively leach resistant.

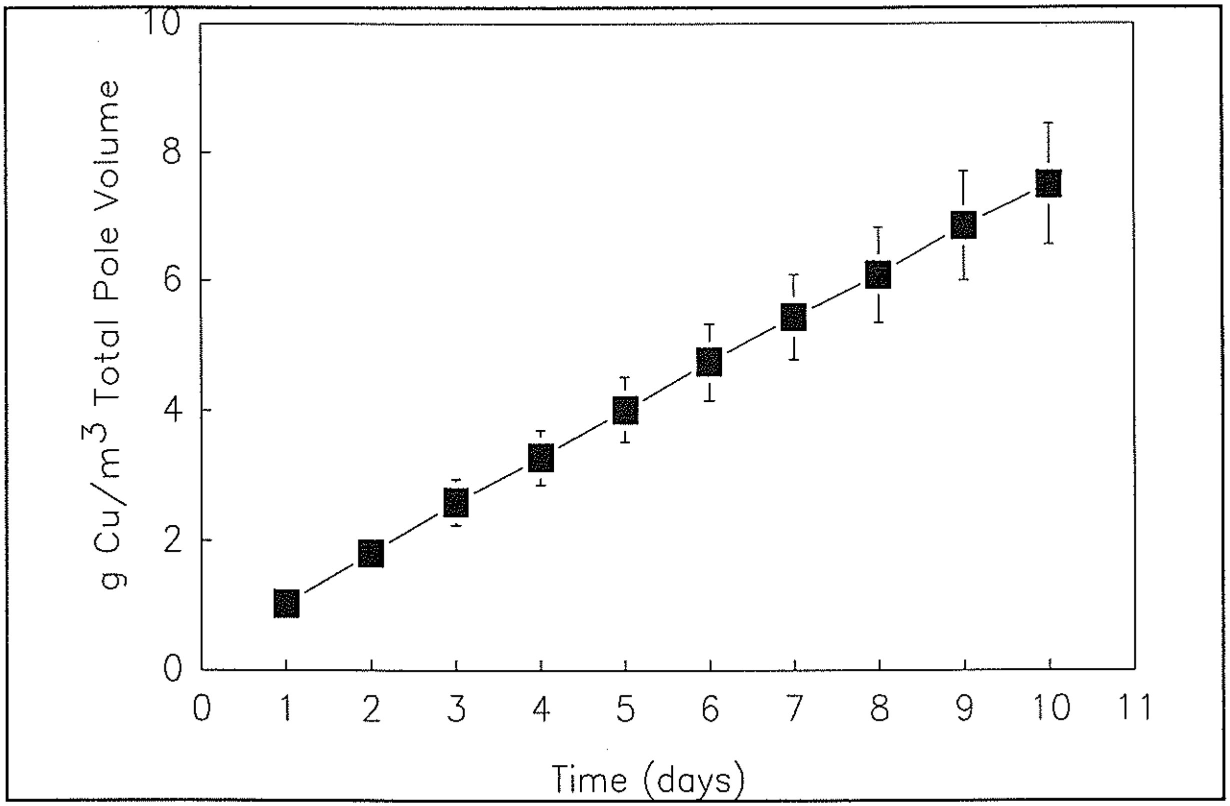

Figure 2 Effect of Simulated Acid Rain on Leaching of Cu From CCA-PEG Treated Utility Poles. Each Point Displays the Mean Value of 6 Poles and 95% Confidence Intervals.

