Leaching of Chromium, Copper and Arsenic from Utility Poles Treated with Chromated Copper Arsenate

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Abstract

The objectives of this study were to examine leaching of chromated copper arsenate (CCA) from treated timber and to determine the cation exchange capacity (CEC), pH and total organic carbon (TOC) of the contaminated soil samples. A total of 114 surface soil samples were collected around 28 Douglas fir utility poles at distances of 0, 0.30, and 0.60 m and 3 background samples were collected at a distance of 7.0 m from the poles. Also a freshly treated, 1.50 m long utility pole section was suspended outside in a large cylinder to collect runoff. The Cu:As:Cr (molar) ratios of the average metal contents in the soil samples collected at a distance of 0 m, and in the runoff from the pole segment, were 100:46:56 and 100:44:57, respectively. At 0.60 m distance the metal concentration had reached background levels. The results suggested that As was more mobile than the Cr and that the metals were being continuously leached from the poles over time. A correlation between the soil CEC and TOC was observed.

Introduction

Timber utility poles in North America are treated with preservatives to reduce bacterial, fungi and insect attack and increase their life expectancy. The wood preservatives are either organic (and oil based) or inorganic (and waterborne). Pentachlorophenol, creosote, chromated copper arsenate (CCA) and ammoniacal copper arsenate (ACA) are the most widely used preservatives, while CCA is the most widely used in aquatic environments (Hingston et al., 2001). CCA is an inorganic wood preservative developed by an Indian scientist, Dr. Sonti Kamesam in 1933 (Lahiry, 1997) and since then has been used extensively although recently its use has been phased out in the United States (Rahman et al., 2004)

Three types of CCA (-A, -B, and -C) are commercially available and they have varying proportions of copper oxide (CuO), chromium oxide or anhydrous chromic acid (CrO_3), and arsenic pentoxide (As_2O_5) present. The CuO ≈ 19% by volume, the CrO_3 varies between 35 and 65% by volume and the As_2O_5 makes up between 46 and 16% by volume. Type CCA-C (with 18.5% CuO, 47.5% CrO_3 and 34% As_2O_5) is most commonly used (Cooper, 1994). The chromic acid (H_2CrO_4) dissociates in water to form the soluble chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) ions.

The copper (Cu) and arsenic (As) in CCA inhibit fungi, bacteria and insects whereas the chromium (Cr) promotes fixation of CCA with the timber (Lebow, 1996) and promotes precipitation. Successful fixation will minimize leaching of metals from the wood. Bull (2001) proposed a simple reaction for CCA fixation in wood and according to his model hexavalent chromium or Cr (VI) is reduced to Cr (III) as shown in the following equation.

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$
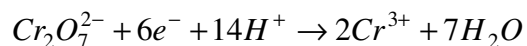
The major fixation products in treated utility poles are comprised of the Cr (III) and they form as Cr (VI) groups are reduced (Hingston et al., 2001). The proposed products include chromium (III) arsenate ($CrAsO_4$), that forms complexes with the lignin, CrO_4^{2-} that also complexes with lignin, Cu (II) precipitates and complexes with lignin and cellulose, and chromium (III) hydroxide (Bull, 2001). X-ray absorption fine structure analysis has revealed that primary alcohol groups in the lignin and carbohydrate fractions in the wood are the electron donors in the reduction reaction (Bull, 2001).

The reduction process occurs in stages. The Cr(VI) and other electron acceptors first become sorbed to the carbohydrates and then they are reduced and form complexes of CrO_4 with lignin and cellulose, and CrO_4^{2-} with lignin. The changes in metal species during fixation and the long-term complex reactions influence the distribution of metals in the wood, the wood toxicity, and the species that may be leached (Hingston et al., 2001). It is believed that metals may be leached as Cu or Cr arsenates, as inorganic complexes, or as organo-metallic complexes bound to water-soluble wood extractives (Lebow, 1996) though little research has been undertaken in this area (Albuquerque and Cragg, 1995).

