

LEACHING OF COPPER, CHROMIUM AND ARSENIC
FROM UTILITY POLES TREATED WITH CHROMATED
COPPER ARSENATE (CCA) IN NEWFOUNDLAND
AND LABRADOR

JOSEPH ABRAHAM ARISI





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Canada

**Leaching of Copper, Chromium and Arsenic from utility
poles treated with Chromated Copper Arsenate (CCA) in
Newfoundland and Labrador.**

By

Joseph Abraham Arisi

Thesis submitted to School of Graduate Studies
In partial fulfillment of the requirements
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St Johns, Newfoundland, Canada.

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Abstract

Chromated Copper Arsenate (CCA) is a timber preservative used to treat utility poles in Canada. The aim of this study was to determine (i) the amount of leaching of Cu, Cr and As from utility poles and diffusion of Cu, Cr and As into soil under natural conditions (ii) the variation in concentration of leaching of Cu, Cr and As with pole age, (iii) the temperature effects on leaching of Cu, Cr and As (iv) the effect of amount of rainfall on the rate of leaching of Cu, Cr and As (v) the other climatic effects on leaching of Cu, Cr and As and (vi) soil properties like 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 three background samples were collected at a distance of 7.0 m from the poles. Also a freshly treated, 1.50 m long wooden log 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 Cu, Cr and As were being continuously leached from the poles over time. 13-yr poles leached the highest amount of concentration of Cu, Cr and As followed by 1-yr old poles and then 2-yr old poles. 1-yr old poles leached more As than Cr. 13-yr-old poles leached the highest amount of Cr. North or South directions from the poles generally

had the highest amount of leaching. The leaching was more dependent on amount of rainfall than temperature. A correlation between the soil CEC and TOC was observed.

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List of Abbreviations and Symbols

CCA	Chromated Copper Arsenate
PMRA	Pesticide Management Regulatory Authority
USEPA	United States Environmental Protection Agency
TOC	Total Organic Carbon
CEC	Cation Exchange capacity
ACQ	Alkaline Cu Quaternary
E_h	Redox Potential
Cu	Copper
Cr	Chromium
As	Arsenic

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Chapter 1

Introduction

1.1 The Problem

Electrical power is a fundamental requirement of a modern society. Utility poles, mostly made of timber in Canada, play a key role in transmitting electrical power to all household users in the society. There are around 200,000 timber utility poles in Eastern Canada alone (Zagury et al., 2003). These poles are treated with wood preservatives to avoid the deterioration due to insect, bacteria, and fungi attack. Chromated Copper Arsenate (CCA) is widely used as a utility pole preservative. (Hingston et al., 2001; Khan et al., 2004). The leaching of CCA from utility poles is a problem as it results in leaching of Copper (Cu), Chromium (Cr), a carcinogen in its (+VI) oxidation state, and Arsenic (As), another carcinogen (Massara et al., 2004; Alloway, 1990).

On April 3, 2002, Health Canada's Pest Management Regulatory Agency (PMRA) in its re-evaluation Note REV2002-03 announced a voluntary ban on CCA treated wood preservative products for non-industrial use by 31 December 2003 (Health Canada, 2002). As part of this ban, wood treaters would no longer use CCA to treat wood for non-industrial uses such as play-structures, decks, and residential fencing, but CCA would still be used for industrial applications such as highway construction, utility poles, and pilings. On June 2, 2006, Health Canada's PMRA issued another re-

evaluation note REV2006-07. In this report it gave guidance to the wood industry about the use of CCA products and stated “All labels are undergoing a second revision to indicate more clearly the permitted uses of CCA”. PMRA is currently working with a United States Environmental Protection Agency (USEPA) organization reviewing a further ban for CCA products for industrial applications like utility poles. Therefore, it is necessary to find clear levels of leaching of CCA from the utility poles and their mobility into soil. In order to clearly know about CCA mobility into soil, it is necessary to know the soil properties. If leaching substances enter the groundwater serious hazards may be present.

The general lifetime of a utility pole is typically 30 to 40 yrs (Stewart, 1996) and that of other treated wood products is estimated to be about 25 yrs (Mulligan et al., 2003). It is then disposed in solid waste landfills. By 2020 around 16 million cubic meters of treated wood would be removed from service and dumped or disposed in Construction and Demolition (C&D) Debris Landfills (Cooper, 1994). There is a serious public concern about disposal of preservative treated wood products into the Construction and Demolition (C&D) Debris landfills (Sharma and Reddy, 2004). The leaching of Cu (Cu), Cr (Cr) and As (As) from the CCA treated utility poles from landfills into soil and entering groundwater table is a definite problem. An estimated amount of 9,425 kg/yr of As, a carcinogenic substance present in CCA treated utility poles is land filled in Construction and Demolition (C&D) Debris landfills (Environment Canada, 2003). Thus there is a serious hazard for the ground water

table due to leaching of carcinogenic substances from utility poles that are disposed as wastes in landfills.

1.2 Background Information

CCA is a PMRA registered pesticide used in timber preservation. The preserved timber is used in a wide range of structures such as decks, playground equipment, fences, docks and utility poles. CCA preserves the timber by killing insects, fungus, and other organisms that attempt to use the timber as food or shelter. Depending upon the amount of Copper oxide CuO , Chromium oxide CrO_3 and Arsenic oxide As_2O_3 present in CCA, it can be divided in to 3 types namely Type A, Type B and Type C. Type A contains 18.1 % CuO , 65.5 % CrO_3 and 16.4 % As_2O_3 , Type B contains 19.6 % CuO , 35.3 % CrO_3 and 45.1 % As_2O_3 and Type C the contains 18.5 % CuO , 47.5 % CrO_3 and 34.0 % of As_2O_3 . Type C is most widely used preservative in Canada (Hingston et al, 2001). In recent years, there has been growing public concern with CCA wood. This is due to findings that Cu, Cr, and As have been leaching from CCA. This indicates that Canada and United States of America are aware of some of the problems associated with the use of CCA, however many other countries will continue to use CCA for some time.

Soil samples were collected to determine the amount of Cu, Cr and As present in soil using acid digestion test followed by Inductively coupled Plasma Mass Spectroscopy Analysis (ICP–MS). Some of the soil properties like pH, Total Organic Carbon

(TOC) and Cation Exchange Capacity (CEC) were found by methods like 1:2 soil: 0.01 M CaCl_2 ratio method, modified Walkely-Black wet oxidation method, $\text{Ca}(\text{OAc})_2 - \text{CaCl}_2$ method respectively.

This work will provide field trial values for leaching of CCA from utility poles and binding of Cu, Cr and As to soil. It also describes the effects of rainfall, wind and pole age on leaching of CCA. It further provides an understanding about the characteristics of the soil around the poles studied. These results of this may help in changing the regulations related to use of CCA in Canada.

1.3 The Objective

The objective of this research is to provide a thorough understanding of leaching of the CCA preservative from utility poles into the soil. To achieve this objective the chemical properties of soil like pH, total organic carbon (TOC) and CEC were examined. Metal concentration variations with distance from the poles were determined. Leaching tests were conducted on a wooden log under conditions that closely resembled natural field conditions. Metal concentrations in runoff from the wooden log were determined to obtain an estimate of runoff in the field. Metal retention in soil was examined. Metal concentration variations with pole age were also determined. The relationship between the soil characteristics and binding of Cu, Cr and As to soil was established. Figure 1.1 shows clearly the different procedures followed in the research.

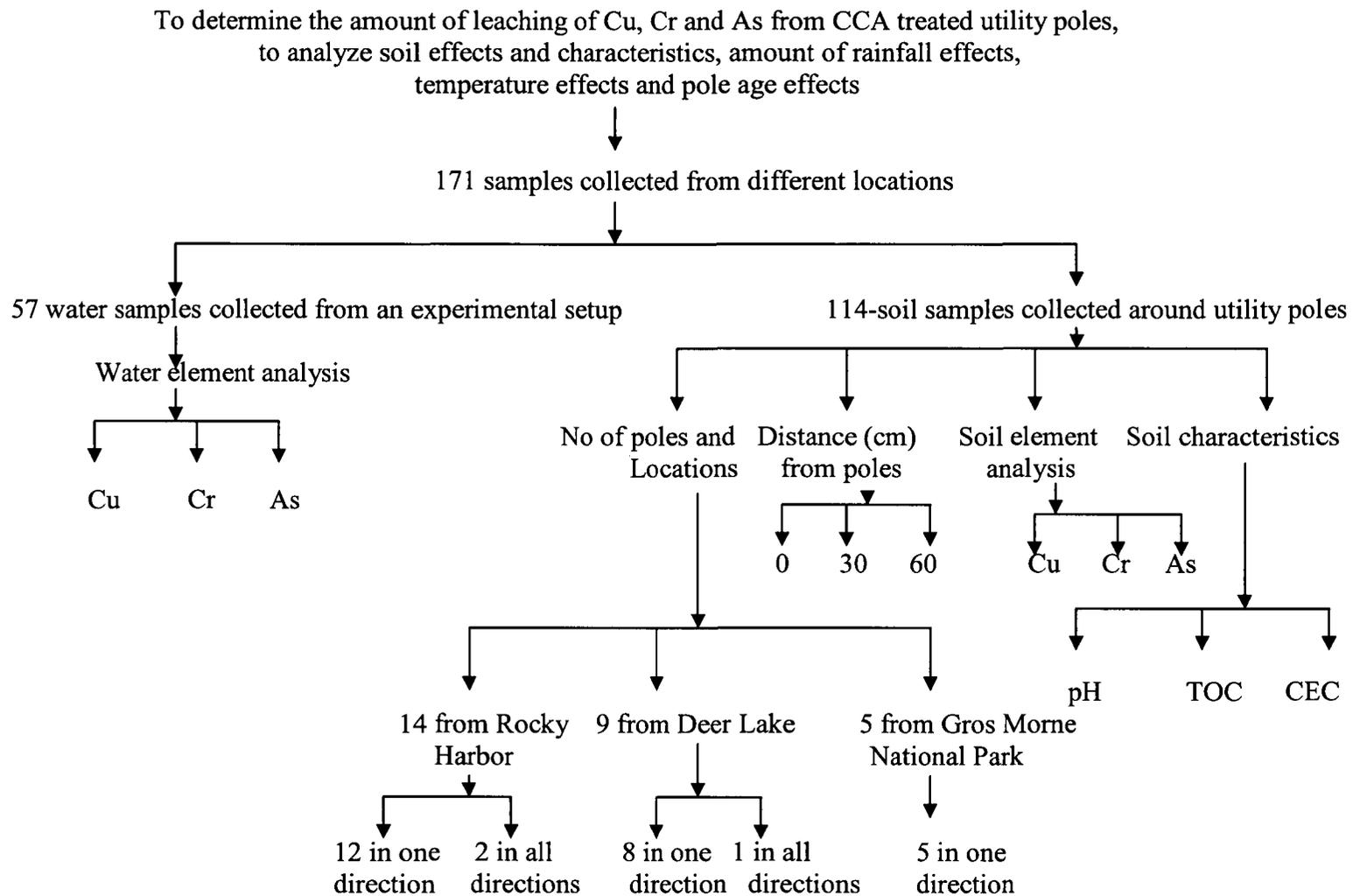


Figure 1.1 Outline of experimental procedure and analysis

1.4 Organization

The chapters in this thesis are organized in the following manner. Chapter 2 contains a literature review and theory for the thesis. Chapter 3 describes the materials and experimental methods used. Chapter 4 contains the results and discussions. Final chapter (Chapter 5) contains conclusions, recommendations and suggestions regarding research. Appendix A contains all data for soil samples 0, 30 and 60 cm away from poles. Appendix B contains all data for water samples collected from a wooden log. Appendix C contains average values of soil characteristics for each pole. Appendix D contains data for drop in concentration of Cu, Cr and As from 0 cm to 30 cm away from each pole.

Chapter 2

Literature Review and Theory

2.1 Soil

Soil is a variable mixture of minerals, organic matter, microorganisms, water and air. It is formed by weathering action of physical, chemical and biological process on rocks. About 90 % of soil is composed of small particles of rocks (Manahan, 1994). The soil particles consist of clay minerals, amorphous materials and different oxides (Yong, 2001). The remaining 10 % consists of organic matter, microorganisms, water and air (Manahan, 1994). The organic matter serves as a source of food for microorganisms and can undergo chemical reactions such as ion exchange. The organic compounds in the soil are humus, fats, resins waxes, saccharides and phosphorous compounds. The amount of organic matter in soil is strongly influenced by temperature and by the availability of oxygen (Manahan, 1994). In colder climates and in water logged soil the biodegradation of organic matter decreases (Manahan, 1994).

Humus is decomposed soil organic matter. It is composed of a strong base soluble fraction called humic acids, an acid soluble fraction called fulvic acids and a strong base insoluble fraction called humin (Yong, 2001). Molecules of humic substances

contain both polar and non-polar structures and are called amphiphiles. Humic materials in soil adsorb heavy polyvalent cations.

Soil pH is a measure of the acidity or alkalinity in the soil. It is a measure of the negative logarithm of the hydronium (H_3O^+) ion concentration. A pH below 7 is acidic and a pH above 7 is alkaline. Soil pH influences the solubility of nutrients, affects the activity of microorganisms responsible for breaking down organic matter and affects most chemical transformations in the soil (Manahan, 1994).

Soil contains particles with variable charges on their surfaces. These charges are due to the presence of inorganic constituents and organic matter. The inorganic constituents such as sesquioxides are amphoteric in nature and hence constitute variable surface charges (Bowden et al., 1980). Iron hydroxides (FeOH) and Aluminium hydroxide (AlOH) groups are predominantly present on the surfaces of the soil particles. Changing the pH of the soil can vary the charges on the surfaces of soil particles. At low pH the soil particle surfaces carry a net positive charge. The pH condition of soil at which the sum of all charges on its surface is equal to zero is called as point of zero charge (p.z.c.) (Bowden et al., 1980).

2.2 Chemistry of Metal Retention

The surfaces of soil particles are very active chemically and the surfaces are negatively or positively charged or electrically neutral. Two mechanisms are involved in the retention of Cu, Cr and As by soil (Evans, 1989). They are:

1. the adsorption reaction mechanism, and
2. the precipitation reaction mechanism.

2.2.1 Adsorption Reaction Mechanism

The Cu, Cr and As are adsorbed either by the formation of relatively weak outer sphere complexes with soil particles through cation exchange reaction or by the formation of strong bond inner sphere complexes through ligand exchange reactions. The weak outer sphere complex occurs when the ions bind indirectly to the surface of soil with intervening water molecules whereas the strong bond inner sphere complexes occur when the ion binds directly to the surface of the soil with out intervening water molecules (Evans, 1989).

