

## Research Article

# Leaching of Chromium, Copper, and Arsenic from CCA-Treated Utility Poles

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Concentrations of Cu, Cr, and As in soils surrounding 26 Douglas Fir Chromated Copper Arsenate (CCA) treated utility poles and in rainwater runoff from a new CCA treated utility pole segment (log) suspended outside in a cylinder were studied. The age of the utility poles, distances from the poles, rainfall amounts, and characteristics of soil samples including cation exchange capacity (CEC), pH, and total organic carbon (TOC) were considered. Heavier rainfall, damp conditions, and more weathered poles contributed to the greatest leaching of Cu, Cr, and As. The maximum measured soil concentrations of Cu, Cr, and As were 37.5, 65.5, and 38.9 mmol/kg and maximum Cu, Cr, and As concentrations in rainwater run-off were 14, 77.7 and 55.8  $\mu\text{mol/L}$ . Metal concentrations decreased with distance from the poles and, except at one utility pole location, Cu was the most leached of the three elements. The As appeared to have greater mobility in the soil than the Cr. Along the transmission line nearest the coast and from which the greatest amount of samples was collected, soil CEC and TOC values were the highest and the CEC and TOC were directly and strongly correlated.

## 1. Introduction

Chromated Copper Arsenate (CCA) has been employed extensively since the 1930s as a wood preservative [1–3] to protect structures such as utility poles, fence posts, backyard decks, playground equipment, and marine structures from fungal and bacterial attack. However, recognition of the hazards of CCA has led to some reduction in its use as, for example, its banning in the residential areas in the U.S. [4, 5]. There is also the problem of retiring CCA-treated structures that are currently in use [6]. CCA-treated wood can have a service life of up to 50 years and its use in post-consumer products (such as landscape mulch), determined to be 0.9% in the UK in 2001, could reach 12.3% in the UK in 2061 [4, 7]. In South Africa, CCA is still commonly used and local food vendors in Cape Town are even cooking food over fires fueled with CCA-treated wood [1].

Slightly different formulations of CCA (CCA-A, CCA-B, and CCA-C) exist but CCA-C containing 18.5% CuO

(copper oxide), 47.5%  $\text{CrO}_3$  (chromium oxide or anhydrous chromic acid), and 34%  $\text{As}_2\text{O}_5$  (arsenic pentoxide) is the most common [8–10]. The role of the Cu and As is to deter fungi and insects, respectively, and the Cr is intended to act as a fixative [11, 12]. During CCA application, Cr (VI) is reduced to Cr (III) and the final products may include Cr (III) arsenate- ( $\text{CrAsO}_4^-$ ) lignin complexes, chromate- ( $\text{CrO}_4^{2-}$ ) lignin and cellulose complexes, Cu (II-) wood carboxylate complexes, and Cr (III) hydroxide [10, 13, 14].

Local climate, leaching media, wood properties, and wood treatment techniques affect leaching of CCA from treated wood [14, and references therein] often as Cu or Cr arsenates and inorganic or organometallic complexes [11]. Leaching of Cu, Cr, and As may also be greater from wood that has been weathered [7]. Although CCA wood waste has been disposed of in approved landfills, preference is moving towards management options which include complete removal of CCA and its products from wood waste before

disposal, both to address the shortage of landfill space and to reassure the public [15].

Cu (II) bonds with soil organic matter and is toxic to aquatic organisms and generally toxic above trace levels [4, 16]. Organic matter and inorganic agents such as Fe can reduce Cr (VI) to the less toxic Cr (III) which forms complexes that are more stable and more retained by soils [17] though Cr speciation will also be influenced by the Eh-pH conditions in soils [18]. Of great concern is As because of exposure effects in humans [19]. Arsenate (V) and arsenite (III) are the most common forms in soils [20] with As (III) being the more toxic and abundant [14]. Both As and Cr are known human carcinogens [4].

A study of 6 CCA/polyethylene glycol (PEG) treated utility poles and found  $23.0 \pm 10.7$  mmol/kg of Cu,  $5.52 \pm 0.62$  mmol/kg of Cr, and  $5.47 \pm 2.00$  mmol/kg of As in adjacent soils [6]. A study of CCA treated fence posts reported a maximum soil concentration of 10.1 mmol/kg of As [19].

One objective of this study was to gain a better appreciation for the amount of leaching of Cu, Cr, and As that could occur from CCA treated utility poles and how the soil could be impacted by this leaching. The field study and measurements of leaching of Cu, Cr, and As from a freshly treated wooden log suspended outside in a cylinder provided some of these answers. For the water and soil samples, efforts were made to determine the effects of temperature, rainfall, and/or pole age on leaching of the metals. Another objective was to understand the nature of the soil environment where the field tests were conducted and to observe what effects, if any, the soil might have on the leaching of the metals. For this purpose soil characteristics such as the pH, cation exchange capacity (CEC), and total organic carbon (TOC) of the soil samples were measured.

## 2. Materials and Methods

**2.1. Site Description.** Soil samples were collected from around utility poles along transmission lines (TLs 227, 259, and 225) in western Newfoundland. Transmission lines 227 and 259 run north out of Berry Hill approximately 30 and 60 m east, respectively, of the Northern Peninsula Highway, that borders the Gulf of St Lawrence and goes north as far as Peter's Barron outside Daniel's Harbour. Sampling along TLs 227 and 259 was only undertaken within Gros Morne National Park and the general area is illustrated in Figure 1(a). Transmission line 225 is a 2.4 km line running out of the Town of Deer Lake and bordering the northern edge of the lake of the same name, as outlined in Figure 1(a) and detailed in Figure 1(b). All of the utility poles along each transmission line were of the same age but each TL was of a different age.

Soil samples around 26 CCA treated utility poles were collected. Eighteen poles were from the Gros Morne National Park area, 14 of which were on TL 227 and 4 from TL 259. The remaining 8 utility poles were part of TL 225 near Deer Lake. The 26 poles were from 24 different sites because 1 site contained three poles. Soil sample locations were selected according to criteria proposed by the Electric Power Research Institute [21] for penta and creosote treated poles. All the poles were Douglas fir (*Pseudotsuga menziesii*), of known

age, were from readily accessible areas having variable soil properties, were far from industrial areas, had not been exposed to pesticides or other contamination, were at least 1.80 m away from a roadway, and were situated in a clearing of at least 1.80 m in diameter.