Chemical leaching of the treated timber also progresses in stages by "loss of surface deposits and unfixed components, penetration of water into the wood and hydrolysis or dissolution of preservatives from the surface of the wood" (Cooper, 1994). Leaching rates are affected by local climate, leaching media, wood properties and wood treatment techniques (Hingston et al., 2001).

CCA exhibits a broad-spectrum of toxicity and the toxic components bond strongly with the wood (Bull, 2001) though recent toxicity tests suggest that in aquatic environments the leaching of preservative components from wood is harmful to the environment (Hingston et al., 2001). Leaching and toxicity of CCA treated wood may be a problem during storage, use and particularly disposal (Riberiro et al., 2000). Approximately 5 million tons of treated timber are landfilled annually in the US (Falk, 1997). Disposal in landfills is expensive and may be prohibited in the future (Riberiro et al., 2000).

Nine different oxidation states exist for Cr (Massara et al., 2004) but only the Cr (VI) and Cr (III) are common in soils (Pagilla, 1999; Massara et al., 2004). Cr (VI) is more toxic and more mobile than Cr (III) which forms stable complexes and is retained in soils. Cr (VI) is reduced to Cr (III) by organic matter (humic and fulvic acids) and inorganic agents (Fe) (Sanders and Reidel, 1987; Pagilla, 1999). Ideally, CCA fixation in wood converts the Cr (VI) to Cr (III) but Nygren and Nilsson (1993) found that 20% of Cr was present in the hexavalent form or incomplete fixation was occurring. Cr (III) may also be mobilized by oxidation to the hexavalent form or its complexation with naturally occurring ligands (Massara et al., 2004). Dichromate, a major constituent of CCA, is generally weakly sorbed to soil and could pose the greatest potential immediate threat to groundwater supplies (Carey et al., 1996).

Cu (II) is an essential micronutrient but is toxic above trace levels. It tends to become bonded to organic material (especially humic acids) in soils (Hung et al., 1993). Cu sorption to soil increases with pH (Carey et al., 1996) and greater Cu leaching from treated wood occurs at lower pH (Hingston et al., 2001). Lebow et al. (1999) found Cu leaching from CCA treated timber was much greater in seawater than in freshwater and their study raised concern about the use of CCA treated wood in marine environments. One study of CCA treated Pine found that 25% of the Cu was leached in the first 6 months, and a maximum of 52% of the Cu was leached within 85 months (Hingston et al., 2001).

There are 4 oxidation states for As and arsenate (V) and arsenite (III) are the most common (Wang and Mulligan, 2004). As (III) is the more toxic and As (V) is the more abundant of the two states (Hingston et al., 2001). Woolson and Gjovik (1981) found As (III) comprised 3% of the As in treated wood although Nyren and Nilsson (1993) found no trivalent As present in commercial wood supplies. In a study on marine piles, leaching of As into the interstitial and overlying waters was found in all cases (Baldwin et al., 1996).

Very little research has dealt with in-situ leaching rates of CCA treated timber and research under actual and different environmental conditions is needed (Lebow, 1996; Hingston et al., 2001). Simple, standard and repeatable laboratory tests on small blocks of wood are not applicable to field conditions and so leaching rates from utility poles are not well defined (Hingston et al., 2001).

Mortimer (1991) investigated CCA/Polyethylene glycol (PEG) treated utility poles, 3 to 36 months in age, and found very low concentrations of Cu, Cr and As near the poles. Cooper et al. (1997) studied 50 CCA-C/PEG poles and found high Cu, Cr and As concentrations near the poles. Zagury et al. (2003) studied soil surrounding 6 CCA/PEG treated utility poles and measured 1460 ± 677 mg/kg of Cu, 410 ± 150 mg/kg of As and 287 ± 32 mg/kg of Cr.

The purpose of this study was to determine the Cu, Cr and As concentrations in soils adjacent to CCA treated utility poles, metal concentration variations with distance from the poles, approximately field scale leaching of metals, and soil properties including cation exchange capacity (CEC), pH and total organic carbon (TOC). Leaching tests were conducted on timber under conditions that closely resembled natural field conditions. Metal concentrations in runoff from an isolated log were determined to obtain an estimate of runoff in the field.