2.2.1.1 Cation Exchange Reaction

Positively charged cations in solution are attracted by electrostatic or columbic forces to the negatively charged edges and surfaces of soil particles. The cations do not form covalent bonds with the surface but rather retain their water of hydration to form outer sphere complexes. Only a weak association is formed between the adsorbed ion and the soil particle. Such adsorption is referred to as non-specific adsorption or cation exchange reaction. Because of the weak association, the adsorbed ions are easily exchanged by other cations to form similar outer spheres complexes. The

cation exchange mechanism is important for alkali elements such as lithium, sodium and potassium and alkaline elements like beryllium, magnesium, calcium, strontium, barium and radium (Evans, 1989).

The cation exchange process is described in terms of the diffuse double layer model in which the exchangeable cations are believed to reside in both of the layers, the one adjacent to the charged surface and the other in an adjacent diffuse layer. For some cations involved in the ion exchange reaction the process is rapid, stoichiometric and readily reversible (Evans, 1989).

2.2.1.2 Ligand Exchange Reaction

Many metallic cations and most anions can form inner sphere complexes with charged mineral surfaces through a process of ligand exchange. The specific adsorption or ligand exchange involves the formation of covalent bonds. The covalent bonds are strong and cannot be easily displaced. Hydrolyzable elements such as transition Cu, Cr and As and rare earths, can form inner sphere complexes with oxides, oxyhydroxides and hydroxides, which are present on the soil surface (Evans, 1989).

2.2.2 Precipitation Reaction Mechanism

In this mechanism Cu, Cr and As are precipitated as secondary minerals in soil and hence called a precipitation reaction mechanism. Oxides, hydroxides and carbonates are mostly precipitated in soil. (Evans, 1989)

2.3 Timber

2.3.1 Timber Structure

Timber is most widely used in the construction and the power industry in North America. The cross section of timber (Figure 2.1) can be divided into four divisions namely bark, Cambium wood pith and wood rays (Desch, 1981). Bark is the outermost part of the timber, Cambium is a thin layer between the bark and the wood, which produces bark on the outside and wood on the inside. Wood is the main part of the timber and is divided into sapwood and heartwood. Sapwood is the youngest layer produced by the cambium. It is softer and lighter. Heartwood provides mechanical rigidity, and is denser and darker in color than sapwood. The dark coloration of the heartwood is due to the presence of complex organic compounds called extractives. The pith is a small center core of the timber. Wood rays are tissues, which connect various layers of cells from pith to bark. Timber is debarked and moisture is removed before being used in the utility pole industry. The chemical composition of timber mainly consists of cellulose, lignin, hemi cellulose extractives and ash forming minerals. Cellulose comprises about 50 %, lignin may range from 16 to 33 %, hemi cellulose may range form 20 to 30 %, extractives may range from 5 to 30 % and Ash-

forming minerals may range from 0.1 to 3 % (US Department of Agriculture Forest products Laboratory, 1974).

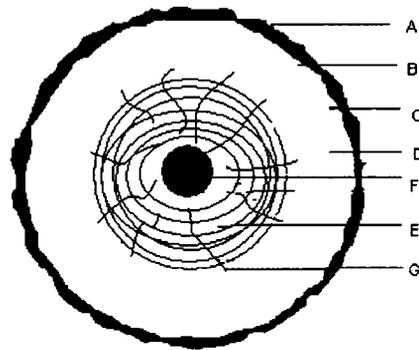


Figure 2.1 Cross section of timber: (A) outer bark, (B) inner bark, (C) cambium, (D) sapwood, (E) heartwood, (F) pith, and (G) wood rays (Adapted from US Department of Agriculture Forest products Laboratory, 1974).

2.3.2 Biodegradation

Dry timber will not undergo decaying. Fungi, insects and marine borers can decay or destroy moist timber (Schwarze et al., 2000). In order to attack timber the moisture content of the wood should be more than 30 % (Schwarze et al., 2000). Fungi attacking timber are divided into (i) Timber decaying fungi and (ii) Timber staining fungi.

Timber decaying fungi may grow in the interior or exterior of the wood. During growth they may form fan, threadlike or root like shapes. They are further divided into white rots, brown rots and soft rots. White rots break down lignin and cellulose.

The decayed timber appears white in color, soft and spongy. Brown rots decay the cellulose and hemi cellulose, leaving behind brownish wood lignin. Timber affected by brown rot is usually dry and fragile and readily crumbles because of longitudinal and transverse cracks (Schwarze et al., 2000). Soft rots decay cellulose, hemi cellulose, and lignin. They usually affect timber with very high moisture content.

Timber staining fungi do not reduce the strength of wood but they affect the appearance by staining the wood. They are divided into sap staining fungi and mold fungi.

Brushing or planing the wood cannot remove the stain caused by sap staining fungi whereas for mold fungi, brushing or planing can remove the stain. The mold fungi increase the moisture content of the wood and thus help wood decaying fungi to develop.

The insects, which affect timber, are ants, termites and beetles (Schwarze et al., 2000). Termites use timber for food and shelter. Termites are able to attack dry or moist wood. Ants use timber for their shelter. Beetles use timber for food and laying eggs. The larvae burrow through wood and the young adults chew timber and make small holes in the timber.

2.3.3 Preservation

Timber must be peeled, dried and conditioned before preservation. There are two types of treatment processes involved in preservation. They are

1. a pressure treatment process and
2. a non-pressure treatment process.

The most common treatment process is the pressure treatment process. In this treatment the timber is immersed into preservatives in an airtight steel cylindrical chamber. Pressure is applied in the chamber to force preservatives into the timber. In the utility pole industry a pressure treatment process is used to treat timber poles. This process gives better penetration and retention of preservatives in the timber. In non-pressure treatments such as brushing, dipping and cold soaking, the penetration and retention of preservatives is not important since preservation is the top priority. These latter types of preservation are used in fencing posts, patios etc. (US Department of Agriculture Forest products Laboratory, 1974)

2.4 Preservatives

Preservatives are natural or synthetic chemicals which are added to different products such as wood or foods to prevent them from degradation. Honey, cold, salt and sugar are natural preservatives whereas sodium benzoate, methylparaben, chromated copper arsenate, and pentachlorophenol are synthetic preservatives. Although preservatives

are meant to be useful, often they are hazardous to the environment. For example, preservatives added to wood may leach from wood, and may reach the ground water table and contaminate it.

2.4.1 Types of Preservatives

The preservatives used for the preservation of timber can be divided mainly into two categories: (i) organic or oil based preservative and (ii) inorganic or waterborne preservatives.

Organic preservatives are compounds containing carbon dissolved in organic solvents. These compounds contain carbon components like phenol, cresols and polycyclic aromatic compounds. For example, pentachlorophenol is a white, crystalline, aromatic compound, dissolved in petroleum oil. It is shown in Figure 2.2

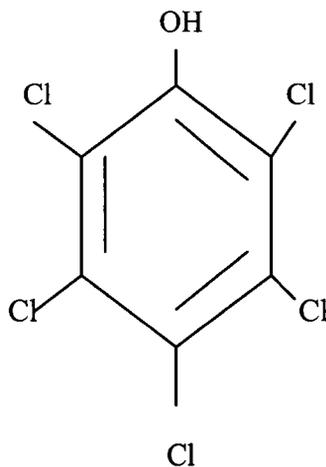


Figure 2.2 Structure of Pentachlorophenol (Modified from Ellis et al., 1998).

Inorganic preservatives are compounds that do not contain carbon components and are dissolved in water. CCA, Amomiacal copper arsenate (ACA), Amomiacal copper zinc arsenate (ACZA) and Boric oxide are some inorganic preservatives. The most commonly used preservative is CCA. It is a mixture of copper salts of chromic acid and arsenic acid (Cox, 1991) or in other words it contains copper arsenate and copper chromate. It was developed by Indian scientist Dr Sonti Kamesam (Arsenault, 1975: Rahman et al., 2004: Lihary, 1997).

Based on the amount of Cu oxide (CuO), Cr oxide or anhydrous chromic acid (CrO₃), and As pentoxide (As₂O₅) present in CCA, it can be further subdivided into 3 types. They are CCA-A, CCA-B, and CCA-C. CCA-C with 18.5% CuO, 47.5% CrO₃ and 34% As₂O₅ is most commonly used in the utility pole industry as a preservative. (Cooper, 1994). The Cu present in CCA acts as a fungicide, As acts as an insecticide whereas the Cr is responsible for fixation of CCA with wood (Lebow, 1996: Stillwell et al., 1997).

2.4.2 Manufacture of CCA

CCA is manufactured by mixing chromic acid, obtained by dissolving CrO₃ in water solution at 60% concentration, arsenic acid, obtained by dissolving As₂O₅ in water solution at 75% concentration and solid copper oxide for 2 hours to form a 50% concentrate (Environment Canada, 2002). The compounds present in the concentrate are copper arsenate and copper chromate. The concentrate is stored in a settling tank,

then filtered and transferred to a storage tank. This process is shown in the Figure

2.3

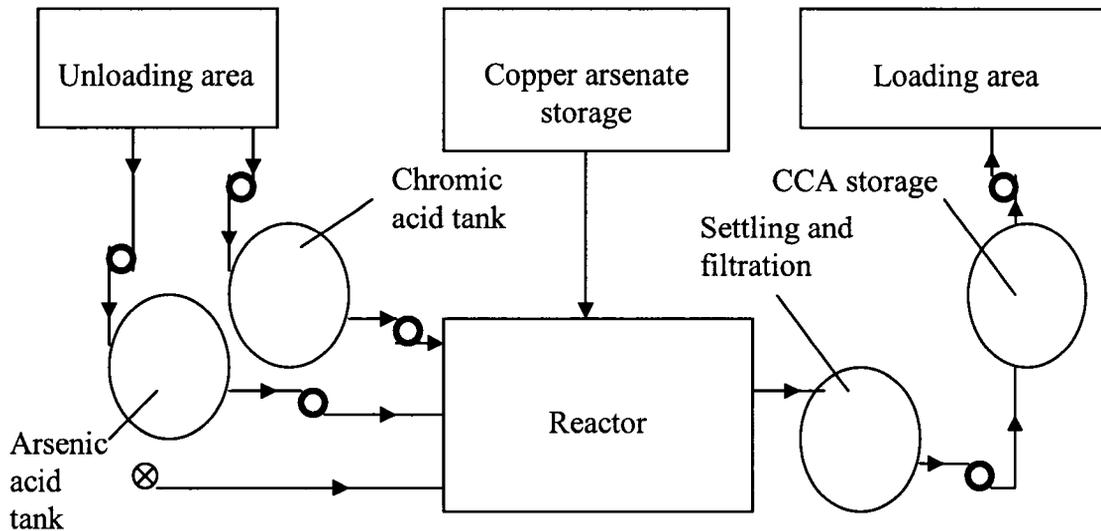


Figure 2.3 Schematic diagram for manufacture of CCA ○ Pump, and ⊗ Water control valve (Modified from Environment Canada, 2002).

2.5 CCA Fixation with Timber Utility Poles

CCA fixation is extremely important in utility pole preservation and affects the amount of Cu, Cr and As that can be leached from the utility pole. There are many factors affecting the fixation of CCA with utility poles. They are

1. wood properties (Pizzi, 1983)
2. treatment techniques (US Department of Agriculture Forest products Laboratory, 1974), and
3. product dimension (Moghaddam, 2002)

During fixation of CCA with utility poles hexavalent Cr (Cr (VI)) is reduced to trivalent Cr (Cr (III)) (Bull., 2001) The important reaction involved in this process is as follows.



According to this fixation model the final fixation products present are mainly Cr (III), Arsenate, Cr (III) hydroxide and Cu (II)- Wood Carboxylate Complexes. The larger number of carboxylate groups are generated as Cr (VI) groups are reduced. Reduction occurs by primary alcohol groups contained in the lignin and carbohydrate fractions. Cr (VI) is also used in oxidation of lignin. X-ray absorption fine structure analysis is used to support this theory (Bull, 2001)

According to Hingston et al., (2001), the fixation of CCA is not well defined; the process generally involves the reduction of hexavalent Cr. The reaction of Cr (VI) is outlined as a series of consecutive steps, which are as follows

1. initial adsorption of carbohydrates
2. reduction and a complexation reaction such as CrO_4 with lignin and cellulose, and CrO_4^{2-} complexation with lignin.

Hingston et al., (2001) also state that long-term reactions will influence the distribution of Cu, Cr and As in wood, which in turn determines the toxicity of the wood.

2.6 Leaching of CCA

After fixation of CCA into utility poles the leaching of the Cu, Cr and As from can be a problem. There are a number of processes involved in the leaching of CCA from timber. Initial reactions involve “loss of surface deposits and unfixed components, penetration of water into the wood and hydrolysis or dissolution of preservatives to the surface of the wood” (Cooper, 1994).

According to Hingston et al., (2001) many factors affect the leaching rates and they are

1. local climate
2. leaching media
3. wood properties, and
4. treatment techniques.

Montimer (1991) investigated 3 to 36 months old CCA/ Polyethylene glycol (PEG) treated utility poles and found very low concentrations of Cu, Cr and As near the poles. Cooper et al. (1997) investigated more than 50 poles and found high concentrations near the poles. Zagury et al. (2003) investigated 6 CCA/PEG treated utility poles in Montreal, Quebec and reported concentrations in soil of 1460 mg/kg for Cu, 410 mg/kg for As and 287 mg/kg for Cr. These studies did not consider the effect of rainfall on leaching of Cu, Cr and As from poles.

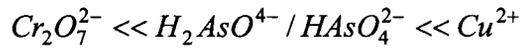
Lab studies on leaching of CCA from timber have been done to determine the effects of pH on CCA leaching rates and it has been found that leaching of Cu from CCA timber increases with reduction in pH (Hingston et al., 2001; Cooper, 1991).

Hingston et al. (2001) also stated that in field trials of Archer and Preston, in 1994, that CCA treated pine leached as much as 25 % Cu during the first six months of service and as much as 52% in the first 85 months, but did not increase beyond this value.

Baldwin et al. (1996) studied partitioning of Cu, Cr and As to sediment during laboratory leaching trials with marine piles and found that Cu bound to both low and high organic carbon sediment to the same degree and did not desorb to the overlying waters. Cr exhibited very low adsorption to high organic sediment and As was found in all cases in the interstitial levels and overlying waters.

Carey et al. (1996) examined sorption characteristics of cupric dichromate $\text{CuCr}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ and arsenate ions in two free draining soils of New Zealand. Sorption was determined both individually and in combination. From the observed sorption behavior an evaluation was made of the likely leaching potential of major elemental species present in CCA contaminated soils. The results of the study indicated that Cu sorption in soil increased with increasing pH. Arsenate sorption to soils changed little with increasing or decreasing soil pH. Less dichromate $\text{Cr}_2\text{O}_7^{2-}$ was absorbed than

arsenate and Cu, and sorption increased with decreasing pH. Carey et al., (1996) concluded the strength of sorption of the compounds for the soil decreased as follows.