To test for the decrease in the metal concentrations with distances from each of the 26 utility poles a least squares linear regression analysis was conducted on the samples.

To compare the effects of rainfall amounts for each metal and among the three TLs at the distance of 0 cm, an unbalanced analysis of variance (ANOVA) (with Excel 2010) was conducted on these samples. Following the ANOVA, Tukey's procedure was employed to determine which TLs had significantly different population means.

To investigate correlations among the soil properties (TOC, CEC, and pH) for each TL, linear regression analysis was employed.

**2.2. Soil Sampling and Characterization.** Soil samples were collected at distances of 0, 30, and 60 cm from the 26 poles and 3 background soil samples were collected at a distance of 7 m for a total of 81 soil samples.

Each sample was collected manually with a cleaned stainless steel spoon and placed in a new Ziploc bag that was sealed and refrigerated at 4°C.

Soil samples were digested by US EPA method 3050 B [22] and stored in the refrigerator at 4°C until analyzed for Cu, Cr, and As. Analyses were carried out on a Perkin-Elmer SCIEX Elan 6100 inductively coupled plasma mass spectrometer (ICP MS) at Fisheries and Oceans Canada's Northwest Atlantic Fisheries Centre trace element lab in St. John's, Newfoundland, Canada. Quality control was monitored by the analyses of the National Institute of Standards and Technology (NIST) certified reference material 1463D. The results in ppb of repeated analyses ( $n = 4$ ) of the NIST 1643D standard were Cr  $18.4 \pm 2.5$ , Cu  $20.0 \pm 2.6$ , and As  $54.6 \pm 7.0$ . Certified ppb values for NIST 1643D were Cr  $18.53 \pm 0.2$ , Cu  $20.5 \pm 3.8$ , and As  $56.2 \pm 0.73$ . Detection limits for all three elements in dilute solutions were <1.0 ppb. Rainwater samples were analyzed in the same lab and using the same equipment as the soil digests. A single NIST 1643 analyses was carried out during the analyses of the water samples for quality control purposes and the results in ppb were Cr 19.1, Cu 21.5, and As 56.8.

Soil samples were analyzed for TOC by the modified Walkely-Black wet oxidation method [23]. The determination of the CEC of the soil samples was according to the Ca (OAc)<sub>2</sub>-CaCl<sub>2</sub> method [23]. Soil pH was determined with a 1:2 ratio of soil:0.01 M CaCl<sub>2</sub> [24]. Concentrations of Cu, Cr, and As and CEC values were measured in duplicate for 10% of the samples. All pH measurements and two thirds of TOC measurements for each sample were conducted in duplicate.

**2.3. Sampling of Runoff from a Freshly Treated Utility Pole Segment.** A 1.50 m long by 0.30 m diameter utility pole segment or log that was freshly treated with CCA was suspended vertically in a 2.40 m high by 1.20 m diameter plastic cylinder that was placed outside to be exposed to

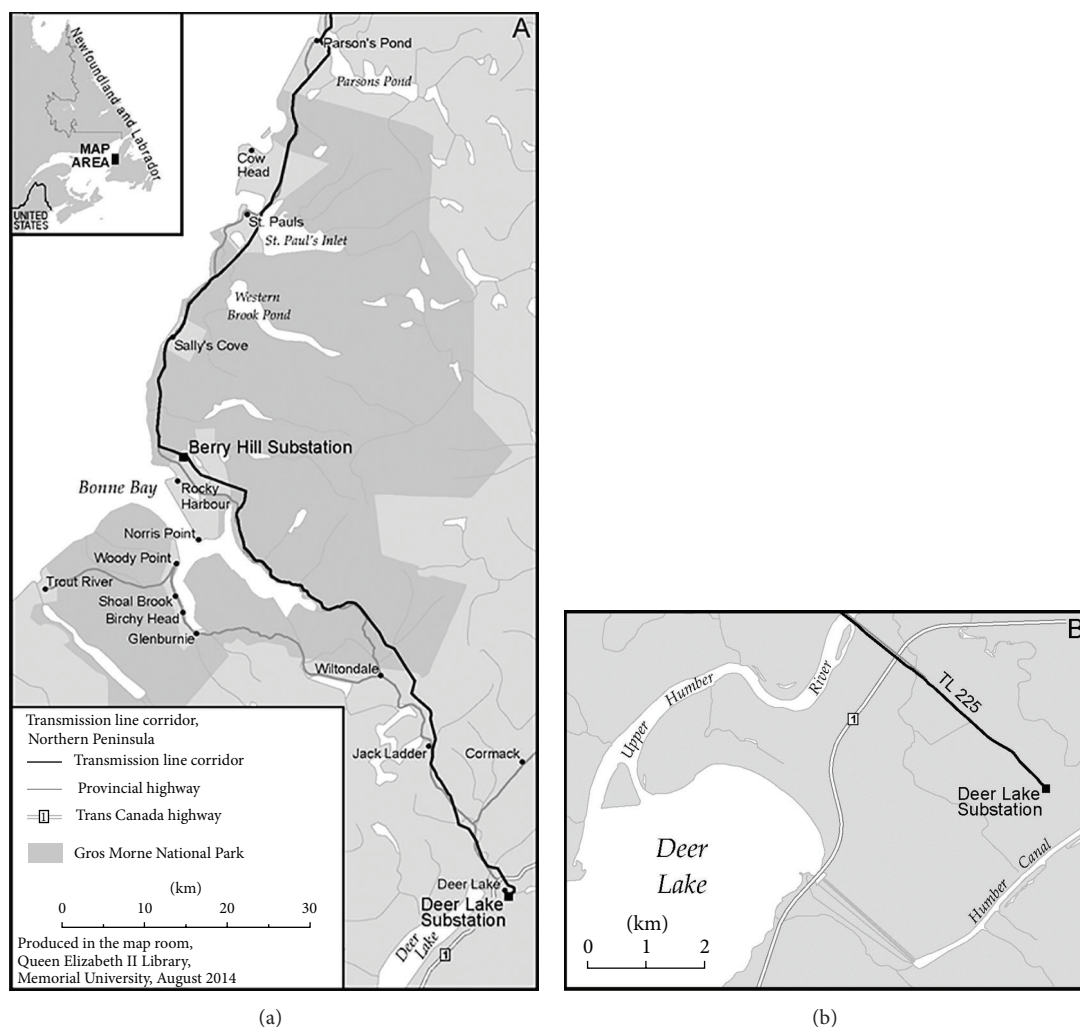


FIGURE 1: Areas of sampling along (a) Tls 227 and 259 and (b) TL 225.

the elements. The bottom of the cylinder was connected to an outlet for runoff collection. Sampling either took place after each rainfall event or after multiple days of rainfall, in which case the total rainfall since the previous sampling time was used. The sampling periods were September 5 to October 28, 2002, inclusive, April 27 to September 30, 2004, inclusive, and June 7 to July 25, 2005, inclusive, for which the rainfall amounts and maximum temperatures were recorded [25]. In 2003 when no samples were collected the log remained outside in the cylinder but the cylinder was covered with a board and the outlet was left open. The runoff samples and one background rainwater sample were acidified with  $\text{HNO}_3$  to less than pH 2 and stored at room temperature until analysis.