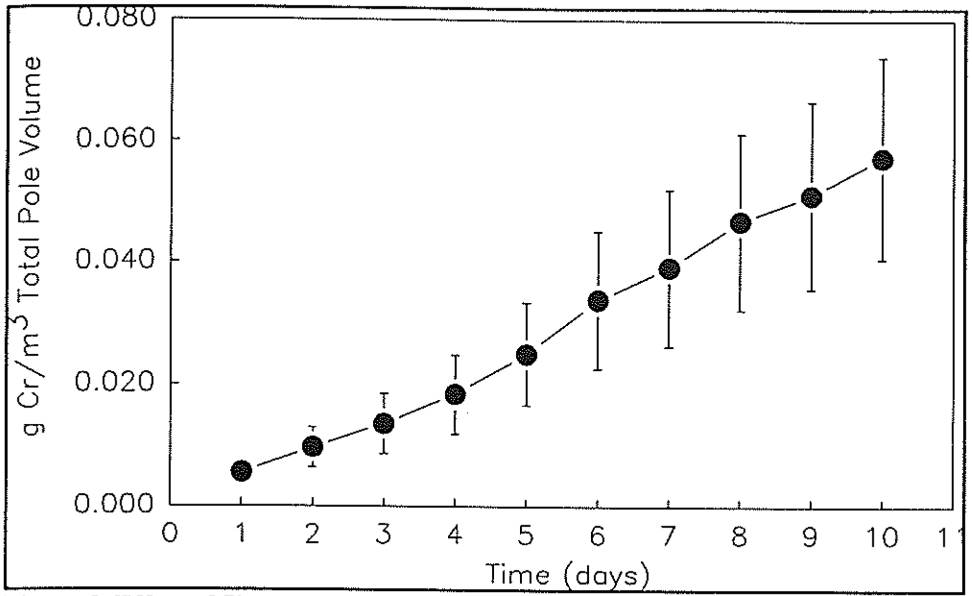

Figure 3 Effect of Simulated Acid Rain on Leaching of Cr From CCA-PEG Treated Utility Poles. Each Point Displays the Mean Value of 6 Poles and 95% Confidence Intervals.

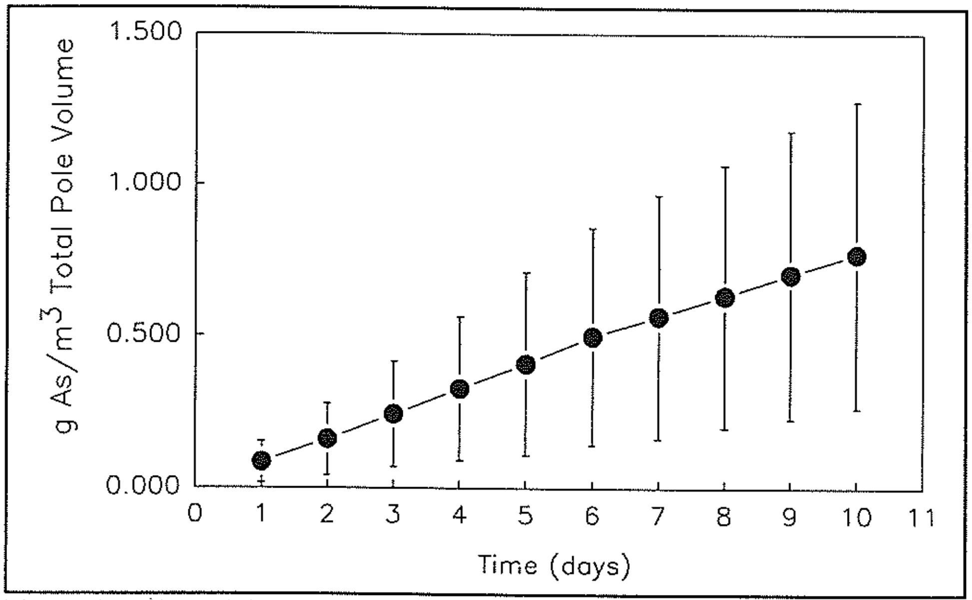

Figure 4 Effect of Simulated Acid Rain on Leaching of Arsenic for CCA-PEG Treated Utility Poles. Each Point Displays the Mean of 6 Poles and 95% Confidence Intervals.

3.1.2 Copper Naphthenate Leaching

Dichloromethane Extract Analysis

Results of preliminary analytical investigations as described in section 2.1.4 indicated that leachate extraction with dichloromethane to determine organic/inorganic copper ratio was unnecessary. Analysis of DCM extracts indicated that virtually all copper in the leachate was in inorganic form, with less than 0.06 mg/L organic copper found. Values for both hydrochloric acid and dichloromethane extracts were extremely low, equating to approximately 0.02 and 0.01 g Cu/m^3 (resp), based on total pole volume. The pH of the SAR (pH 4.2), was sufficient to result in near complete dissociation of copper naphthenate into Cu ions and free naphthenic acids. The literature lends support to this finding, indicating that acidification of copper naphthenate by many different acids results in complete dissociation of the copper ion from naphthenic acids.

Copper Naphthenate Leachate Analysis Results

Analytical comparisons between acidified and nonacidified leachate as described in section 2.1.4, indicate that samples (at pH 4.2) which were further acidified with HCl resulted in only slightly higher copper levels as compared to non acidified. The increase, on average, was less than the detection limit for copper, however, all results displayed are from acidified leachate samples, thus ensuring more complete results.