They found the sorption of Cu^{2+} was pH dependent and had the highest sorption potential in high pH soils. The degree of Cu sorption was governed by the organic matter content and pH. Dichromate was weakly sorbed to the soil and is a major constituent of CCA. Since Dichromate is not retained by soil particles, it poses the greatest immediate potential threat to groundwater supplies. The sorption of arsenate depended on the presence of Fe and Al oxides. The pH of the soil had the smallest influence on the sorption of arsenate.

Lebow (1996) reported that despite the larger number of laboratory studies that had been conducted on leaching of different types of preservatives, data could not be applied to in-situ leaching rates. He also recommended further research to address the effects of different environmental conditions. Hingston et al. (2001) in his review also stated that insufficient data existed to determine leaching rates.

There are standard leaching procedures existing for laboratory tests but they are relatively simple and designed to provide easily repeatable results. These results, however, do not give accurate estimation of losses from commercial sizes of timber due to differences in size, physical stresses and environmental conditions (Hingston et

al. 2001). As a result, despite a considerable amount of literature available, the leaching rates of CCA from timber still remain poorly defined.

2.7 Toxicity of CCA

Recent toxicity tests suggest that leaching of preservative components such as Cu from wood used in aquatic environments may be harmful to the environment (Hingston et al., 2001).

CCA toxicity due to leaching concerns exist in areas where treated utility poles are stored, used and disposed. Disposal of timber treated with CCA is expected to increase in volume in the next few years (Ribeiro et al., 2000). Nearly 5 million tons of preservative treated timber is disposed of annually in US landfills (Falk, 1997) and there are growing concerns about managing wood wastes. Disposal is also expensive and approved landfills sites are scarce and will even be forbidden in some countries in the future (Ribeiro et al., 2000). As well, reactions that take place in the wood during fixation of CCA have a great influence on the metal species that are emitted from the wood (Hingston et al., 2001).

2.8 Speciation

In determining the amount of CCA released into the environment it is also important to understand the species of the components that are released. It is not clear if Cu, Cr and As are leached as individual elements, as Cu or Cr arsenates, as inorganic

complexes, or possibly as organometallic complexes bound to water-soluble wood extractives (Lebow, 1996).

2.8.1 Copper

Cu belongs to the d-block transition elements and has an atomic number of 29. Mostly Cu is specifically fixed in soils (Alloway, B.J., 1995). It hardly moves in the soil. The total Cu in soil consists of (i) exchangeable Cu, (ii) stable organic complexes in humus, (iii) Cu adsorbed by oxides of Mn, Fe and Al, (iv) Cu adsorbed on the clay humus colloidal complex, (v) soluble ions and inorganic complexes in soil and (vi) the crystal lattice bonded Cu in soil minerals. Cu fixed to organics, Fe/Mn oxides and clay minerals is hard to separate. While Cu is an essential micronutrient Cu^{2+} is toxic above trace levels. In general, Cu tends to become bonded to organic material (especially humic acids) in soils (Hung et al., 1993).

2.8.2 Chromium

Cr is a d-block transition metal with an atomic number of 24. It can be found in 9 different oxidation states (Massara et al., 2004), however in the soil two forms predominate, hexavalent and trivalent (Pagilla 1999, Massara et al., 2004). The most stable oxidation states of Cr are Cr (III) and Cr (VI). Cr (VI) exists as anions such as chromates CrO_4^{2-} , and dichromates $\text{Cr}_2\text{O}_7^{2-}$. Cr (VI) is a known carcinogen and mutagenic but when reduced to Cr (III) as in the CCA fixation process, it may be significantly less harmful (Massara et al., 2004). Cr (VI) is a strong oxidizing agent

and hence in soil Cr (VI) is reduced to form Cr (III) in the presence of soil organic matter.

Cr (III) is less mobile and adsorbs to soil particles strongly. The solubility of Cr (III) decreases above pH 4 and at pH greater than 5.5 complete precipitation occurs. Cr (III) forms stable complexes, which are retained in the soil by adsorption (Pagilla, 1999). On the other hand Cr (III) can also be mobile by oxidation to the hexavalent form or by forming complexes with naturally occurring ligands (Massara et al., 2004). When a soil's pH increases the Cr toxicity also increases (Alloway, 1995) and this is due to the formation of Cr (VI) ions in soil.

2.9.3 Arsenic

As is a p-block element, present in the nitrogen group, which constitutes the 15 (VA) group in the periodic table. As has both the properties of Cu, Cr and As and non-Cu, Cr and As (Alloway, 1995). As exists in four oxidation states (Wang et al., 2004), of which Arsenate (V) and Arsenite (III) are the predominating forms (Wang et al., 2004). Of these predominant oxidation states As (V) is thought to be the more prevalent and less toxic form than As (III) (Hingston et al., 2001). Woolson and Gjovik (1981) found As (III) comprised 3% of the As in treated wood but Nyren and Nilsson (1993) found no trivalent As present in commercial wood supplies. As has a high affinity to organic matter in the soil. This is evident by the presence of highs

level of As in alluvial and organic soil, which contains large amount of organic matter (Frankenberger, 2002). It is also known that As binds with iron and sulphur in soils.

Redox potential E_h is the tendency of elements to acquire electrons and thereby be reduced. As the redox potential increases, the electron affinity of elements increases. A reduction potential is measured in milli volts (mv).

Depending on pH and E_h values of soil, As can exist in trivalent or pentavalent forms. In oxidizing soil where E_h lies between +300 mv and +800 mv and between pH 4 to 8, one of the pentavalent forms of As acid such as H_3AsO_4 , $H_2AsO_4^-$, $HAsO_4^{2-}$, or AsO_4^{3-} will predominate (Frankenberger, 2002). In reducing soil conditions at E_h below +300 mv and pH below 4 and at E_h above 100 mv at pH=8, one of the trivalent forms of arsenious acid such as H_3AsO_3 , $H_2AsO_3^-$ and $HAsO_3^{2-}$ will predominate. The change of As (V) to As (III) is also influenced by the presence of microorganisms. Under aerobic conditions the methylation of As compounds results in the formation of monomethyl arsonic acid ($CH_3AsO(OH)_2$), dimethyl arsinic acid ($(CH_3)_2As(OH)$) and trimethyl As oxides ($(CH_3)_3AsO$). Under anerobic conditions methylarsine gas, trimethyl arsine and dimethyl arsine are formed and they are highly toxic, volatile and flammable.

The presence of clay minerals, organic matter, Fe oxides and Al oxides affect the As oxidation rate (Frankenberger, 2002). Mobility of As in soil is dependent on the stability of parent minerals and electrochemical properties. In some types of soil this As remains bound to particles and is not very mobile but in other soils the As may be

mobile and pose a hazard to ground water supplies. As is a known human carcinogen and it is acutely toxic

There are three possible main mechanisms for the As interaction with minerals. In the first mechanism the entire surface of Fe and Al oxides, which predominates the surface of soils, has bonding sites with uniform attraction towards As. This attraction can explain only a small percentage of total bound As present in soil (Frankenberger, 2002).

In the second mechanism the hydrated As ions freely diffuse throughout the loose and hydrated Fe and Al compounds. For the adsorption in this mechanism, soil pH is important. At pH 4, the pentavalent As or H_2AsO_4 is adsorbed to the maximum. At pH 7, the trivalent As or H_3AsO_3 is adsorbed to the maximum. Overall, pentavalent As shows greater capacity to be adsorbed than the trivalent As (Frankenberger, 2002).

The third mechanism can be considered for soil containing different types of minerals. Each mineral has its own attraction energies and quantities of surface hydrated oxides of Fe, Mn and Al; hence they attract differently according to their capacity (Inskeep, 2001).

Chapter 3

Materials and Methods

3.1 Materials

The materials related to this research include CCA treated utility poles, above ground soil samples collected around CCA utility poles, acids such as 36-38 wt % of hydrochloric acid (HCl), 69-wt % of nitric acid, 85 wt % phosphoric acid of (H₃PO₄) and 98 wt % of sulfuric acid (H₂SO₄), a CCA treated wooden log, sodium chloride, calcium chloride, calcium acetate, ferrous sulphate, potassium dichromate dissolved in water. The materials are described below.

3.1.1 Utility Poles

Utility poles selected for this research were from parts of the power transmission grid of Newfoundland and Labrador. The power transmission grid for the province of Newfoundland and Labrador is shown in Figure 3.1. From the above grid, 28 utility poles belonging to 3 different transmission lines (TLs) in western Newfoundland, namely Gros Morne (TL 259), Rocky Harbour (TL 227) and Deer Lake (TL 225) were selected. A closer view of these transmission lines is shown in the Figure 3.2. The Utility poles were all Douglas fir [*Pseudotsuga menziesii* (Mirb.) Franco] poles treated with CCA preservative. The transmission lines used were selected according to criteria proposed by the Electric Power Research Institute (EPRI, 1997) for penta and creosote treated poles. All poles had not been exposed to pesticides and other

contamination. They 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.

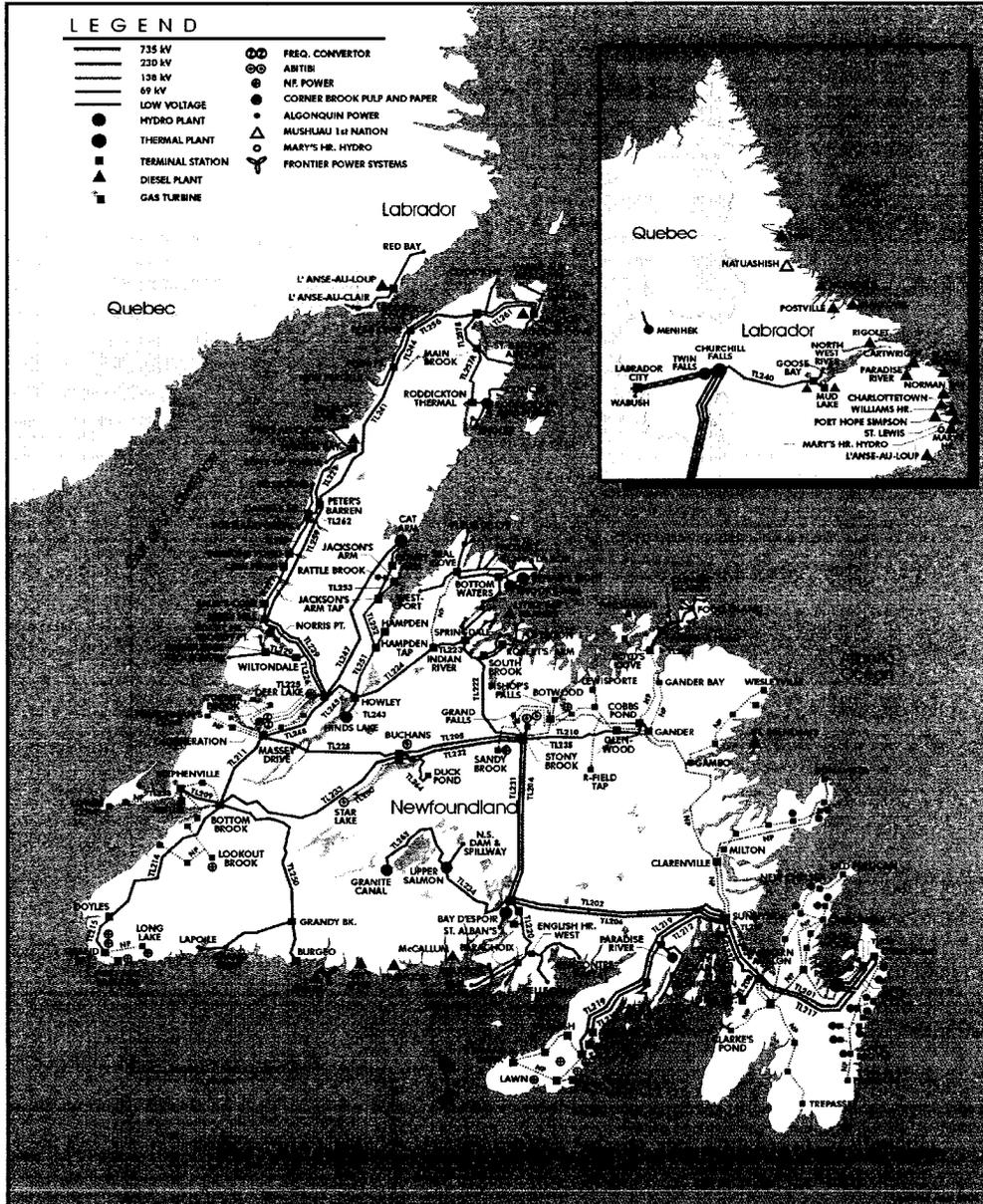


Figure 3.1 Newfoundland and Labrador power generation and transmission grid (used with permission from John Mallam, Vice President Engineering Services Newfoundland and Labrador Hydro department)

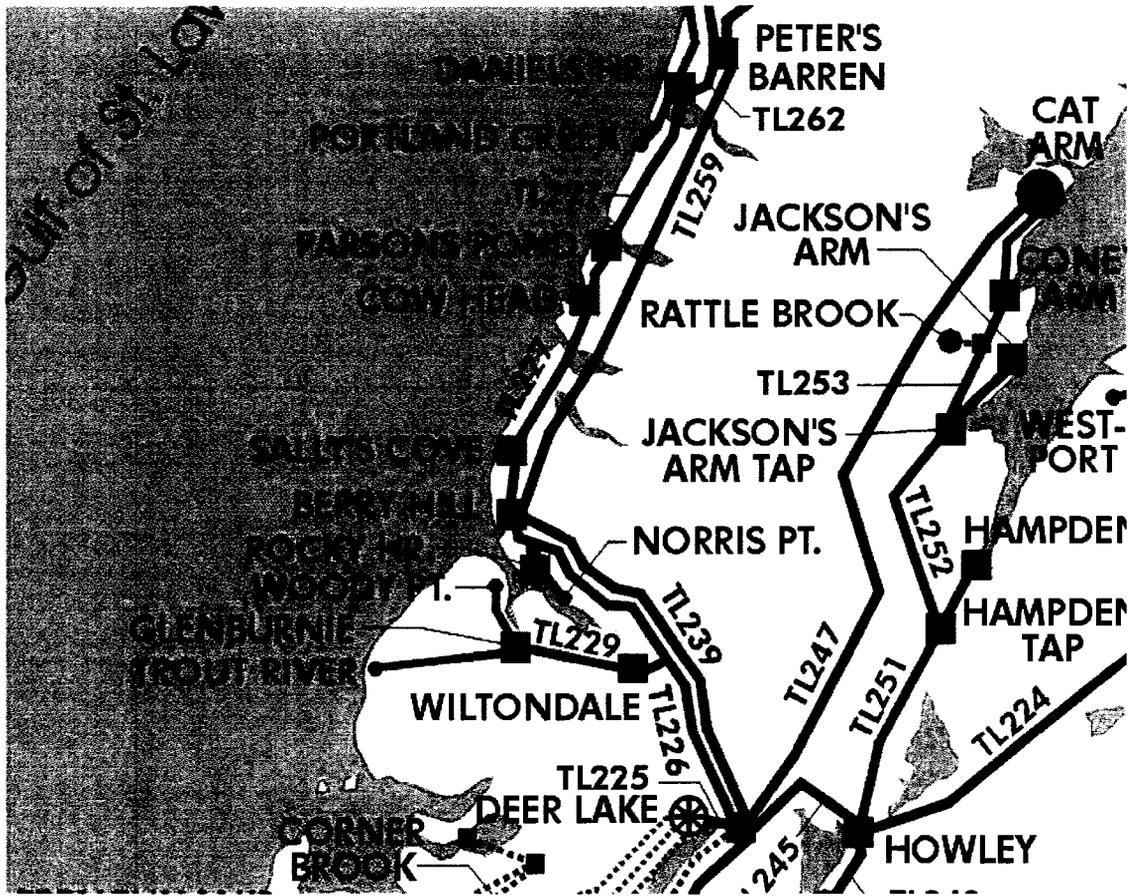


Figure 3.2 Closer view of transmission line from Rocky harbor (TL 227), Deer lake (TL 225) and Gros Morne (TL 259). (used with permission from John Mallam, Vice President Engineering Services Newfoundland and Labrador Hydro department)

3.1.2 Soil Samples

Soil samples used in this research were taken at 0, 30 and 60 cm distances from the base of 28 different utility poles. The soil particle size used in the research was <2 mm. It was obtained by sieving the samples.