### 3. Results and Discussion

#### 3.1. Runoff from the Suspended Log

**3.1.1. Trends in Leaching of Metals with Rainfall Amounts.** To observe trends in leaching of Cu, Cr, and As from the pole

segment with rainfall amount, water samples were considered separately in each of the three years so that pole age might be isolated as a factor, and only rainfall amounts  $\geq 10$  mm were used. The 10 mm cut-off was selected (1) to ensure rainfall amounts would be sufficiently measureable and (2) to give the log enough time to be well soaked in case this was required for leaching of the metals. The results from 2002, 2004, and 2005 are shown in Figures 2(a), 2(b), and 2(c), respectively.

In 2002 the greatest rainfall of 36.4 mm gave the greatest amount of leaching of Cu, Cr, and As from the log in that year. In 2004 the rainfall amounts of 22.8 mm, 30.6, and 100.9 mm gave the three highest amounts of leached metals in that year. In 2005 the maximum rainfall of 42.6 mm produced the most leaching of metals from the log in that year.

The concentrations of leached Cu, Cr, and As were similar in 2002 and 2005 (Figures 2(a) and 2(c)). However, one difference was that in 2002 Cu concentrations were greater than the two other elements and in 2005 As concentrations were less than the two other elements. Leaching of Cu was most pronounced in all years but especially in the first year. By the last year leaching of Cr became more similar to that of Cu.



In 2004 there were 7 instances when concentrations of the leached elements exceeded maximum amounts in 2002 and 2005 and the three events that showed the greatest leaching are examined and discussed in chronological order. These events were on August 31, September 5, and September 20 as shown in Figure 2(b) and each of the rainfall amounts happened to represent multiple days of rain.

With the first event on August 31, 2004, there was a total rainfall of 30.6 mm (trace, 1.2 mm, trace, 16.4 mm, and 13.0 mm on August 27, 28, 29, 30, and 31) and concentrations of Cu, Cr, and As leached from the suspended log were 29.4, 13.6, and 8.87  $\mu\text{mol/L}$ , respectively. The previous sampling and emptying of the collection cylinder had been on Aug 26. Rainfall occurred every day from August 17 to 31 inclusive and totaled 58.6 mm. Fifteen consecutive days of damp conditions culminated in the great amount of leached metals observed on August 31.

On September 5, 2004 (the second event), there was a rainfall amount of 22.8 mm (16.2 and 6.6 mm on September 4 and 5) and the concentrations of Cu, Cr, and As leached from the log were 149, 77.7, and 55.8  $\mu\text{mol/L}$ , respectively. However, this time there had been 20 consecutive days of rain from August 17 to September 5 inclusive giving a total rainfall of 83.6 mm. The extended period of damp conditions prior to sampling may have enhanced the removal of the Cu, Cr, and As from the log.

On September 4 and 5 the maximum temperatures were only 11.9°C and 11.1°C, following three weeks with an average maximum temperature of 19.5°C. After the 20 days of warm, damp weather, contraction of the wood with cooler temperatures might have forced some long retained water to be expelled and this might have also contributed to the highest recorded concentrations of Cu, Cr, and As leached from the suspended log. Others have observed that Cu and As leached more as the temperature rose whereas Cr leached slightly less at 30°C [26].

On September 20, 2004 (the third event), there was a rainfall amount of 100.9 mm (trace, 2.3 mm, 0 mm, 0 mm, trace, 6.4 mm, 62 mm, and 30.2 mm on September 13, 14, 15, 16, 17, 18, 19, and 20). Concentrations of Cu, Cr, and As leached from the log were 60.8, 46.2, and 50.5  $\mu\text{mol/L}$ , respectively. The 98.6 mm of rain that fell on the 4 consecutive days prior to sampling was the greatest amount of precipitation observed for any of the sample measurements and this high rainfall amount could have been important. The previous sampling had been on September 12 or 8 days prior.

These three instances of the greatest leaching of Cu, Cr, and As might be attributed to the total rainfall amounts, the long damp periods preceding the sample measurements, and possibly a drop in temperature. Given that prolonged dampness appears to enhance the leaching and that acids have been employed intentionally to extract CCA from wood waste [15], damp, acidic landfill environments would create ideal conditions for leaching of CCA from wood waste in landfills.

In each of 2002, 2004, and 2005 when sampling was being conducted, the full or partial months when rainfall was the highest were September 5–30, 2002 (104.6 mm), September

2004 (205.7 mm), and June 7–30, 2005 (103 mm). In September 2004 the rainfall accumulation was approximately double the highest measured months in 2002 and 2005 and this likely contributed to two instances of the maximum leaching from the suspended log. From 1981 to 2010 the average precipitation in St. John's during September was 129.6 mm [27]. The rainfall accumulation in September 2004 was clearly exceptional.

From a total of 57 samples of runoff from the log, the average amounts of Cu, Cr, and As were 8.98, 5.30, and 3.88  $\mu\text{mol/L}$ , respectively. The one background rainwater sample contained Cu, Cr, and As concentrations of 1.134, 0.015, and 0.002  $\mu\text{mol/L}$ , respectively. However, 5 of the 57 runoff samples contained less Cu than in the background water, with the lowest Cu concentration being 0.52  $\mu\text{mol/L}$ . There could have been small variations in the rainwater concentrations and for the purpose of this study these concentrations were taken to be negligible.

*3.1.2. Metal Concentrations in Runoff from the Log Compared to Water Quality Guidelines.* Annual average, maximum, and standard deviations of concentrations of Cu, Cr, and As measured in runoff from the suspended log are reported in Table 1. Water quality guidelines for Cu, Cr, and As for the protection of drinking water, freshwater and marine life, and agricultural livestock and crops [28] are also included for comparison.