Results of leachate analytical data as shown in Figure 5 illustrate the leaching tendencies of copper naphthenate from treated utility poles. The mean CCA loss per leaching event, was approximately 1.32 mg/L (ppm) Cu, with a range of 0.77 - 2.23 mg/L Cu. The mean total accumulated copper loss over the duration of the study was determined to be approximately 4.67 g/m^3 Cu, as based on total pole volume (Table 2). This value expresses the approximate total above ground leaching loss over a one year period in southern Ontario. Concentrations of copper in SAR leachate approach that of the water solubility of copper naphthenate.

The release of copper naphthenate from treated utility poles appears relatively constant between poles and leaching events. The maximum rate of leaching for any particular pole appears limited to the water solubility of copper naphthenate. The typical loss of copper from an individual pole section, over the duration of the study, is shown in Figure 6.

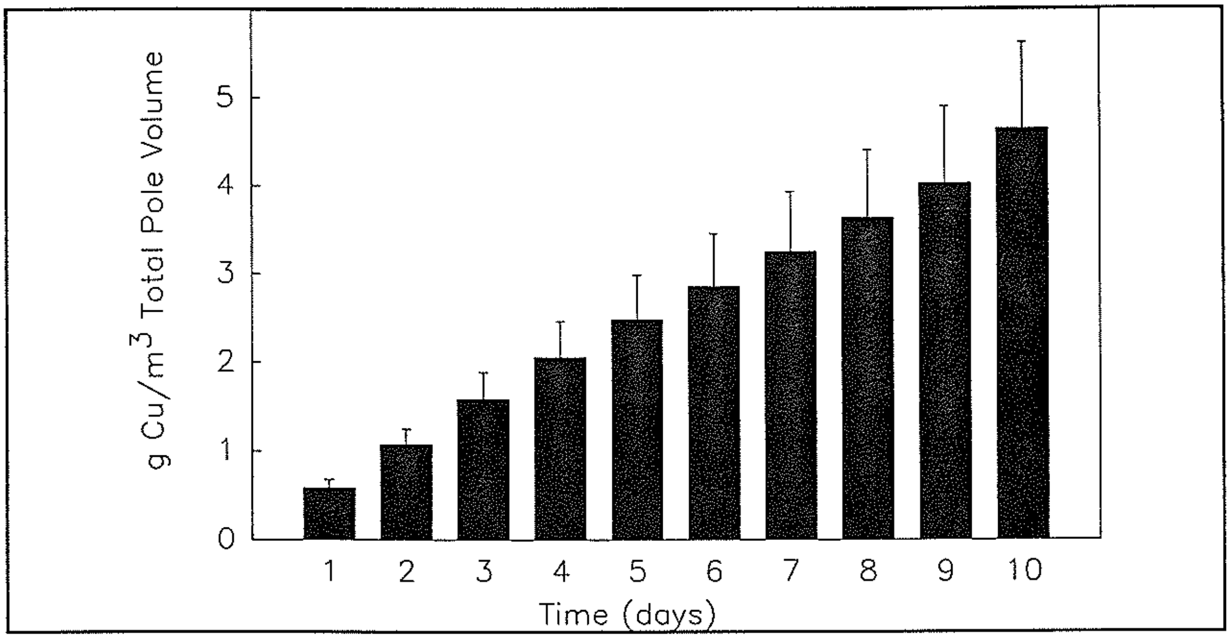

Figure 5
Effect of Simulated Acid Rain on Leaching of Copper From Copper Naphthenate Treated Utility Poles. Each Bar Displays the Mean of 6 Poles and 95% Confidence Intervals.

Table 2 Total Copper Loss - Copper Naphthenate Treated Poles
Based on Total Pole Volume

	Leaching Event #											
Pole #	1	2	3	4	5	6	7	8	9	10	HCl*	DCM*
						g/m³ Cu						
1	0.58	0.45	0.49	0.45	0.37	0.34	0.35	0.35	0.38	0.55	0.02	0.00
2	0.40	0.31	0.29	0.28	0.24	0.22	0.24	0.25	0.26	0.40	0.01	0.01
3	0.66	0.54	0.51	0.50	0.44	0.39	0.36	0.41	0.38	0.68	0.02	0.01
4	0.52	0.44	0.41	0.37	0.38	0.35	0.35	0.29	0.31	0.56	0.02	0.00
5	0.75	0.62	0.76	0.67	0.59	0.54	0.57	0.56	0.60	0.82	0.03	0.00
6	0.61	0.52	0.62	0.52	0.56	0.44	0.47	0.44	0.45	0.67	0.02	0.01
Mean	0.59	0.48	0.51	0.47	0.43	0.38	0.39	0.38	0.40	0.61	0.02	0.01
SE	0.044	0.039	0.061	0.050	0.049	0.041	0.043	0.042	0.045	0.054	0.002	0.000