3.1.3 Chemicals

All chemicals used in this research were high purity chemicals substances obtained from Fisher Scientific, A and C Chemicals or VWR.

3.1.3.1 Acids

The acids used in the research were 36-38 wt % of hydrochloric acid (HCl), 69-wt % of nitric acid, 85 wt % of phosphoric acid (H₃PO₄) and 98 wt % of sulfuric acid (H₂SO₄). 36-38 wt % of hydrochloric acid (HCl) and 69-wt % of nitric acid were used for acid digestion for soil samples. 85 wt % phosphoric acid and 98 wt % sulfuric acid were used in the estimation of soil TOC.

3.1.3.2 Other Chemicals

The chemicals used in the research were 2 N sodium chloride, 0.01 M calcium chloride, 0.9 N calcium acetate, a few drops of barium diphenylamine sulphonate as indicator, 0.5 N ferrous sulphate solutions, and 1 N potassium dichromate solution. 0.1 N Calcium chloride was used both in pH and CEC analysis and 0.9 N calcium acetate was used in the CEC analysis. Barium diphenylamine sulphonate, ferrous sulphate (FeSO₄.H₂O) solution and potassium dichromate solution were used in the TOC analysis.

3.1.4 Wooden Log

A wooden log that had been freshly treated with CCA with a length of 1.50 m and a diameter of 0.30 m in diameter, was used in this study. It was suspended vertically outside in a large plastic cylinder measuring 2.40 m high and 1.20 m in diameter. The bottom of the cylinder was connected with an outlet for runoff collection. The wooden log and cylinder were exposed to rain and snow. Runoff from the log was collected regularly over a period of 2.5 yrs. This setup is shown in Figure 3.3.

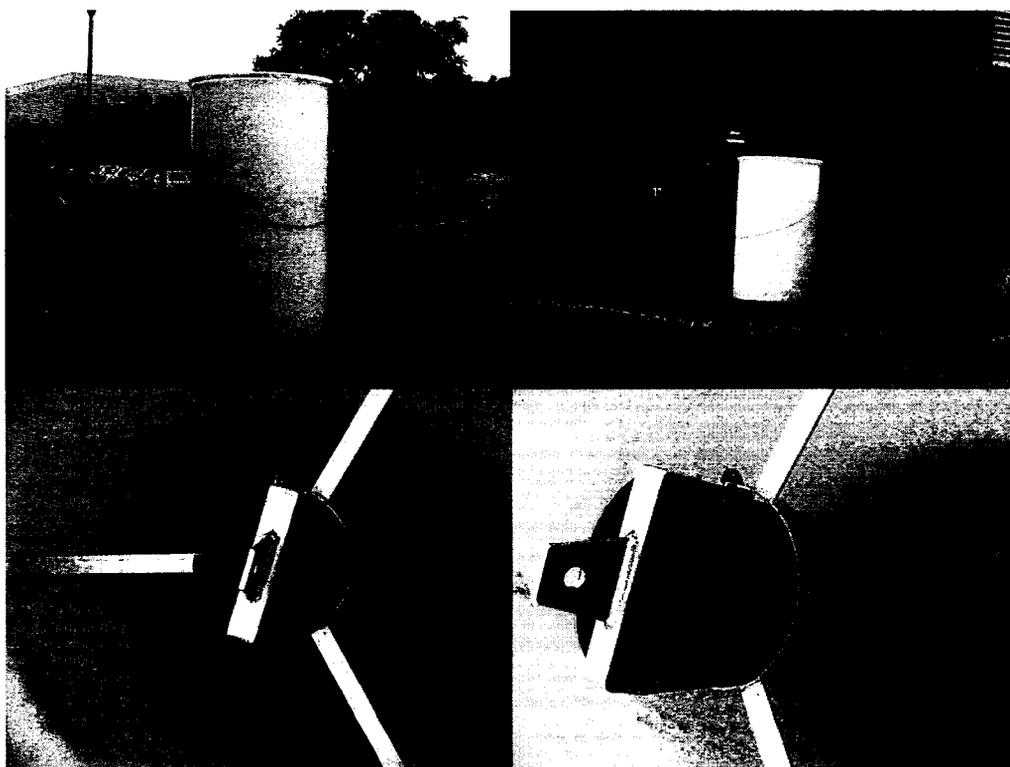


Figure 3.3 Experimental set-up for collecting Cu, Cr and As leached from CCA treated wooden log.

3.2 Methods

Based on the reading and research of several studies a methodology for sampling and analysis of soil and water was developed. The methods used are described in the following section.

3.2.1 Soil Sampling

Soil Samples were collected around 28 poles along three different transmission lines (259, 227, 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, 3 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. The plan view for one of these sites is shown in the Figure 3.2. 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 3 pole locations, soil samples were also collected at 7 m from the poles to obtain background soil conditions. 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. Samples were taken in 4 different directions at 3 different poles to see if climatic condition could affect results.

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 labeled with the date of collection, a code for each pole, the pole age, the distance, and where applicable, the direction from the pole. The code for each pole was written to identify each pole. For example 1- 32 means 32nd pole in the first kilometer of that particular transmission line. This system of coding was used because in the hydro industry, when a transmission line is under construction, the poles are initially coded by the kilometer, followed by the pole number. The poles that are only a yr old are numbered in this way. The symbols, N, E, S and W appearing in the appendices after some of the pole indicate the North, East, South and West directions.

When construction of transmission line is finished the poles are renumbered from 1 onward. Therefore for the 2 and 13 yr old poles, 19 in the coding means 19th pole in the that particular transmission line. Some poles, which do not have a pole number, are represented by a street location

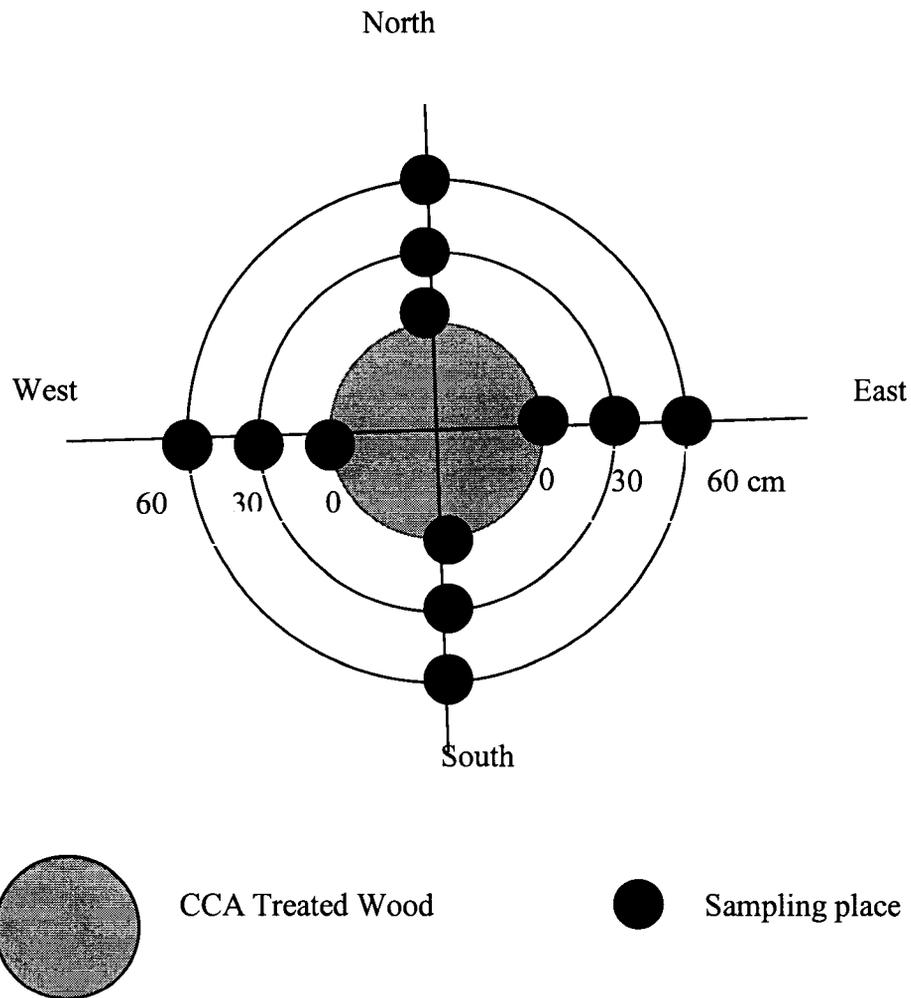


Figure 3.4 Plan view of the sampling site showing the four directions (North, South East and West) of soil collection.

3.2.2 pH Determination

The pH of all soil samples was determined by the 1:2 soil:0.01M CaCl₂ ratio method (Sheldrick, ed. 1984). Soil samples were mixed in a beaker with a 0.01M of CaCl₂ solution. A soil to solution ratio of 1 to 2 was used. After partial settling of the

suspension an electrode was immersed into the soil solution. The pH of the solution is the pH of the soil. All the samples were duplicated and the average pH was found.

3.2.3 Total Organic Carbon (TOC) Determination

The TOC determination test was conducted on soil to give an approximate indication of the total amount of the organic matter present in the soil. In this method soil samples were analyzed by the modified Walkely-Black wet oxidation method (Sheldrick, ed. 1984). 20 mg soil samples were measured and transferred into a 250 ml conical flask. 10 ml of 1 N potassium dichromate and 20 ml concentrated sulphuric acid were added to the soil under a fume hood. The contents were then mixed for 1 minute by swirling and were allowed to stand for 30 minutes. 10 ml of orthophosphoric acid was added, 150 ml of water was also added and a few drops of indicator (barium diphenylamine sulphonate) were then added and stirred using a magnetic stirrer. The flask contents were titrated against 0.5 N ferrous sulphate solutions. When the colour changed from mud brown to blue 0.5 ml of potassium dichromate was added and again titrated until the appearance of green colour in the solution. The end point was noted and used for calculating the TOC of the samples. In TOC experiments 68 % of samples were done in duplicate and the average error was 13.7 %.

3.2.4 Cation Exchange Capacity (CEC) Determination

The CEC determination test was conducted on all soil samples according to the $\text{Ca}(\text{OAc})_2 - \text{CaCl}_2$ method (Sheldrick, ed. 1984). In this method 1.0 g of soil was weighed and transferred into a 50 ml centrifugal tube. 10 ml of 0.9 N $\text{Ca}(\text{OAc})_2 + 0.1$ N CaCl_2 solution at pH 7 was added and the mixture was shaken for 30 minutes. This step was repeated once then samples were washed 3 times with 30 ml distilled water to remove free Cl^- . 15 ml of 2 N NaCl was added and shaken 30 minutes on the shaker and centrifuged. The centrifugate was transferred into a 50 ml volumetric flask. Again 15 ml of 2 N NaCl was added and shaken in a shaker for overnight. The centrifugate was then transferred to a 50 ml volumetric flask. The volumetric flask was made up to its volume by adding distilled water and stored at 4 ° C until analysis. The solution was analyzed for calcium using Inductively Coupled Mass Spectroscopy (ICP-MS). CEC for the soil was calculated based on the calcium concentration. CEC determinations were conducted in duplicate for only 10% of the samples since at least 3 samples (similar to triplicates) were available for each pole. The average error for all duplicate results was 28.7 %.

3.2.5 Acid Digestion

The acid digestion test was used to determine the amount of Cu, Cr and As in the soil samples. The method used in the research was US EPA METHOD 3050B, Acid Digestion of Sediments and Sludges and Soils 3050 B (American Chemical Society, 1986).

In this method, a block digester able to hold 20 test tubes of 250 ml was used to digest the soil samples. The soil samples were placed inside the 20 test tubes and concentrated nitric acid, concentrated hydrochloric acid and 30% hydrogen peroxide were added during digestion to oxidize all Cu, Cr and As in the soil. The temperature in the digester was kept at $95 \pm 5^\circ \text{C}$ without boiling. The digestate was filtered and diluted with water to make up to 100ml in the volumetric flasks and samples were analyzed by ICP- MS to determine levels of analysis of Cr, Cu and As.

3.2.6 Inductively Coupled Mass Spectroscopy Analysis

The CEC solutions and the digestate samples from the acid digestion were delivered to Dr Geoff Veinott at the Department of Fisheries and Ocean (DFO) where they were analysed on Perkin – Elmer SCIEX Elan 6100. The ICP-MS was calibrated with 3 different standards of Cu, Cr or As concentrations in the ranges being analyzed. The standards were prepared by dissolving known concentrations of metal in acid and water. The digestate from acid digestion was diluted further to obtain optimum concentrations to be fed to the ICP-MS. The ICP-MS is computerized so that a printout of the metal concentrations is produced when samples are aspirated. Only 10% of acid digestion experiments (for soil metal determination) were conducted in duplicate since it is known that the Cu, Cr and As concentrations tend to decrease with distance from the poles and the error was only 7 %.

3.2.7 Water Sample Collection

Water samples of approximately 200 ml were collected from the outside drum containing the wooden log after the precipitation events and were then acidified with HNO₃ to <pH 2 and stored in plastic containers at room temperature. They were water analyzed for Cr, Cu and As using the ICP-MS. One background water sample was also collected for analysis.