As with Figure 2, Table 1 is showing similar metal concentrations in the runoff in 2002 and 2005 and higher amounts in 2004. The guideline for Cu in drinking water is for aesthetic purposes as Cu is an essential nutrient (high Cu concentrations might cause a green coating to form on bathroom and kitchen fixtures). In each year the average Cr concentrations in the runoff were higher than permissible for drinking water.

The average As concentration in each year exceeded all of the permissible limits for water with one exception being the 2005 average which was below the permissible limit for irrigation water. It is well known that As can migrate to the groundwater and cause contamination. This has been especially true in Florida where pesticides containing As have been applied to golf courses and because of frequent irrigation, a porous underlying soil system, and a shallow groundwater table, the groundwater has become contaminated [29].

*3.2. Characteristics of the Soil Samples.* The averages and ranges of values of pH, CEC, and TOC determined for each TL and for each of the three distances from each utility pole, are presented in Table 2. Regression analysis revealed that the TOC and CEC values were significantly and positively correlated for TL 227 at 0, 30, and 60 cm and the linear trend lines for these correlations had *P* values of 0.00152, 0.00864, and  $6.56 \times 10^{-7}$ , respectively, and *R*<sup>2</sup> values of 0.581, 0.450, and 0.882, respectively. No such correlations were found for the less sampled TLs 225 and 259 and no significant correlations were found among the other soil properties.

The strong positive correlation between CEC and TOC may be explained by the fact that the soil organic matter

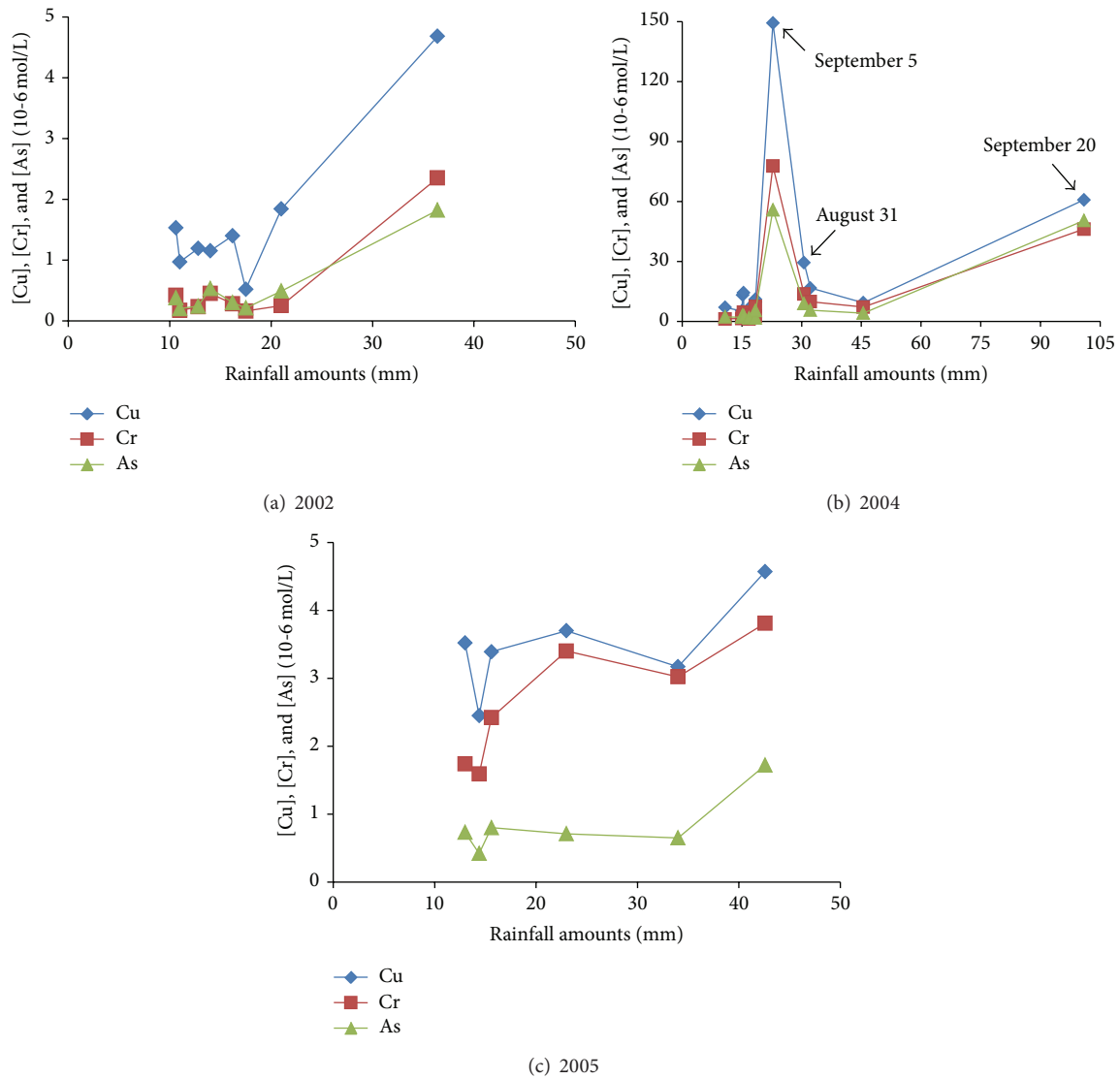


FIGURE 2: Rainfall amount of  $\geq 10$  mm and corresponding leaching of Cu, Cr, and As from the suspended log in (a) 2002, (b) 2004, and (c) 2005.

TABLE 1: Average, maximum, and standard deviation (stdev) values of Cu, Cr, and As concentrations in runoff from the suspended log and water quality guidelines [28].

	2002 Average, maximum, and stdev (of 14)	2004 Average, maximum, and stdev (of 33)	2005 Average, maximum, and stdsev (of 11)	Limit for drinking water	Limit for fresh water	Limit for marine water	Limit for livestock	Limit for irrigation
Cu ( $\mu\text{mol/L}$ )	3.85 33.4 8.56	12.8 149 26.9	3.26 5.17 1.00	15.7 <sup>1</sup>				
Cr ( $\mu\text{mol/L}$ )	2.74 31.5 8.31	7.08 77.7 15.0	2.79 5.48 1.23	0.961				
As ( $\mu\text{mol/L}$ )	1.53 14.0 3.63	5.70 55.8 12.4	1.13 2.60 0.625	0.133	0.067	0.167	0.334	1.33

<sup>1</sup> Aesthetic objective, [28].