Materials and Methods

The transmission lines used in this study were selected according to criteria proposed by the Electric Power Research Institute (EPRI, 1997) for penta and creosote treated poles. The CCA treated poles in this study were all Douglas fir and of known age, came from readily accessible areas having variable soil properties, had not been exposed to pesticides and other contamination, were far from industrial areas, were at least 6 ft away from a roadway and were situated in a clearing of at least 6 ft in diameter.

Samples were collected around 28 poles along three different transmission lines (227, 259, 225) situated in Gros Morne National Park, at Rocky Harbour and at Deer Lake, respectively. The 28 poles were located at 24 sites and a total of 114 samples were collected.

For 21 sites with 23 poles, three samples were taken at distances of 0, 30 and 60 cm from the poles and 2 of these sites had double poles. At 2 other sites that had 1 pole each, samples were taken at distances of 0, 30 and 60 cm in north, south, east and west directions from the

pole for a total of 12 samples per pole. At 1 site with 3 poles, 3 samples each were taken for 2 of the poles and 12 samples were taken for the other pole. At least 3 samples were collected at 3 distances from each pole to determine the variation in soil metal concentrations with distance from the pole. At 3 pole locations, soil samples were also collected at 7 m from the poles to obtain background soil conditions.

Surface soil samples were collected with a spoon, placed in clean Ziploc bags, sealed and refrigerated at 4°C. The spoon was cleaned between sampling locations. Each Ziploc bag was labelled with the date of collection, a code for each pole, the pole age, the distance, and where applicable, the direction from the pole.

Soil samples were analyzed for TOC by the modified Walkely-Black wet oxidation method and for CEC according to the $Ca(OAc)_2 – CaCl_2$ method (Sheldrick, ed. 1984). Soil pH was determined using a ratio of 1:2 soil:0.01M $CaCl_2$ (Sheldrick, ed. 1984). Soil samples were digested using US EPA method 3050 B (American Chemical Society, 1986).   Samples were stored in the refrigerator at 4°C until analysis with a Perkin-Elmer SCIEX Elan 6100 inductively coupled plasma mass spectrometer (ICP MS). All pH measurements and 68% of TOC measurements for each sample were conducted in duplicate. CEC determinations were conducted in duplicate for only 10% of the samples since at least 3 samples were available for each pole.   Only 10% of acid digestion experiments (for soil metal determination) were conducted in duplicate since it is known that metal concentration tends to decrease as distance from the pole increases (Cooper et al., 1997; Hingston et al., 2001; Zagury et al., 2003).

A freshly treated section of a utility pole, 1.50 m long and 0.30 m in diameter, was suspended vertically outside in a large plastic cylinder measuring 2.40 m high by 1.20 m in diameter. The bottom of the cylinder was connected with an outlet for runoff collection and the pole and cylinder were exposed to rain and snow. Runoff from the pole segment was collected regularly over a period of 2.5 years. The water samples were then acidified with HNO_3 to < pH 2 and stored at room temperature until they were analyzed for Cr, Cu and As. One backgound water sample was also collected for analysis.

Results and Discussion

At all 28 poles metal concentrations were highest adjacent to the poles and decreased with distance from the poles. This was similarly observed in previous studies (Cooper et al., 1997; EPRI, 1997; Hingston et al., 2001; Zagury et al., 2003). This phenomenon at pole 1-32 is illustrated in Figure 1 and the trends seen in this figure are typical results for this study and are the same trends that were seen when measured values from all samples in this study were averaged.