3.2.8 X- ray Diffraction

Eight randomly selected soil samples were ground by mortar and pestle and analyzed using an X-ray Diffractometer (XRD) to identify the mineral phases (chemical phases) present in the soil. A Regaku D/MAX 2200V – PC XRD was employed that used Cu as a target operating at 40 kV and 40 mA and computer auto search and match software tool to find the different mineral phases present in the system.

Chapter 4

Results and Discussion

4.1. Introduction

A total of 114 surface soil samples were collected around 28 Douglas fir utility poles treated with CCA, located along transmission lines 227, 259, 225, situated in Gros Morne National Park, Rocky Harbor and Deer Lake, respectively, in the province of Newfoundland and Labrador. They were analyzed for soil chemical properties such as pH, TOC and CEC and heavy concentrations of Cu, Cr and As. These results are summarized in Appendix A. The minimum, maximum and mean values of pH, TOC and CEC present in the surface soil samples are shown in the Table 4.1.

Table 4.1, Minimum, maximum and mean of pH, TOC and CEC values for all soil sample.

Amount	pH	TOC %	CEC (meq/100 g)
Minimum	4.0	0	0
Maximum	7.6	12.5	71.31
Mean	5.5	2.16	19.70

4.2 Soil Characterization Results

4.2.1. pH results

The pHs of the soil samples ranged from 4.0 to 7.6, with a mean of 5.5, as is shown in Table 4.1. Figure 4.1 shows the range of pH values and the percentage of samples present in that range for the 114 locations. From the Figure 4.1, it can be seen that the higher percentage (59.39 %) of soil samples are present in the pH range of 4-5. This clearly shows that majority of soil samples are highly acidic and about 11.4 % of soil samples are highly alkaline.

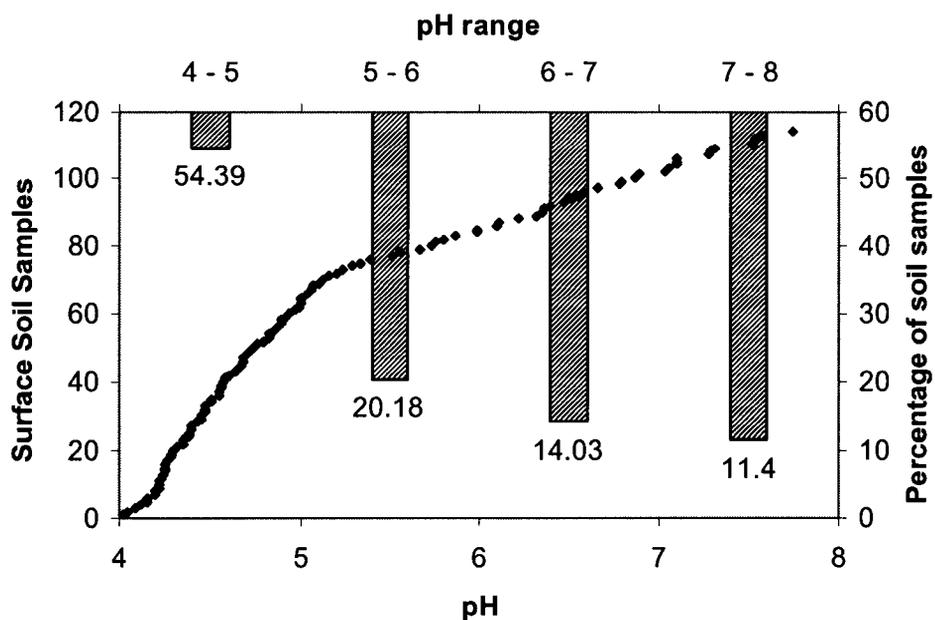


Figure 4.1 pH values for 114 surface soil samples

4.2.2 TOC Results

TOC is the total amount of organic carbon present in soil. The total organic carbon is measured because of its ability to form water insoluble complexes with leached metal ions and hydrous oxides and to interact with clay minerals and bind particles together (Schumacher, 2002).

The percentage TOC present in all soils ranged from 0 to 12.5 % with a mean of 2.6 % as shown in Table 4.1. Figure 4.2 shows the distribution of TOC present in the 114 surface soil samples.

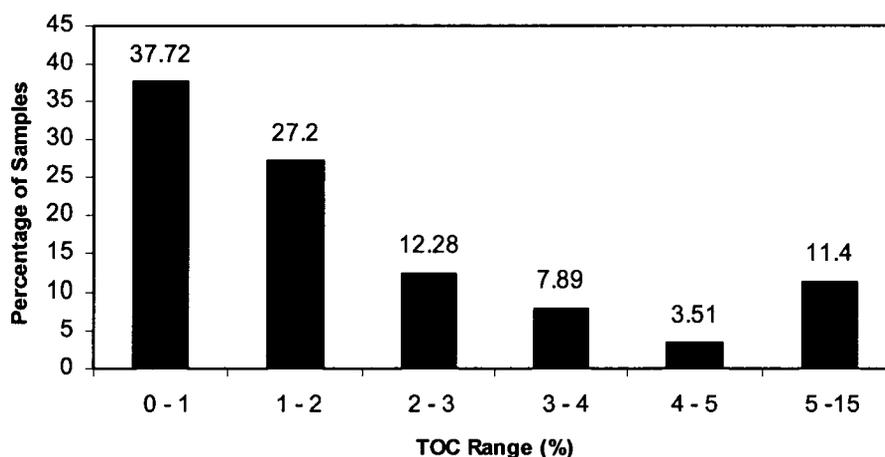


Figure 4.2 Distribution of Total Organic Carbon (TOC) in the 114 soil samples.

4.2.3. CEC Results

CEC is the capacity of soil to exchange positively charged ions (cations) between the soil and the soil solution. Soil particles and organic matter have negative charges on their surfaces. These negative charges adsorb positively charged cations. Once

adsorbed, these cations are not easily desorbed and are retained in the soil. Depending on the type of soil particles CEC may vary (Reiner 2006). For example, clay and organic soil particles have high CEC.

The CEC values ranged from 0 to 71.31-meq/100 g, with a mean of 19.70 meq/100 g as given in Table 4.1. The soil CEC values are quite variable and their distribution is shown in Figure 4.3.

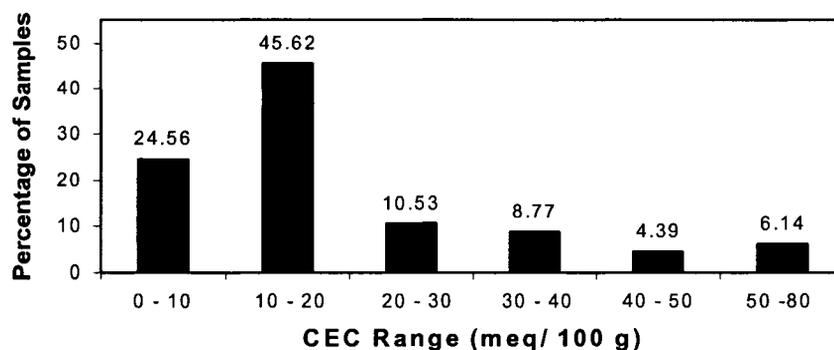


Figure 4.3 Distribution of Cation Exchange Capacity (CEC) results in 114 soil samples.

4.2.4 X- ray Diffraction Results

X-ray diffraction measurements were performed on eight different randomly selected soil in order to identify mineral phases (chemical) phases present it. Table 4.2 shows different mineral phases present in those soil. Mainly Quartz (SiO_2) was present in all the samples. Clay minerals like chlorite, illite and montmorillonite were also present in small quantities.

Table 4.2 Mineral phases present in random soil samples

Samples	Dis ¹ (cm)	TL ²	Quartz	Albite	Chlorite_ serpentine	illite	Chlorite- Vermiculite montmorillonite
P 1-4	700	227	89%	-	6%	4%	1%
P 1-12	60	227	78%	11%	8%	2%	1%
P 1-16	30	227	86%	-	7%	6%	1%
P 1-17	0	227	87%	-	9%	3%	1%
P 1-31 E	60	227	57%	27%	8%	7%	1%
P 1-32	30	227	80%	-	9%	10%	1%
P 19 L	0	225	94%	-	3%	2%	1%
P101	0	259	95%	-	2%	1%	2%

¹Dist = distance from utility poles

²TL = transmission line

4.3 Analysis of Water Samples

4.3.1 Leaching of Cu, Cr and As from a Freshly Treated Wooden

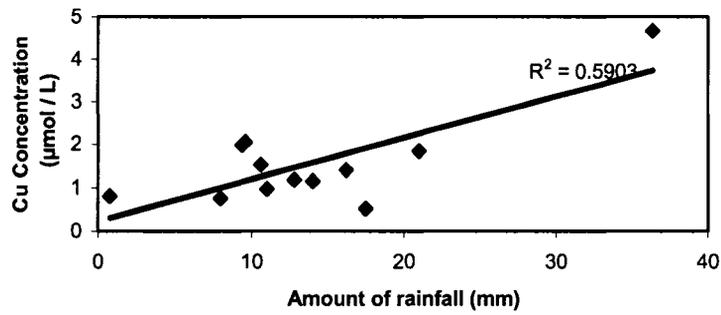
Log

Cu, Cr and As concentrations in water samples collected from drum containing the suspended wooden log that had been freshly treated with CCA were analyzed. The results, along with the date of rainfall, time of observation and temperature are summarized in appendix B. The average amounts of Cu, Cr and As leached from the log are 8.98 $\mu\text{moles} / \text{L}$, 5.31 $\mu\text{moles} / \text{L}$, and 3.87 $\mu\text{moles} / \text{L}$ respectively. The Cu: As: Cr molar ratio of these average amounts is 100:43:58. It will be seen from section 4.4 that this is nearly the same as the molar ratio of the average contents in the soil samples collected at a distance of 0 cm away from the poles, 100:46:57. This may indicate that there is continuous leaching from the poles over time.

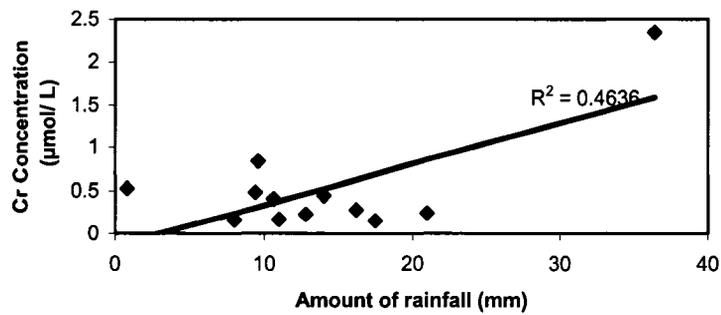
4.3.2 Leaching of Cu, Cr and As with Amount of rainfall

The concentrations of Cu, Cr and As leached from the suspended log are plotted against the amount of rainfall. Figure 4.4 and Figure 4.5 shows the leaching of CCA for two different (2002 and 2004) yrs. In Figures 4.4a, b and c the R^2 values for the amount of leaching of Cu, Cr and As for the first yr (2002) covering two months of data are 0.59, 0.46 and 0.3 respectively. These values are too low and hence there is no linear relationship between the leaching of Cu, Cr and As and the amount of rainfall but in Figures 4.5a, b and c the R^2 values have increased to 0.81, 0.84 and 0.78 respectively for the next yr (2004) covering five months of data and hence there is a linear relationship between the amount of rainfall the 2nd yr leaching of CCA from poles and hence improper leaching of preservatives with amount of rainfall from suspended log was observed. The reason that 2004 was the second or next yr is that after October 2002 (1st yr) the experiment set-up was closed off with a wooden lid and reopened for sampling only in April 2004 (2nd yr). One value water in each yr had a very high concentration of Cu, Cr and As and was omitted while finding the relationships shown in Figure 4.4 and Figure 4.5. The 2 outliers may be due to a chip of wood fallen into the water in the bottom of the drum, resulting in high concentration of Cu, Cr and As in the sample.

(a)



(b)



(c)

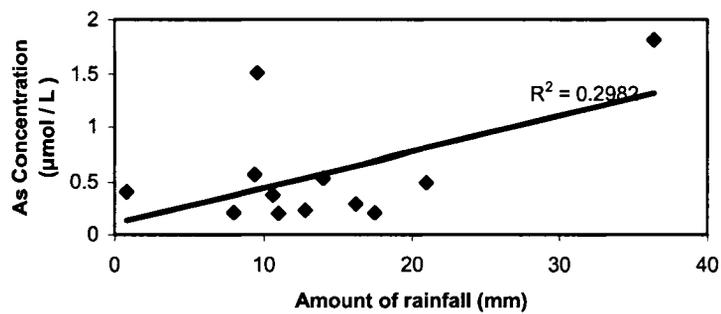
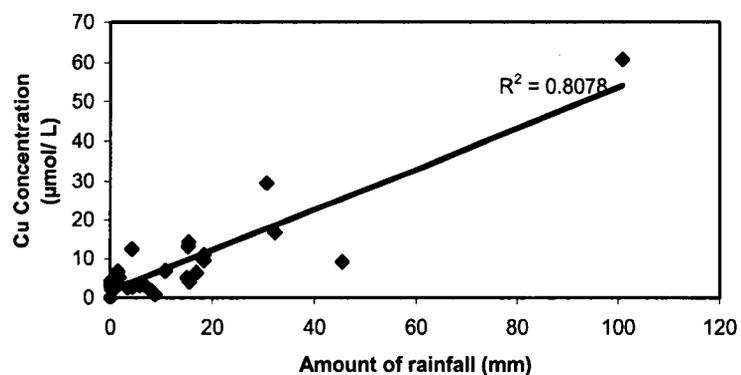
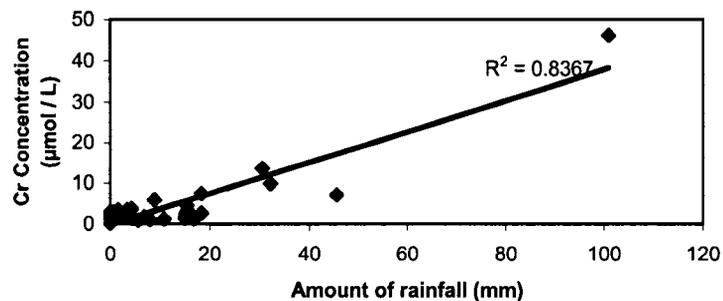


Figure 4.4.a, b, c Leaching of (a) Cu (b) Cr (c) As from the freshly treated 1.5 m long wooden log for the 1st yr (2002) vs. Amount of rainfall received.