* Hydrochloric acid and Dichloromethane glassware extractions

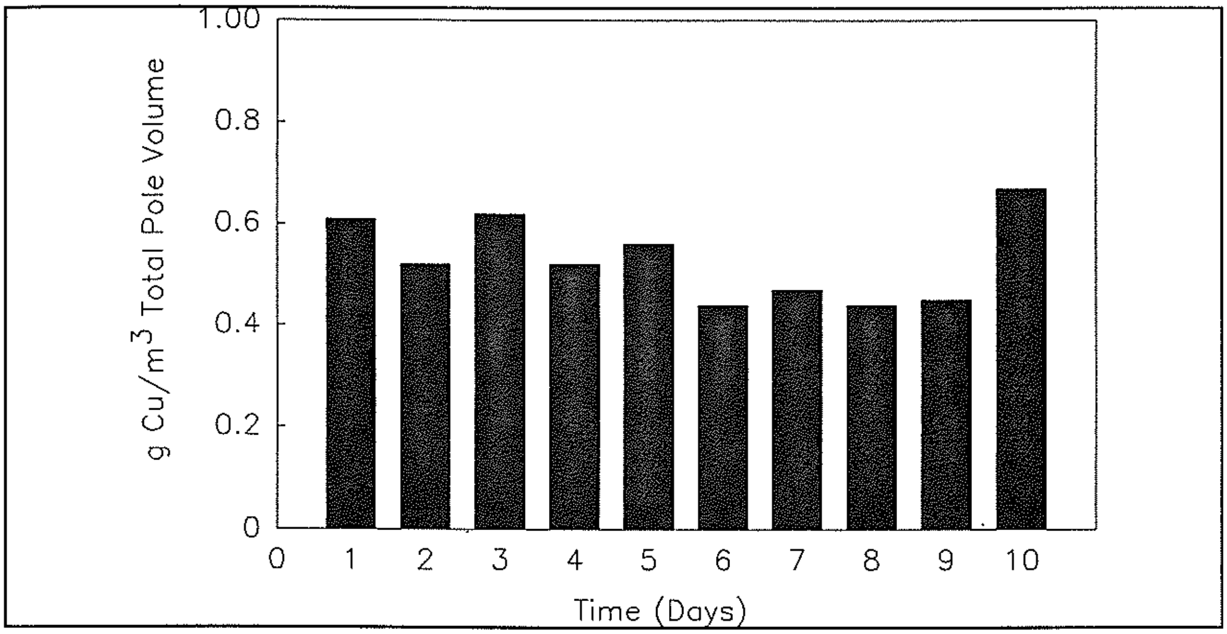

Figure 6 Effect of Simulated Acid Rain on Leaching of Copper From Copper Naphthenate Treated Utility Poles. Each Point Displays the Daily Loss of Copper From Pole # 6.

3.2 *Daphnia magna* Static Acute Toxicity Tests

The various mechanisms involved in metal contaminant interactions remains relatively unknown. Therefore, extrapolation of laboratory assessment to field situations is difficult due to the complexity of the interactions. Verriopoulos and Dimas (1988), describe the interaction of two pollutants as generally being additive. This may also be the case for three toxicants, as found with CCA leachate.

3.2.1 CCA Bioassay Results (48hr LC50)

Results of preliminary LC50 determinations for Cu, Cr and As in this study are shown in Table 4. The resultant mean LC50 values found were approximately 0.053 mg/L Cu, 0.49 mg/L Cr and 8.21 mg/L As. These responses can be explained in part by known mechanisms of toxicity of the various metals. In general metals exhibit multiple organ toxicity mainly due to inhibition or alteration of enzymes and/or biological membranes (Goyer, 1986).