TABLE 2: Average and standard deviation values of pH, CEC, and TOC for soil samples collected along each transmission line.

TL	pH average, stdev, and range	CEC average, stdev, and range (meq/100 g)	TOC average, stdev, and range (%)
227	4.9	29.3	3.71
	0.789	19.2	2.94
	4.1–7.3	0–71.3	0–10.2
225	6.1	12.2	1.45
	1.05	4.71	0.889
	4.2–7.6	5.5–23.3	0–10.2
259	5.0	13.9	1.56
	0.870	7.30	1.20
	4.1–6.3	5.7–21.5	0.4–3.9

TABLE 3: Details related to the sampling of soils along the three TLs.

TL	Age (y)	Poles sampled	Location	Comments	Precipitation, monthly average (mm)
227	1	14	Gros Morne	Coastal	95.2
225	2	8	Deer Lake	Inland	88.8
259	13	4	Gros Morne	Coastal	102.5

contains a large proportion of carboxyl groups that dissociate and contribute to negative charge and result in a high CEC [30]. It was determined by Zagury et al. [6] that organic soils had higher CEC values than clay soils and that an organic matter contribution to CEC would be greater than a clay contribution.

Table 2 is showing more similar pHs of soils along the parallel TLs 227 and 259, though soils along the more coastal TL 227 had double the organic matter content, indicating more organic enrichment of soils nearer the coast.

Most of the soil samples were slightly acidic in pH and about 40% had TOC contents in the range of 0 to 1%. It has been found that leaching of Cu from CCA timber increased in more acidic soils [31] whereas [32] found the leaching of Cu increased in more alkaline soils. As was seen with the suspended log, heavy precipitation and damp conditions appeared to have a significant effect on the leaching of Cu, Cr, and As.

**3.3. Soil Sampling at 0, 30, and 60 cm Distances from the Utility Poles and Precipitation Effects.** Details related to the sampling of soils are summarized in Table 3. The ages of the poles indicate how long they had been exposed to precipitation at the time that the sampling was undertaken in July 2002. The last column of the table is the estimated average monthly precipitation from the time that the pole was installed until the time that the samples were collected. The Deer Lake A station (49°13' N, 57°24' W, and EL 21.90 m) was used to determine the precipitation for TL 225. The station at Cow Head (49°54'42 N, 57°47'20 W, EL 15.2 m, Figure 1(a)), through which TL 227 runs, was used to determine the precipitation for TL 227 and parallel TL 259 [25].

TABLE 4: Mean and standard deviation (stdev) values and results of an unbalanced ANOVA of the Cu, Cr, and As concentrations at 0 cm from the utility poles of TLs 227, 225, and 259.

TL	Mean and stdev [Cu] (mmol/kg)	Mean and stdev [Cr] (mmol/kg)	Mean and stdev [As] (mmol/kg)
227	10.8	3.57	4.12
	9.37	3.74	3.60
225	4.11	1.55	1.20
	1.80	0.960	0.957
259	19.1	21.8	13.7
	10.7	29.3	16.9
P values	0.019292	0.014372	0.018510

The results of the least squares linear regression analysis of soil samples with distance from the utility poles for Cu, Cr, and As concentrations are shown in Figures 3, 4, and 5, respectively. These figures indicate trends of decreasing Cu, Cr, and As concentrations with distance from the poles since, for all but two metals on TL 259 for which only four poles were sampled, this trend is statistically significant. Usually both linear and exponential decreases in metal concentrations fit the data but in each case the line that gave the best fit or highest  $R^2$  value is shown on the figure. Decreasing Cu, Cr, and As concentrations with distance from the poles was also reported by Zagury et al. and Hingston et al. [6, 14].

Figures 3, 4, and 5 show that the greatest scatter for each TL and for each metal is at the 0 cm distance and the trend in metal reduction with distance from the pole is most pronounced for Cu.

The results of the ANOVA comparing the effects of rainfall amounts among the three TLs, along with the mean and standard deviation values for each TL at 0 cm (Table 4), indicate that at least two of the TLs are different from each other for each metal and show that for all three metals the average metal concentrations are highest along TL 259 (also apparent from Figures 3, 4, and 5) and lowest along TL 225. These relative metal concentrations can be seen to be in proportion to the average monthly precipitation amounts in Table 3.

The results of the pairwise comparison of the TLs using Tukey's procedure, required to confirm significantly dissimilar leaching of metals from the TLs, are presented in Table 5. The minimum differences in means or  $T$ -values between TLs compared to the actual differences in means confirm with 95% confidence that TLs 225 and 259 are different for all metals (bolded fonts) and that TLs 227 and 259 are different for Cr and As (bolded fonts). The least dissimilar TLs were TLs 227 and 225. These results could be explained by combinations of pole age, average monthly rainfall, and excess CCA being leached out of the newest poles.

Ultraviolet exposure plays a major role in the weathering of CCA-treated wood and the leaching of Cu, Cr, and As and [7, 33, and a reference therein] report that leaching is greater from weathered wood. Weathering by rain, wind, sun, salts, and temperature changes could assist in releasing the CCA components from the wood. Increasing pole age would