(a)



(b)



(c)

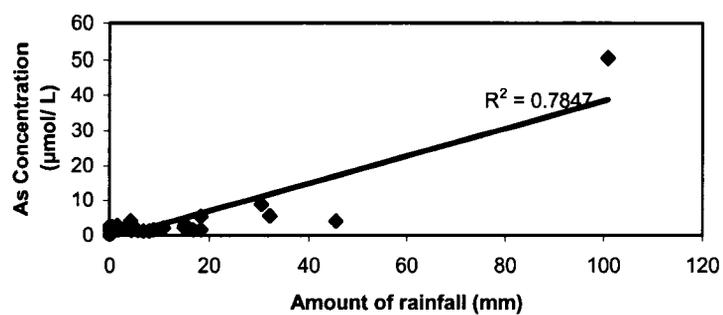
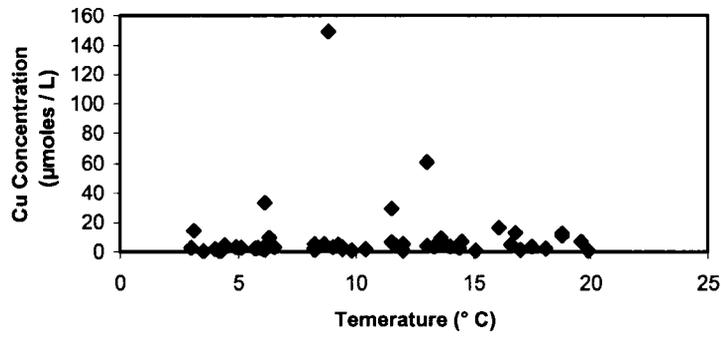


Figure 4.5.a, b, c Leaching of (a) Cu (b) Cr (c) As from the freshly treated 1.5 m long wooden log for the 2nd yr (2004) vs. Amount of rainfall received.

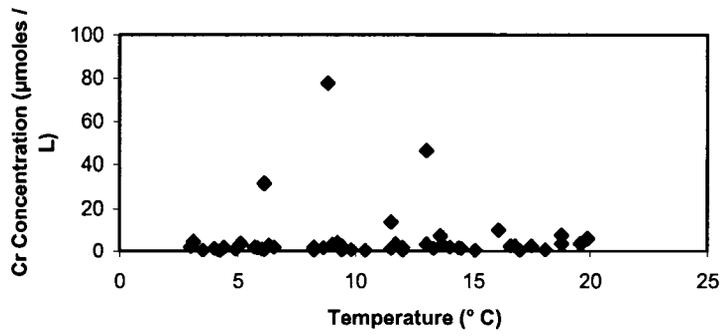
4.6.2 Leaching of Cu, Cr and As with Temperature

The concentrations of Cu, Cr and As that were compared to the ambient temperature during the rainfall. Waldron et al., (2004) found Cu and As leached more as the temperature rose where as Cr leached slightly less at 30° C. Figures 4.6a, b and c show the leaching of Cu, Cr and As for different temperatures during rainfall. From those Figures there is no visible trend. The reason is likely due to the fact that different amounts of rainfall were also occurring so it was not just the temperatures that were different, and it has been seen that the amount of rainfall and its duration are also important factors. For example more leaching was seen when the rainfall was 100.9 mm at 13° C than when it was 1.5 mm at 19.6° C.

(a)



(b)



(c)

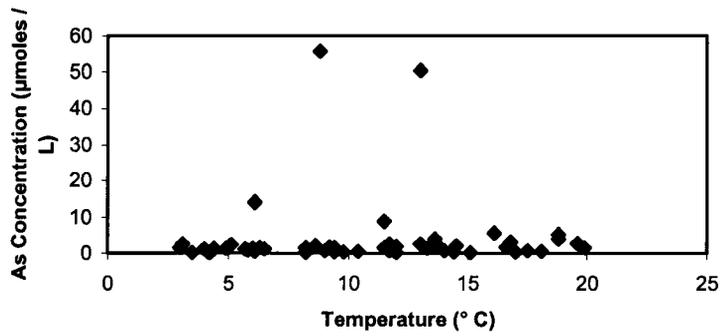


Figure 4.6a, b c Leaching of (a) Cu, (b) Cr (c) As concentration for the freshly treated 1.5 m long wooden log. vs. Amount of rainfall received.

4.4 Analysis of soil samples

4.4.1 Cu, Cr and As in Soils

Soil Cu concentrations ranged from 39 mmol/g to 37,506 mmol/g. Soil Cr concentrations ranged from 0 mmol/g to 65,518 mmol/g. Soil As concentrations ranged from 4.65 μ mmol/g to 38,930 mmol/g. The percentage of samples present in different concentration ranges is shown in Figure 4.7. From this Figure it can be seen that the highest percentage of Cu and Cr Concentrations falls in the range of 100 – 1,000 mmol/g whereas for As the highest percentage of samples were in 0 – 100 mmol/g concentration range.

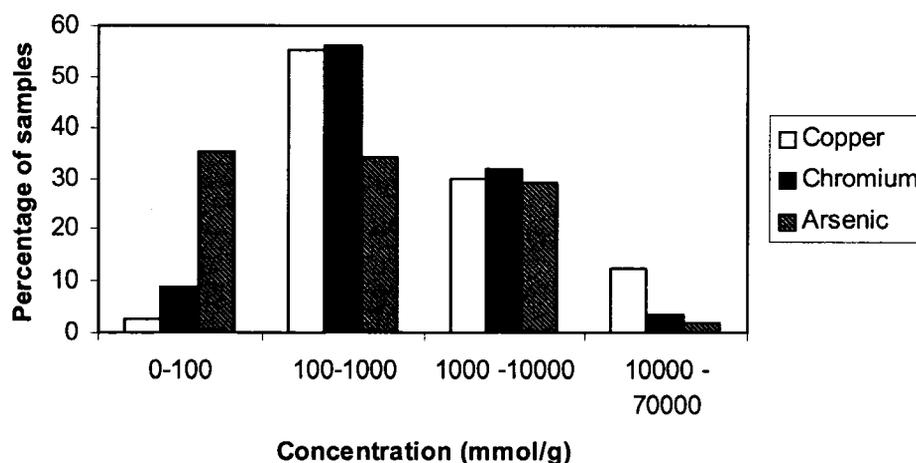


Figure 4.7 Distribution of Cu, Cr and As concentrations in 114 soil samples.

4.4.2 Cu, Cr and As Concentrations with Distance from Pole

Cu, Cr and As concentrations, in surface soils generally decreased rapidly over short distances from the poles. Table 4.3 shows the average values observed at distances of 0, 30 and 60 cm from the pole.

Table 4.3 Average Cu, Cr and As concentrations at three distances from the utility poles.

Distance cm	Cu (mmol/g)	Cr (mmol/g)	As (mmol/g)
0	9040	5010	4130
30	1230	680	460
60	540	460	190

At 0, 30 and 60 cm the concentration of Cu was the highest followed by Cr and As. Similar results were also obtained by Zagury et al., (2003).

To illustrate this rapid decrease in Cu, Cr and As concentration with distance from the utility pole the average values at the three different distances from the poles are plotted in Figure 4.8. The average Cu, Cr and As concentration decreased in an exponential manner in the interval from 0 cm to 60 cm.

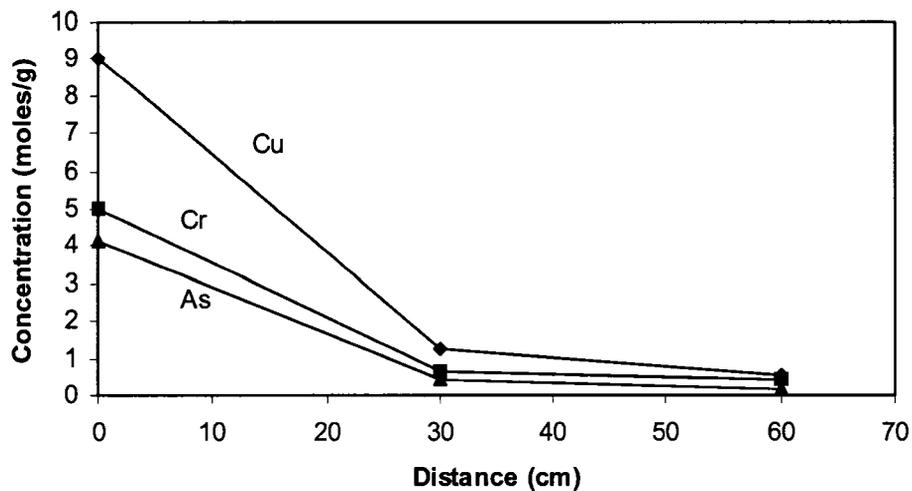


Figure 4.8 Average Cu, Cr and As concentrations in 114 surface soil samples at three distances from the utility poles.

Figure 4.9 shows the change in Cu, Cr and As concentration with distance from pole 1-32. For soil samples from 26 of the 28 poles, Cu concentrations were higher than the Cr and As concentrations and a similar result was also observed by Cooper et al. (1997) and Zagury et al. (2003). For approximately 60% of the poles the As concentration exceeded the Cr concentration immediately next to the pole but at 30 cm from these same poles, the Cr concentration was greater than the As concentration. These results suggest that As is more mobile in soil than Cr and could therefore be more likely to move towards the ground water table.

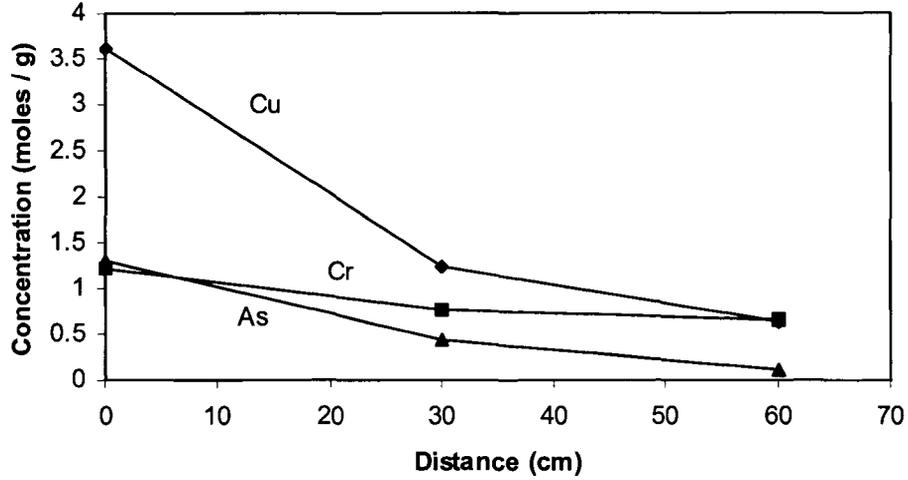


Figure 4.9 Reduction in Cu, Cr and As concentration with distance from pole 1 –32.

Stilwell and Gorny (1997) and Zagury et al. (2003) also found As to be more mobile than Cr. For soil samples from the remaining 40% of the poles, the As concentration remained greater than the Cr concentration, at a distance of 30 cm from the poles.

The pie charts in Figure 4.10 provide a clear view of the distribution of Cu, Cr and As concentrations in soil samples at the three different sampling locations or distances from the utility poles. It can be seen in this Figure that the highest concentrations of Cu, Cr and As occurred usually nearest to the pole and the lowest Cu, Cr and As concentrations usually occurred at the farthest location from the pole.

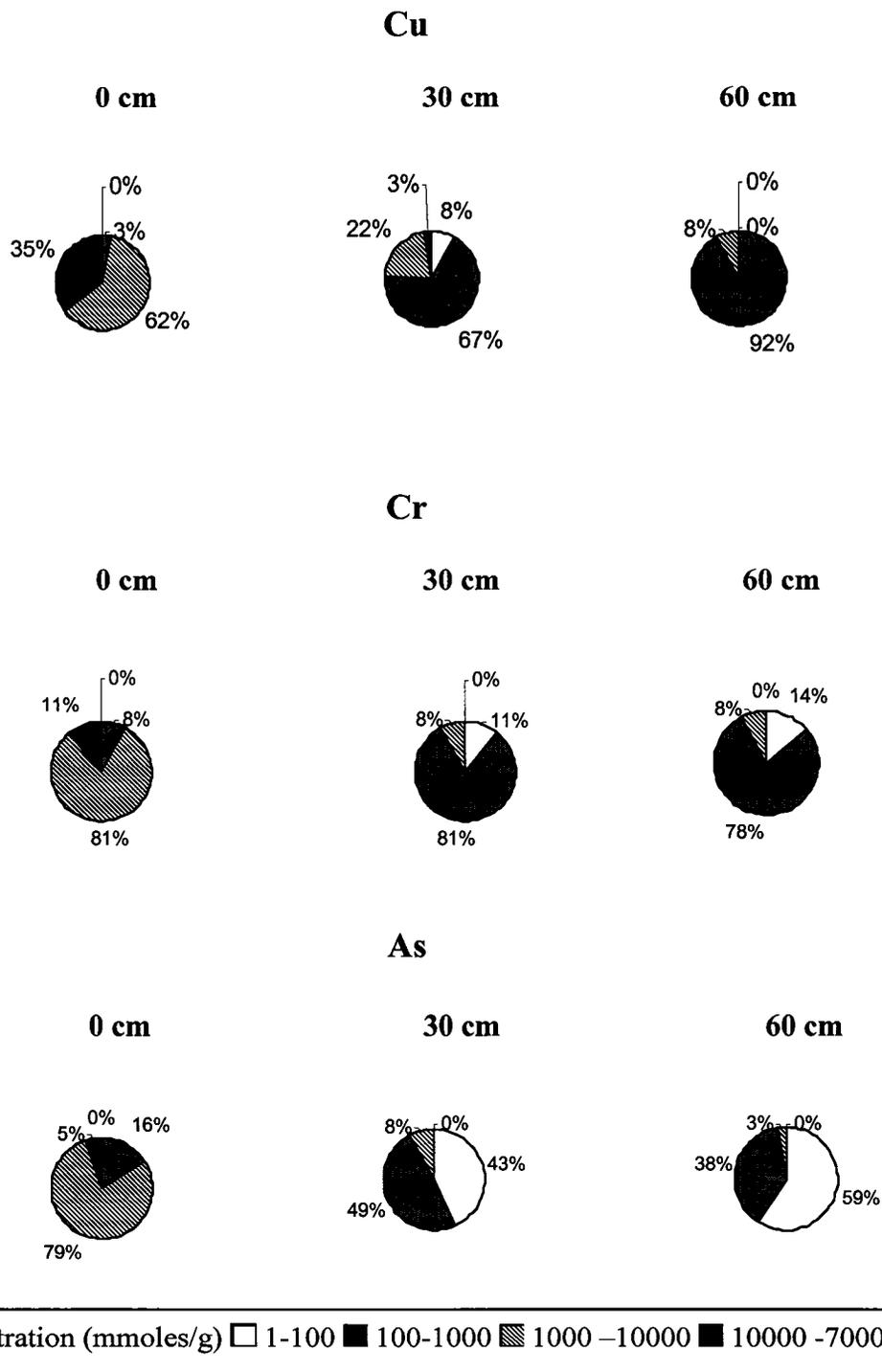


Figure 4.10 Distribution of Cu, Cr and As concentrations in soil samples at the three different sampling locations

4.4.3 Cu, Cr and As concentrations in East, West North and South directions

In addition to distance another variable direction, viz., Cu, Cr and As concentration with respect to direction was also examined. Soil samples were collected from east west, north and south directions of 3 utility poles. Prior to initiating this study, it was thought that direction might be important with respect to the leaching levels of Cu, Cr and As in the soil. For example, one suggested premise was that wind direction during rainfall could cause excessive leaching of Cu, Cr and As from the utility pole in one direction. In Newfoundland, winds are predominantly from the west yr-round, but variations are common both from location to location and from month to month. Prevailing wind directions are from the west in winter and from the west-southwest in summer (Environment Canada, 2006). With the wind coming from the west or west-southwest, it is expected that the precipitation will be carried around the sides of the utility poles and will be deposited on the north and south sides of the poles. Therefore higher amounts of Cu, Cr and As should be observed in soil samples obtained from south or north sides of the poles This phenomena is observed in pole 1-4 (227) and pole 1-31 (227) where the highest amounts of Cu, Cr and As occur in the south direction and for pole 19 (225) where the highest amounts of Cu, Cr and As occur in the north direction. Figures 4.11, 4.12 and 4.13 show the amounts of Cu, Cr and As respectively, in samples taken from the east, west, north and south faces of the 3 utility poles.