Table 4 Preliminary Static Acute *Daphnia* Bioassay Results

Toxicant	Mean (mg/L)	Range (mg/L)
Cu^{2+}	0.053	0.049-0.062
Cr^{6+}	0.49	0.47-0.52
As^{5+}	8.21	7.44-9.15

Bioassay contaminant concentrations for this study were defined as a percentage of the mean Cu-Cr-As loss per leaching event. Under simulated acid rain conditions, the mean daily loss of CCA components was approximately, 1.68, 0.02, and 0.18 mg/L Cu, Cr, and As respectively. The resultant combined LD50 for 15 tests was found at 2.14% of the original leachate CCA concentrations. This value equates to approximately 0.036, 0.00047, and 0.00385 mg/L Cu, Cr, and As (resp). Since Cr and As concentrations at this level are far below either of their individual LC50 values, the resulting toxicity seen above can undoubtedly be attributed to copper. There may however be a slight interaction between metal components, since the LC50 of the CCA mixture was slightly below that of copper alone.

3.2.2 CuNap Bioassay Results (48hr LC50)

All bioassays were conducted using serially diluted well water leachate of CuNap treated poles. The total mean daily copper concentrations found in the leachate was approximately 0.21 mg/L. However, nonacidified leachate samples showed only 0.132 mg/L Cu. Since these bioassays were conducted using well water as a diluent with a pH 7.6 it might be assumed that only the inorganic copper present could display its toxic effects. However, well water leachate of copper naphthenate treated poles had the peculiar capacity to pull all neonate *Daphnia* to the surface of the containment beakers. This phenomenon was noticed even at extremely low concentrations of CuNap leachate (2.5%), indicating that some other component of the leachate was affecting the surface tension of the diluent water. An obvious oily film was present on all test beakers, and the presence of petroleum vapours was apparent. It is hypothesized that *Daphnia* swimming near the surface would contact this organic film and be unable to escape from it, as would appear to be the case. This in itself did not appear to have a significant detrimental effect on survival since *Daphnia* exposed to lower concentrations (5-15%) were still very much alive on the water surface after 48 hours.

The resultant combined LC50 value of 15 bioassays was determined at 32.34% of the well water leachate. This equates to approximately 0.07 mg/L Cu based on total copper values above. However, if we disregard the organic copper present this value equates to only 0.044 mg/L Cu. Insofar as this case is concerned, the preliminary LC50 values found for copper ranged from 0.049 to 0.062 mg/L, thus an LC50 value based on total copper for copper naphthenate leachate would lie outside this range. This would indicate an LC50 value based only on inorganic copper concentrations to be more representative of the actual toxicity expected.

The toxic reactions seen above, appear to be mainly attributed to copper content of the leachate with other CuNap leachate components playing only insignificant roles.

4 Conclusions

Previous leaching studies have shown that leaching in an acidic environment has substantial effects on CCA depletion, with the source of the acidity playing the most important role. Organic acids have been found to remove more that 10 times the amount of CCA components as compared to sulfuric acid alone.

Studies with simulated acid rain (SAR) solutions at pH 4.2, have shown CCA components to be relatively resistant to leaching when exposed to a volume of water equal that of the mean annual rainfall in southern Ontario. Copper was the only component to be released in concentrations above the detection limits of the atomic absorption unit used.

The leaching rate of copper naphthenate throughout the duration of study was relatively constant between leaching events and poles. This may be the result of the low water solubility of copper naphthenate or an indication of uniformity among poles being tested. The total amount of copper lost in a simulated year of rainfall exposure was approximately 4.75 g/m^3, compared to 7.50 g/m^3 (total pole volume) found with the CCA study. If based solely on the values above, copper naphthenate would appear to present less of a leaching hazard than CCA. Although CCA leachate contains Cr and As in addition to Cu, it is also true that copper naphthenate contains both metal ions and naphthenic acids, both of which play important roles in the effectiveness and thus overall toxicity of the preservative.

Daphnia bioassay results indicate the risk associated with leachate from CCA-PEG treated utility poles to be only slightly higher than that for CuNap. LC50 values were found at 2.14% and 9.48% percent of original SAR leachate concentrations for CCA and CuNap respectively. These values equate to approximately 0.036 and 0.044 mg/L Cu respectively, as determined by SAR leachate analysis.

It should be considered that all leaching losses described in this study pertain only to the above ground portion of treated poles. Many studies have indicated the dissociation capacity of a variety of acids on copper naphthenate as well as the sequestering capacity of organic acids for metals, especially copper, from treated wood. Poles exposed to such conditions in service may result in much higher preservative losses below ground than above.

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