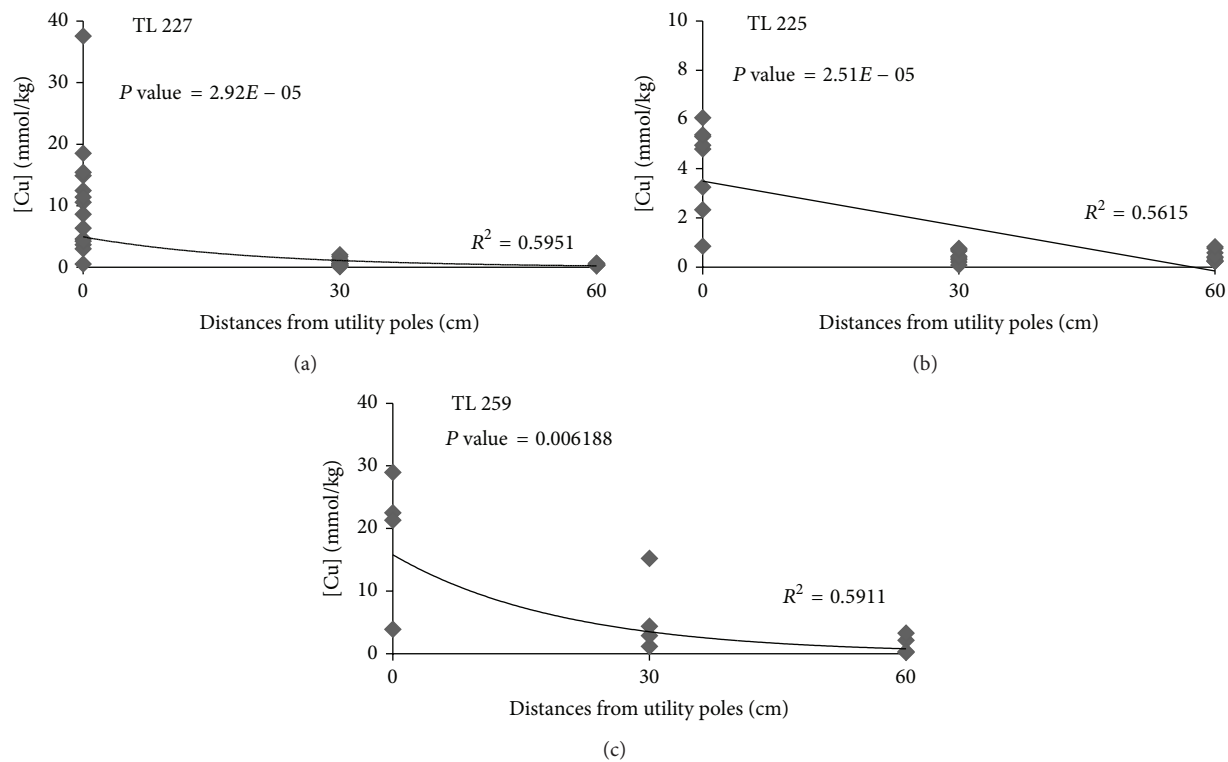


FIGURE 3: Concentrations of Cu at 0, 30, and 60 cm from TLs 227, 225, and 259 with *P* values from the regression analysis and *R*<sup>2</sup> values for the trend line fit.

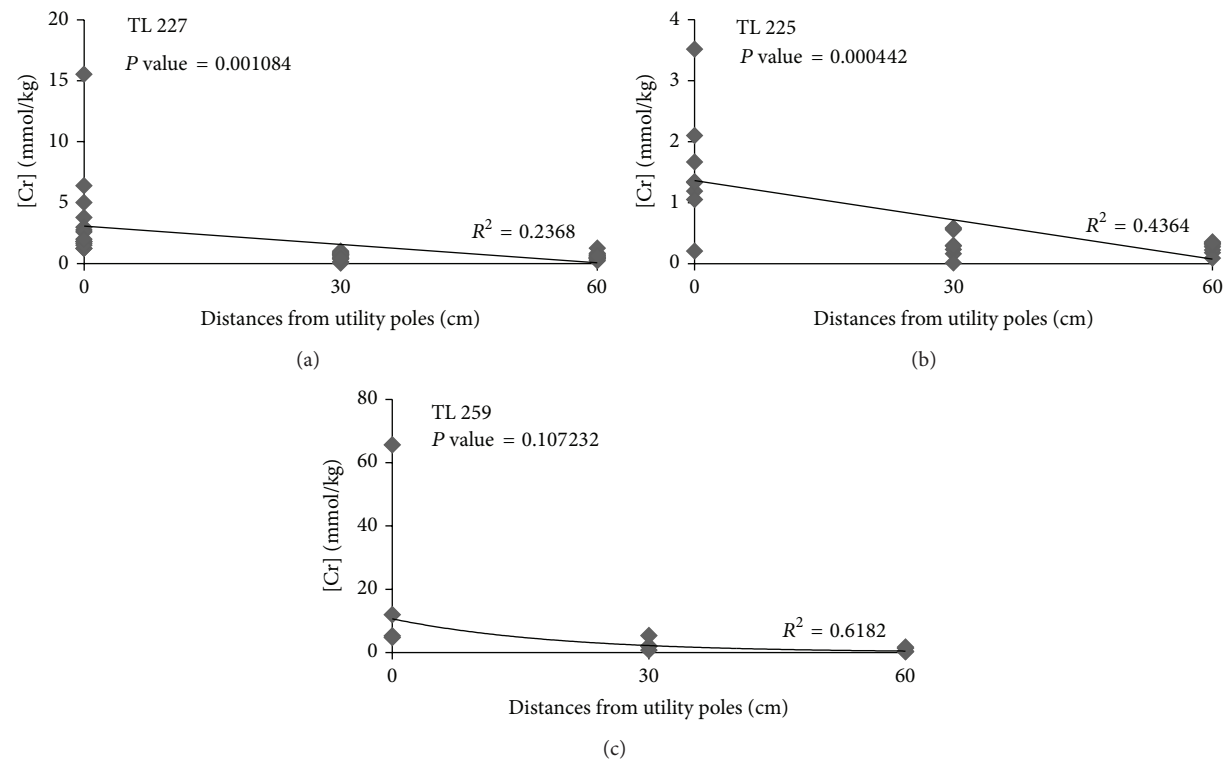


FIGURE 4: Concentrations of Cr at 0, 30, and 60 cm from TLs 227, 225, and 259 with *P* values from the regression analysis and *R*<sup>2</sup> values for the trend line fit.