For 27 of the 28 poles Cu concentrations were higher than the Cr and As concentrations and this was also observed by Cooper et al. (1997) and Zagury et al. (2003). For approximately 80% of the poles, the As concentration exceeded the Cr concentration immediately next to the pole but at 30 cm from the poles, the Cr concentration was greater than the As concentration (when concentrations are measured in mg/kg). These results suggest As is more mobile than Cr and could therefore be more likely to contaminate groundwater. Stilwell and Gorny (1997) and Zagury et al. (2003) also found As to be more mobile than Cr.
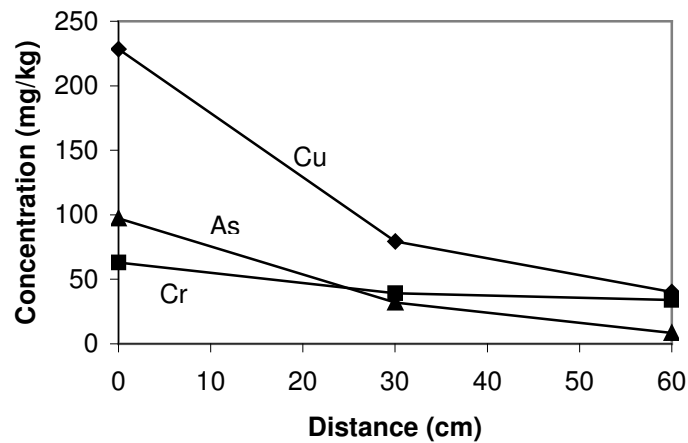
Figure 1. Reduction in metal concentration with distance from pole 1-32

An overall trend in soil immediately adjacent to the utility poles was observed whereby Cu had the highest average concentration of 574 ± 58 mg/kg, followed by As with an average concentration of 309 ± 33 mg/kg and finally by Cr with an average concentration of 261 ± 27 mg/kg. It can be seen from Table 1 below, these concentrations in soils are considerably higher than Canadian maximum acceptable levels. There can be significant variation in the relative amounts of As and Cr applied to the timber depending on the type of CCA used, and so these values for As and Cr might not necessarily be exactly comparable for studies using different types of CCA.

Table 1. Maximum acceptable levels of Cu, As and Cr (Environment Canada and Canadian Council of Ministers of Environment, (CCME), 2003)

Metals	Water (µg/L)					Soil (mg/kg)	
	Community	Aquatic life		Agriculture		Agriculture	Commercial
	MAC[a]/ IMAC[b]/AO[c]	Fresh-water	Marine	Irrigation	Livestock	Residential Parkland	Industrial
Cu	≤ 1000 (AO)	2-4	-	200-1000	500-1000	63	91
As	25 (IMAC)	5	12.5	100	25	12	12
Cr	50 (MAC)	-	-	-	-	64	87

[a] MAC = Maximum acceptable concentration.
[b] IMAC = Interim maximum acceptable concentration.
[c] AO = Aesthetic objective

The metal concentrations in soils at 7.0 m from the utility poles were comparable to metal concentrations in the soils at 0.60 m from the poles, as shown in Table 2. Therefore, metal background levels in surface soils were reached at about 0.60 m from the poles.

Average values of pH, CEC and TOC for soil at each pole were calculated and Figure 2 shows a direct correlation between the CEC and TOC of each soil. This might be explained by the fact that the TOC is a function of the total organic matter in the soil and the soil organic matter contains a large proportion of carboxyl groups that dissociate and contribute to negative charge and result in a high CEC. Zagury et al. (2003) compared different soils and found that organic soils had higher CEC values than clay soils. They concluded that an organic matter contribution to CEC would be greater than a clay contribution.

Table 2. Metal concentrations in surface soils at 3 pole locations

Pole No.	Metal	Metal concentrations at four distances from poles (mg/kg)			
		0 m	0.30 m	0.60 m	7.00 m
P 1-31(S)	Cu	1257	117	24.1	18.6
	As	487	42.4	2.43	24.2
	Cr	232	47.4	20.5	24.3
P 1-4 (S)	Cu	575	14.8	18.6	24.6
	As	375	4.38	3.68	6.77
	Cr	117	20.0	27.7	25.2
P 19L(S)	Cu	512	5.52	7.52	11.6
	As	79.8	1.00	2.25	4.11
	Cr	140	1.01	2.18	3.38
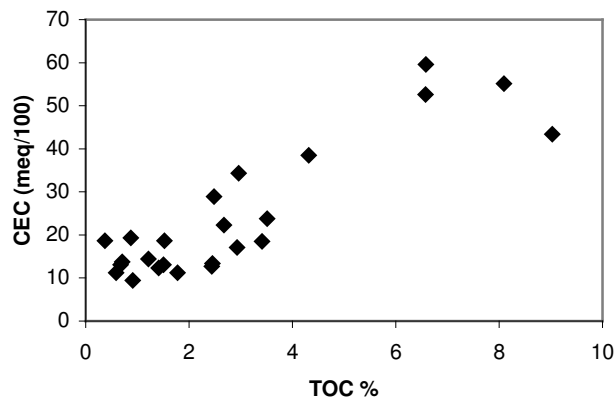
Figure 2. Average of all TOC site values against average of all CEC site values