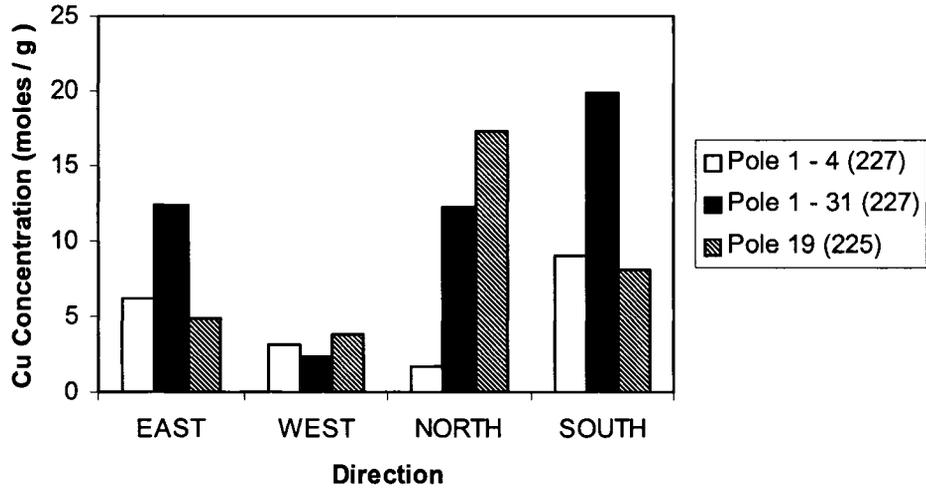


Figure 4.11 Leaching of Cu in four directions from 3 utility poles

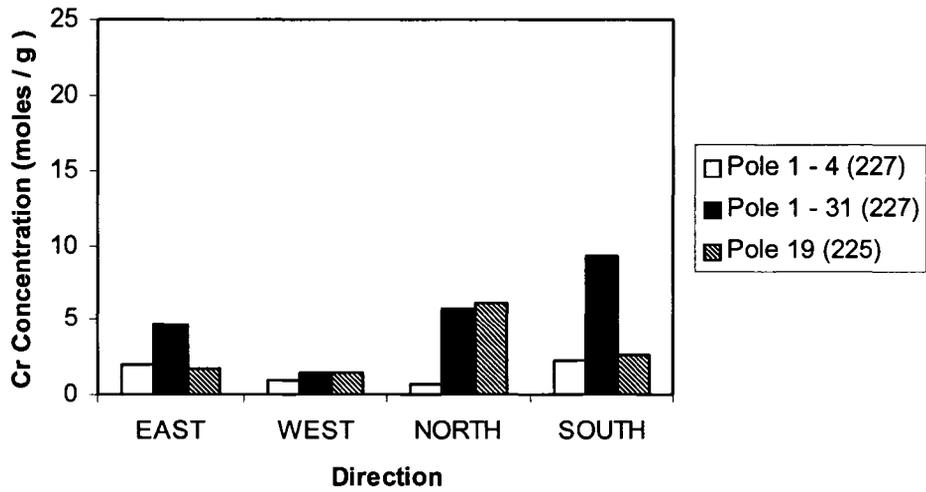


Figure 4.12 Leaching of Cr in four directions from 3 utility poles.

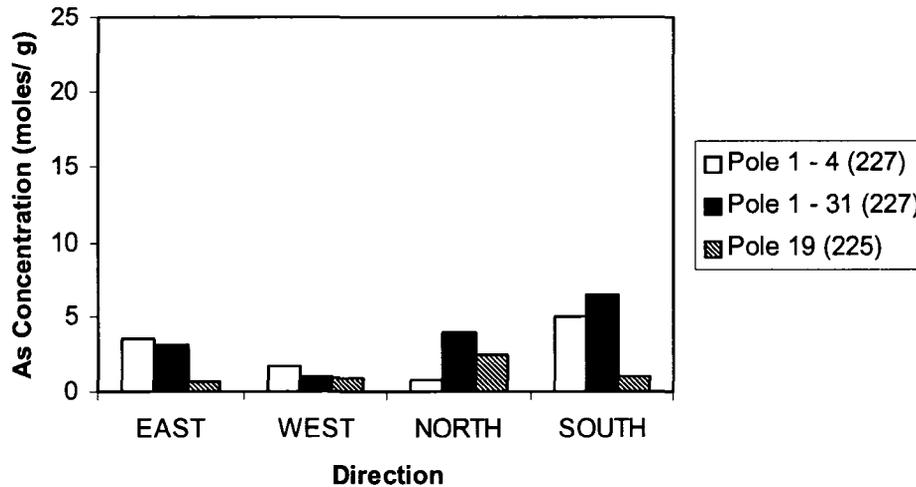


Figure 4.13 Leaching of As in four directions from 3 utility poles

4.4.4 Effect of Pole age on leaching of CCA

Cu, Cr and As concentrations in soil samples were studied in terms of pole age to determine if leaching was related to the age of the pole. Pole age data were available for all 28 poles. The average amounts of Cu, Cr and As in soil samples collected at 0 cm from the poles that were 1, 2 and 13 yrs old is shown in the Table 4.4. From the table it is seen that greater leaching occurs for freshly treated poles (1 yr old) than for slightly aged poles (2 yrs old) but the greatest leaching occurs for the most aged poles. One possible reason for this is that during the first yr the pole is in service, the portion of Cu, Cr and As that are weakly bonded to the poles are removed easily, and hence lower amounts of leaching are seen in the second yr the pole is in service. However, after 13 yrs a large amount of Cu, Cr and As is again being leached from the wood. A possible reason for the highest leaching at 13 yrs, is that the wood has become more weathered by wind, rainfall, sun exposure and change in temperatures

over time and is gradually being broken down and thus the Cu, Cr and As are becoming more weakly bonded to the wood. Lebow et al., (2003) studied the effect of weathering on CCA treated wood in terms of UV exposure and found that UV radiation plays an important role in the leaching of Cu, Cr and As

Table 4.4. Average amounts of leaching Cu, Cr and As for utility poles that are 1, 2 and 13 yrs old.

Age	Location	Cu (mmol/g)	Cr (mmol/g)	As (mmol/g)
1	Rocky harbor	10180	3090	3830
2	Deer Lake	5610	2130	1330
13	Gros Morne	16760	20610	12690

For 1-yr-old poles, As leached more than Cr near (0 cm away from) the poles. A possible reason is that As may not be properly fixed with the timber and hence an excess amount is leached from the poles. For 13-yr-old poles, Cr leached highest near the poles. A possible reason may be that over time Cr losses its fixation characteristics and is more freely available for leaching.

The permissible amount of Cu, Cr and As in soil for an industrial location is 1430 mmol/ g, 1670 mmol/ g, and As 160 mmol/ g respectively (Environment Canada, 2003: Canadian Council of Ministers of Environment, (CCME), 2003). This clearly shows that the levels of these elements is higher than the permissible level The average background concentrations of these elements in soil samples were 287 mmol/

g for Cu, 339 mmol / g for Cr, and 156 mmol / g for As. The background concentrations of these elements in water were only 72 µg/L of Cu, 0.17 µg/L of As and 0.80 µg/L of Cr.

4.3.5 Effect of Rainfall and Temperature on Leaching of CCA

Leaching of Cu, Cr and As from poles was studied in terms of rainfall and temperature in the like Rocky Harbor, Gros Morne National Park and Deer Lake regions to determine if any changes of leaching occur due to environmental conditions.

The weather recording stations available near the sampling regions are in Rocky Harbor and Deer Lake. Rocky Harbor's weather recording station is located in Latitude 49° 34' N, Longitude 57° 52' W and at Elevation of 67.70 m whereas Deer Lake's weather recording station is located in Latitude 49° 13' N, Longitude 57° 24' W and at Elevation of 21.90 m. Sampling locations from Rocky Harbor and Gros Morne National Park were very close and hence the same environmental data is used for both places. Environment Canada uses Climate normal or averages to describe the average climatic conditions of a particular location. Tables 4.4 and 4.5 show climate normal for monthly temperature average and monthly rainfall for Rocky harbor (or Gros Morne) and Deer Lake. These data are based on at least 15 yrs of information between 1971-2000.

The annual average rainfall in Rocky Harbor or Gros Morne National Park area is 898.6 mm and for Deer Lake 718.3 mm. Deer Lake area poles (2 yrs old) may have received around 1436.6 mm (2×718.3 mm) of rainfall whereas Rocky Harbor area poles (one yr old poles), which only received 898.6 mm, however soils around the 1 – yr old poles were more heavily contaminated. A possible reasons is that the weakly bonded fractions of the CCA elements (Cu, Cr and As) are easily leached during the 1st yr of rainfall. Light rain showers of long duration may also cause more leaching than short, heavy rain showers (Taylor, 2001) although there is no information available to indicate any differences in average duration of rainfalls between the two places.

Table 4.4 Climatic normal shows the monthly average of temperatures and the amount of rainfall for Rocky Harbor or Gros Morne area.

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
MA ¹	-7.5	-8.9	-4.8	1.6	6.4	11.3	15.4	15.2	11.4	6	1.2	-4.3
Rf ²	30.3	20.9	35.3	43.3	68.7	105.3	99.6	110.5	112.1	130.9	96.7	45

¹MA- Daily Average in ° C

²Rf- rainfall in mm

Table 4.5 Climatic normal shows the monthly average of temperatures and the amount of rainfall for Deer Lake.

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
MA ¹	-8.9	-9.8	-5	1.4	6.9	12	16.1	15.4	10.9	5.3	0.5	-5.4
Rf ²	20.5	12.4	27.1	41.5	67.5	79.9	91.6	100.1	96.1	92.4	60.6	28.6

¹MA- Daily Average in ° C

²Rf- rainfall in mm

Temperature effects on the leaching of CCA from poles were considered however during the eight months from April to November the number of degree days of freezing were approximately equal for both places. Therefore no conclusions could be made regarding the effect of temperature upon leaching.

4.5 Soil, pH, CEC and TOC relationships

The pH, CEC and TOC were measured for all of the soil samples and average values for each pole were calculated to study the correlation between the parameters. These values for each pole are shown in Appendix C.

4.5.1 TOC and CEC relationship

There was found to be a direct correlation between the CEC and TOC as shown in Figure 4.14. This relationship might be explained by the fact that there is a relationship between CEC and total organic matter that contains a large proportion of carboxyl groups. They dissociate and contribute to negative charge in the soil and hence result in a high CEC value.

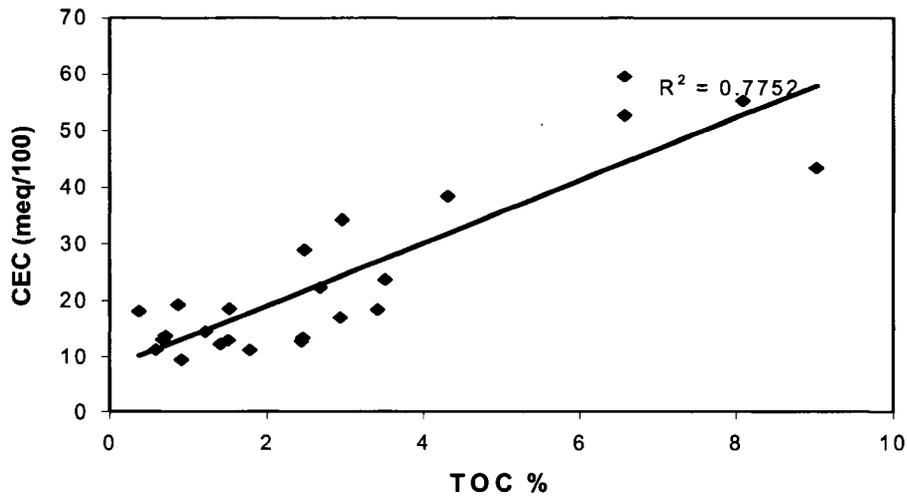


Figure 4.14. Average of all TOC site values against average of all CEC site values.

When Zagury et al. (2003) compared different soils, they determined that organic soils had higher CEC values than clay soils and they indicated that an organic matter contribution to CEC would be greater than a clay contribution.

4.5.2 pH and TOC relationship

The average pH values for all of the pole sites ranged between pH 4.1 and pH 7.2 and so all of the soils were in the acid to neutral pH range. There was no direct relationship between the TOC and the pH as can be seen from Figures 4.15. However, wherever there was a high TOC there was also a low pH. This could be due to the fact that probably because organic matter tends to lower soil pH.

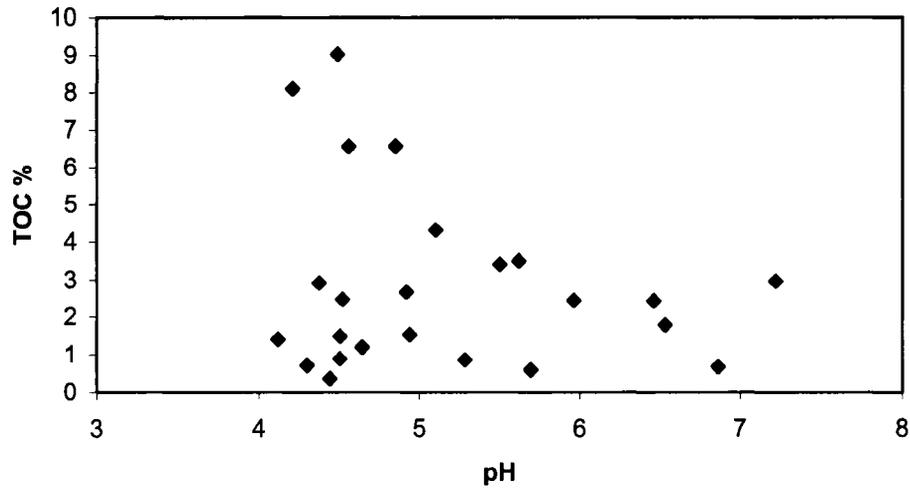


Figure 4.15. Average pH values against average of TOC values

4.5.3 pH and CEC relationship

There was no direct relationship between the pH and CEC. However where there was high CEC there was low pH. This may occur when organic matter is a major contributor to the CEC as the presence of organic matter lowers soil pH.