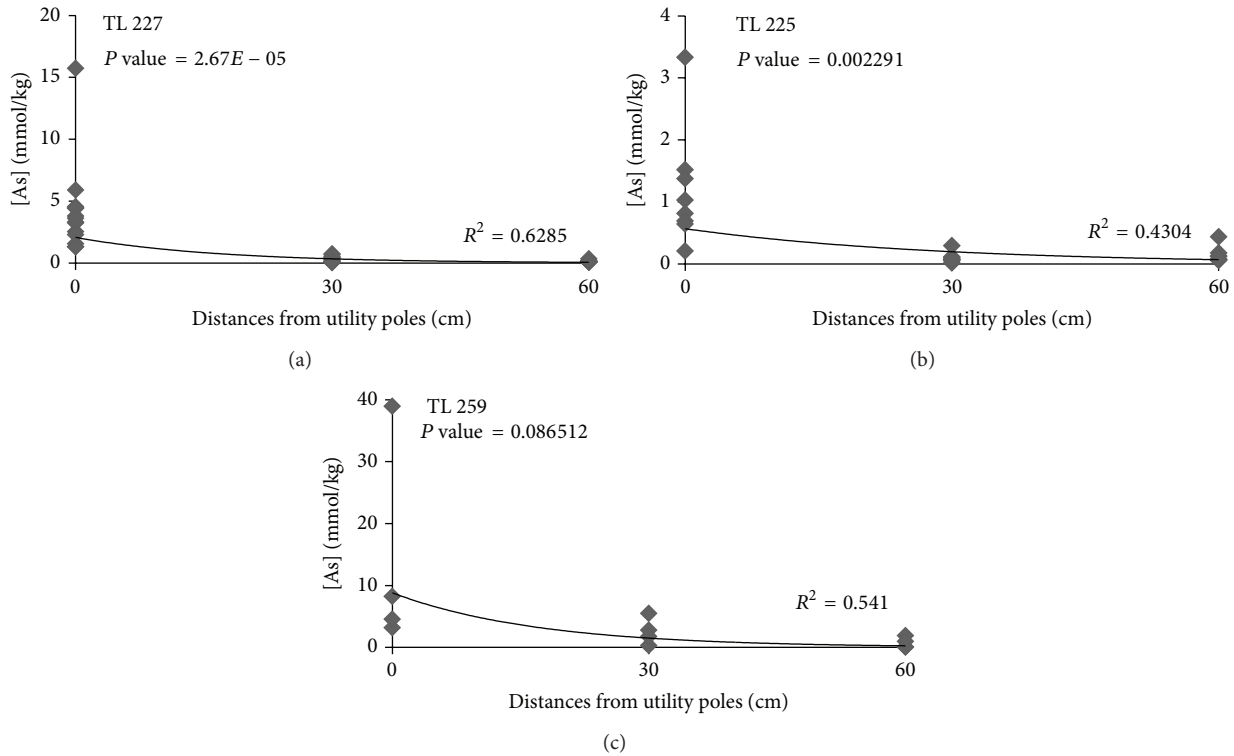


FIGURE 5: Concentrations of As at 0, 30, and 60 cm from TLs 227, 225, and 259 with  $P$  values from the regression analyses and  $R^2$  values for the trend line fit.

TABLE 5: Results of pairwise comparison of TLs with Tukey's procedure show the minimum differences in means ( $T$ -values) necessary for TLs to be significantly different (with 95% confidence) with shaded areas showing dissimilar pairs.

TLs compared	[Cu] (mmol/kg)		[Cr] (mmol/kg)		[As] (mmol/kg)	
	$T$ -values	Actual	$T$ -values	Actual	$T$ -values	Actual
227 & 225	8.98	6.67	10.0	2.02	6.14	2.92
227 & 259	11.5	8.32	15.5	<b>18.2</b>	9.52	<b>9.61</b>
225 & 259	12.4	<b>15.0</b>	16.8	<b>20.2</b>	10.3	<b>12.5</b>

normally increase the exposure of the pole to weathering. There may also be a "significant wash-off effect" with newly treated poles [4].

The least dissimilar and closest in age TLs were the 1-year- and 2-year-old TLs (227 and 225). The most dissimilar pair of TLs, 225 and 259, experienced the greatest difference in average monthly rainfall amounts (13.7 mm) in addition to having an age gap of 11 years. The reason TLs 227 and 259 were less dissimilar than TLs 225 and 259, despite the age gap of 12 years, was likely due to extra leaching from the 1-year-old poles and less difference in the average monthly rainfall amounts (7.3 mm). Rainfall amount was also important for leaching of metals from the suspended log.

With partitioning of metals between the soil and pore fluid phases, one portion of the metals is retained and another portion migrates, and to some extent metal retention by soils increases with metal concentration. More metals could have been able to accumulate in the soils of the 13-year-old poles

(TL 259). Using the mean metal concentrations in Table 4, the ratio of metals in the soils at 13 years compared to 1 year are 1.77 (Cu), 6.10 (Cr), and 3.33 (As) and compared to 2 years are 4.64 (Cu), 14.0 (Cr), and 11.4 (As). More Cu being removed early on from the suspended log could explain the more similar Cu removal at 1 and 13 years (Tables 4 and 5). The greatest relative accumulation of Cr in the soils by 13 years may be indicating that Cr was the least mobile. There was less As than Cr accumulation in soils by 13 years which could mean that As was more mobile than Cr, something also noted by Zagury et al. and Stilwell and Gorney [6, 12].

Under flooding, anaerobic conditions (such as a torrential and prolonged rainfall that is causing the soil to become saturated), arsenate (V) is reduced to arsenite (III) and any As (V) bonded to the soil could be released as As (III) [34]. Such mobilization of As (III) could facilitate its downward migration (potentially to the groundwater) as long as the heavy rainfall persists. If reducing conditions are combined



with lower pH as observed for the coastal soils along TLs 227 and 259, arsine gas, and dimethylarsine could also form and be released to the atmosphere [34].

The less mobile Cr (III) is likely to occur when organic matter and inorganic iron compounds are present in soils [17]. Anthropogenic Cr (VI) discharged to the environment is usually converted to Cr (III) which is the more commonly occurring in the environment [35]. The use of wood vinegar to extract Cu, Cr, and As from CCA-treated wood waste was the least successful for Cr [15]. Thus, there is some body of literature that supports that As could be more mobile in the environment than Cr.

When anthropogenic Cu is introduced to surface soils it has a strong affinity for organic matter and clays [36]. Even if released by surface soils it can become bonded to any reactive fine particulate soils, including organic and clay soils at depth and is not usually mobile [36]. Of the three metals, the leaching of Cu may be of least concern because it tends to remain bonded to the soil.