The average pH values for all of the sites ranged between pH 4.1 and pH 7.2 and were therefore in the acid to neutral pH range for all soils. There was no direct relationship between the TOC and the pH or between CEC and pH, as can be seen from Figures 3 and 4 respectively. However, wherever there was a high TOC, and thus a high CEC, there was also a low pH. This may be explained by the fact organic matter can have a significant affect on the lowering of pH.
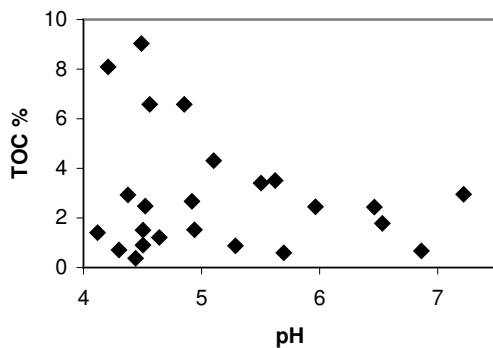

Figure 3. Average of pH values against average of TOC values
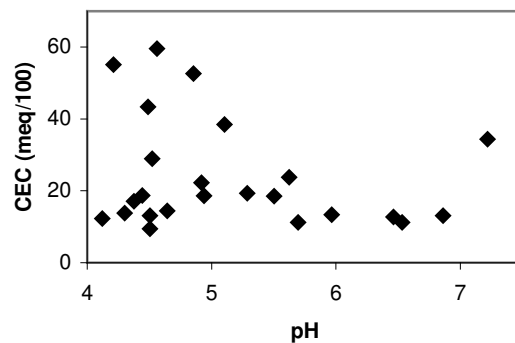

Figure 4. Average of pH values against average of CEC values

Between 5 September 2002 and 12 February 2004 water samples were collected from the utility log that had been suspended outside. Cu was found to be the most abundant metal to be leached. The average amount of Cu found in the water samples was 641 μg/L and the average amounts of As and Cr leached were 331 and 300 μg/L respectively. Based on the recommended maximum levels in Table 1, leaching of these metals could be unsafe, particularly in freshwater or marine environments, where toxic levels of Cu and As (and possibly Cr) could be released in the immediate vicinity of the treated timber. The trends and proportions of metal leaching into the water and into the soil immediately adjacent to the poles, were similar. The background concentrations of these metals in water were only 72 μg/L of Cu, 0.17 μg/L of As and 0.80 μg/L of Cr.

Conclusions

The average metal contents in soil collected immediately adjacent to the utility poles gave concentrations of 574 ± 58 mg/kg Cu, 309 ± 33 mg/kg As, and 261 ± 27 mg/kg Cr or a Cu:As:Cr molar ratio of 100:46:57. A similar trend of leaching of the metals from the suspended log was observed as the average concentrations in the water samples were 641 μg/L Cu, 331 μg/L As and 300 μg/L Cr or a Cu:As:Cr molar ratio of 100:44:57. The metal concentrations in soil samples immediately adjacent to the utility poles were accurately reflecting the same relative proportions of metal leaching from the suspended log. This could mean there is a continuous leaching of the metals over time since the results also suggested that As was more mobile than Cr. It appeared that soil background conditions in surface soils were reached at a distance of only 0.60 m from the utility poles.

Acknowledgements

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