Comparing the proportions of Cu, Cr, and As in the CCA-C (18.5% CuO, 47.5% CrO<sub>3</sub>, and 34% As<sub>2</sub>O<sub>5</sub>) with the soil samples in this study (Table 4) leads to the conclusion that Cu was the most readily removed from the poles throughout the time periods under consideration. Another study of metal leaching from CCA treated utility poles [6] found that Cu concentrations in the soil samples were always higher than the Cr and As concentrations and [36] suggest Cu is not mobilized in soils that contain fine reactive soil particles such as organic matter or clays. For 25 of the 26 poles in this study Cu concentrations were the highest but this is not apparent for the 13-year-old poles along TL 259 (Table 4 and Figure 4) because at 0 cm from one pole (P 101) the Cr concentration was the highest and was so high that it changed the observed trend in the average values. If this particular utility pole was of low quality wood so that it was more prone to becoming weathered or if it was installed in an especially exposed location where it was more susceptible to weathering, this might explain the high levels of leaching of all metals. Among the three metals, wood vinegar most successfully removed Cu from the CCA-treated wood waste [15]. Though Cu could be the most readily removed from the utility poles, it may be well retained by the soil.

**3.4. Maximum Cu, Cr, and As Concentrations in Soils.** Table 6 shows the most extreme cases of leaching of Cu, Cr, and As from the utility poles. Only pole P101 exhibited greater leaching of Cr than Cu. Although the Cr concentration here was unexpectedly high, of all the soil samples measured at 30 and 60 cm, the highest Cr concentrations at these two distances were also observed at this pole and so this number in Table 6 is reasonable.

Although sampling was only conducted at 4 poles along TL 259, it is noteworthy that soil samples surrounding 3 of the 4 poles contained some of the highest metal concentrations. This appears to be evidence of greater leaching from the utility poles that were older, more exposed to rainfall, and more weathered as also supported by Mercer and Frostick [7].

TABLE 6: Extreme Cu, Cr, and As concentrations in soils near 1-, 2-, and 13-year-old poles.

Approximate pole age (years)	TL	Pole	Cu (mmol/kg)	Cr (mmol/kg)	As (mmol/kg)
1	227	P1-8	37.5	15.5	15.7
2	225	P19L (N)	17.3	6.12	2.48
		P121	22.4	5.19	3.19
13	259	P87	21.3	11.8	8.25
		P101	28.9	65.5	38.9

**3.5. Soil Sample Measurements at All Distances and Compared to Guidelines.** Table 7 contains the average, standard deviation, and maximum values of metal concentrations at 0, 30, and 60 cm from all of the utility poles and at 7 m from three of the utility poles. The metal concentrations at 7 m were taken to approximate the natural background concentrations of the Cu, Cr, and As in soils. For all of the samples collected at 0, 30, and 60 cm, seven of the nine highest metal concentrations were associated with pole P 101.

Arsenic is of great concern because of its known toxicity and the average As concentrations at 0 cm, 30 cm, 60 cm, and 7 m all exceeded the permissible limit in soils. The highest As soil concentration measured was 2,431 times the permissible level. Soil concentrations of As in Newfoundland and Labrador are typically high and often above the guidelines. Average Cu concentrations at 0 and 30 cm exceeded the permissible limit for Cu in agricultural and residential soils and the average Cr concentration at 0 cm also exceeded the limits for Cr in soil.

## 4. Conclusion

With regard to runoff from the suspended log, Cu leached the most in the first year, and in the final (fourth) year the Cr leached almost as much as the Cu and the As leached noticeably less than the two other metals. The wettest month in 2004 saw 205.7 mm of rain, it compared with the 29 year average for that month of 129.6 mm, it was almost twice as wet as other months during which rainfall runoff samples were collected, and it was associated with the two highest incidents of total leaching of metals from the log. Heavier rainfalls and longer durations of dampness preceding sample measurements appeared to increase the metals in the runoff. It is also possible that some contraction of the wood when warm temperatures turned cold may have squeezed more metals out of the log.

With regards to the water quality guidelines, the greatest exceedances were for As in the rainwater runoff. The average As concentration was greater than all the permissible water limits except for irrigation water and only in 2005 and exceeded by approximately 8 to 42 times the drinking water guideline limits. The average Cr concentrations in the rainwater runoff were approximately 3 to 7 times greater than the drinking water guideline limits while the average Cu concentrations in the rainwater runoff were all less than the drinking water guideline limits.

TABLE 7: Average, standard deviation, and maximum values of all Cu, Cr, and As concentrations in soils at different distances from the poles compared with permissible soil concentrations.

Average, standard deviation, and maximum values of metal concentrations of all soil samples (mmol/kg)					Permitted soil concentrations [25, 28] (mmol/kg)	
Distance from poles	0 cm	30 cm	60 cm	7 m	Agricultural, residential	Commercial, industrial
Cu	9.52	1.23	0.543	0.287	0.991	1.43
	8.34	2.52	0.595	0.102		
	37.5	15.2 <sup>1</sup>	3.20 <sup>1</sup>	0.386		
Cr	5.15	0.673	0.46	0.339	1.23	1.67
	10.8	0.879	0.340	0.237		
	65.5 <sup>1</sup>	5.24 <sup>1</sup>	1.62 <sup>1</sup>	0.484		
As	4.22	0.459	0.183	0.126	0.016	0.016
	6.57	1.00	0.337	0.173		
	38.9 <sup>1</sup>	5.51 <sup>1</sup>	1.92	0.323		

<sup>1</sup> Pole P 101 along TL 259 where most of the highest concentrations were detected.

With regards to the soil samples, there was a significant trend in decreasing metal concentration with distance from the utility poles and the greatest scatter in metal concentrations occurred at the 0 cm distance. TL 259 soil samples at 0 cm from the utility poles contained the highest metal concentrations and these poles were the most weathered because they were the oldest and had been exposed to the highest cumulative rainfall. TL 227 soil samples at 0 cm contained the second highest metal concentrations which may have been a result of a “wash-off” effect from the new poles. TL 225 soil samples had the lowest metal concentrations and these poles were exposed to the lowest average monthly precipitation.

With regards to the soil concentrations of the three metals, Cu was normally the most leached into the soil, and though the average Cu concentrations exceeded soil quality guideline limits at 0 cm and residential/agricultural guideline limits at 0 cm and 30 cm, it may have been of least concern as it tends to be more retained by the soil (or less mobile within the soil). Soil As was the most critical because the average soil concentrations of As at all distances from the poles exceeded the acceptable allowable concentrations and As appeared to be the most mobile in the soil as well. There could be cause for concern that As could leach from CCA treated timber, migrate to groundwater, and reach wells or ponds, especially if the underlying soil is porous. Soil Cr only exceeded the acceptable allowable concentrations at the 0 cm distance and appeared to be less mobile than As so of less concern than As.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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