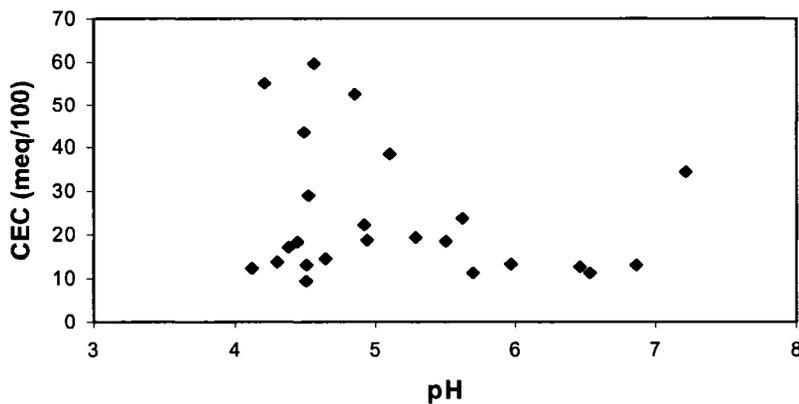
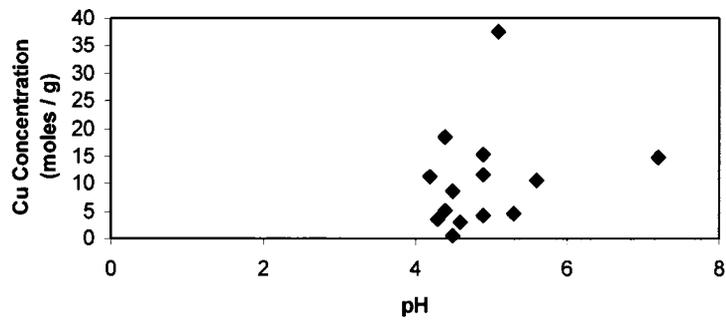


Figure 4.16 Average of pH values against average of CEC values

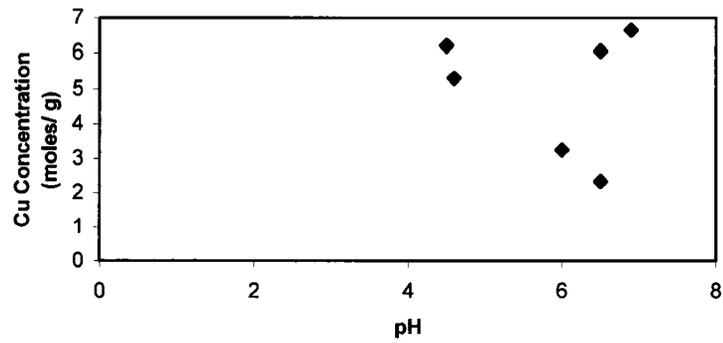
4.5.4 pH and Leaching of Cu, Cr and As from utility poles

For all soil samples that were taken immediately adjacent to the utility poles, the pH values for the three different ages of utility poles are plotted against the concentrations of Cu (Figure 4.17), Cr (Figure 4.18) and As (Figure 4.19). Cooper (1991) and Mulligan et al., (2003) found that leaching of Cu from CCA timber increases with reduction in pH. However, from the results of this study, no relationship between pH and either Cu, Cr and As concentrations in the soil samples can be seen.

(a)



(b)



(c)

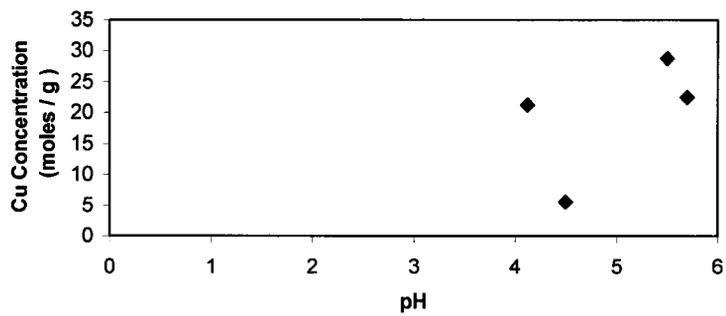
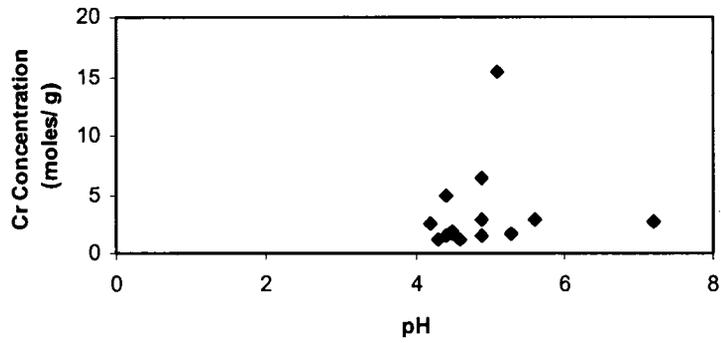
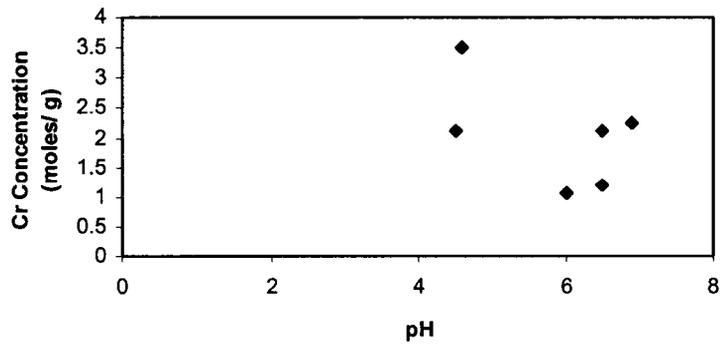


Figure 4.17 Average pH values for (a) 1 yr (b) 2 yr and (c) 13-yr old poles vs. Cu concentrations in soil samples.

(a)



(b)



(c)

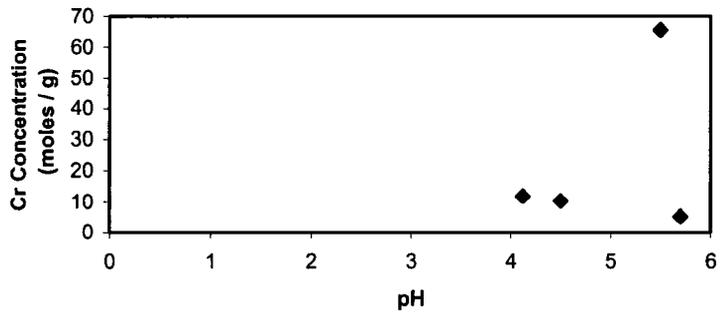
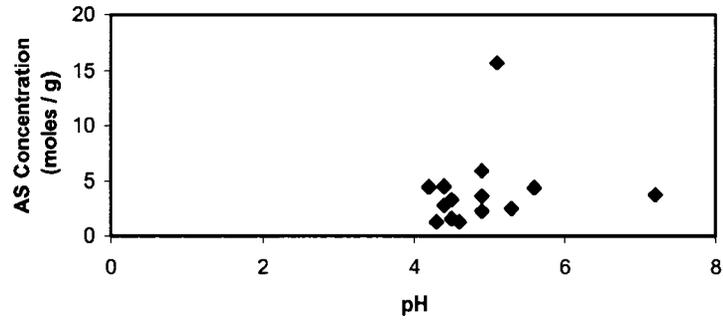
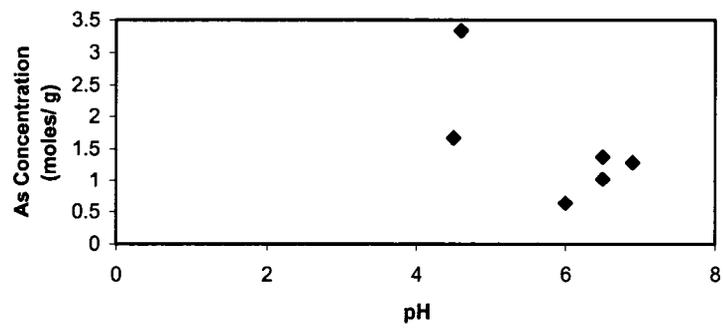


Figure 4.18 Average pH values for (a) 1 yr (b) 2 yr old (c) 13 yr old poles vs. Cr concentrations in soil samples.

(a)



(b)



(c)

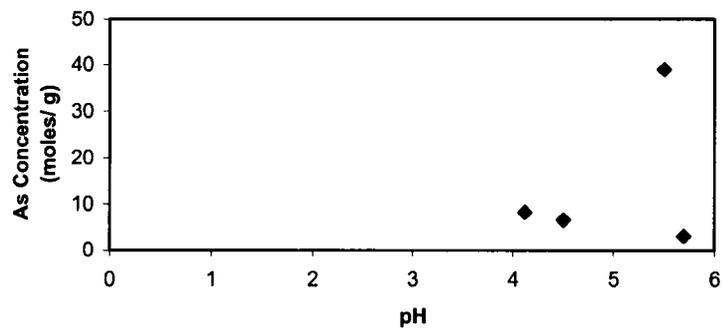


Figure 4.19 Average pH values for (a) 1 yr (b) 2 yr (c) 3 yr old poles vs. As concentration in soil samples.

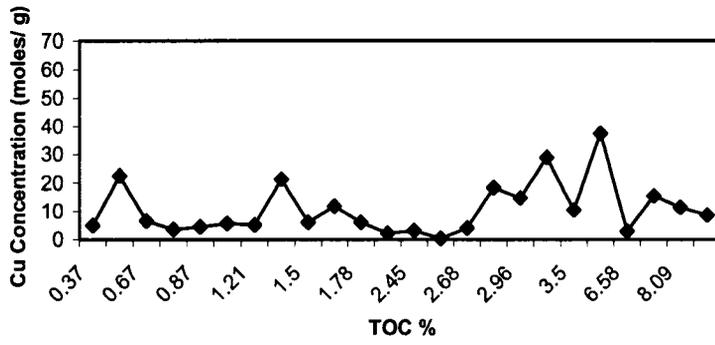
4.5.7 TOC, CEC and leaching of Cu, Cr and As

By considering soil samples collected at 0 cm leaching of Cu, Cr and As was analyzed in terms of soil CEC and TOC values. As seen in Figure 4.20 and Figure 4.21 TOC and CEC effect on leaching of Cu, Cr and As does not show any trend.

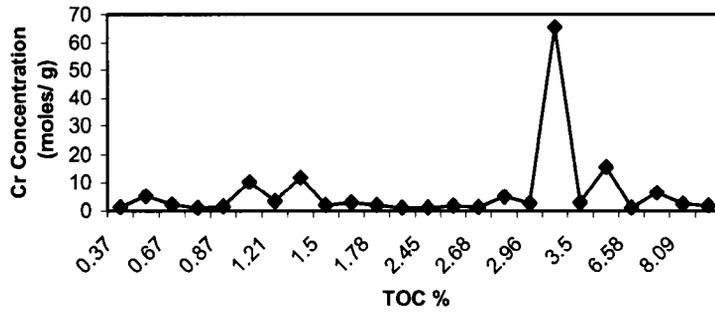
4.5.8 CEC, TOC, pH and Drop in concentration of Cu, Cr and As

The CEC, pH and TOC values of all the samples were plotted against drop in concentration of Cu, Cr and As in soil samples with increase in distance (i.e. 0 to 30 cm) from the utility pole. As seen in the Figures 4.22 to 4.24 no direct correlation was found.

(a)



(b)



(c)

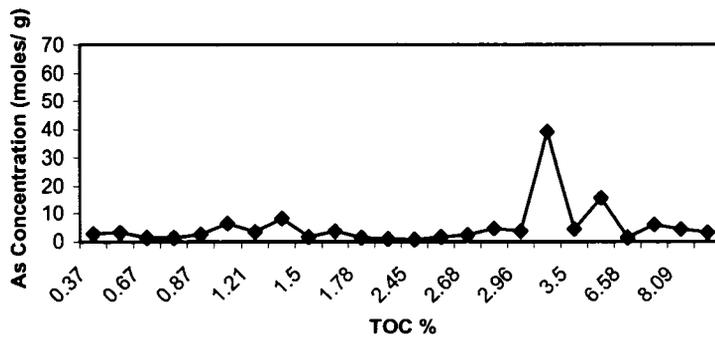
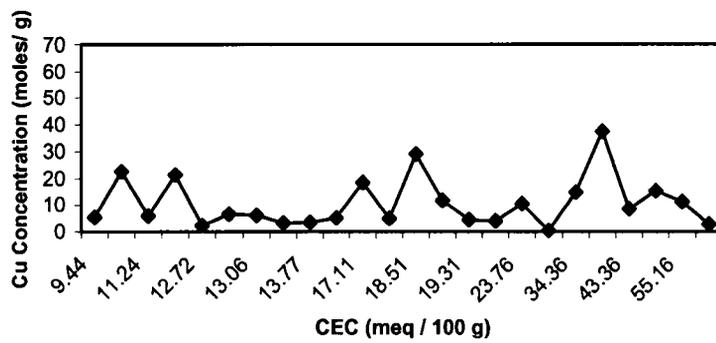
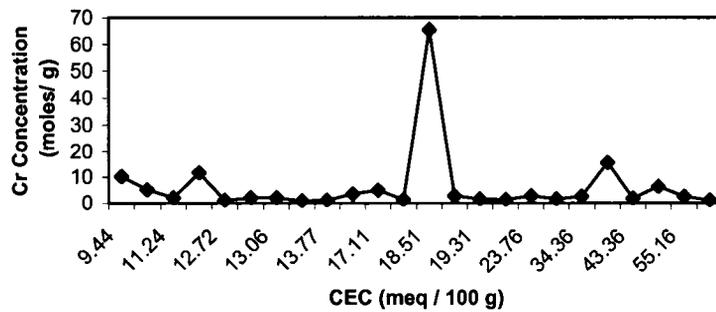


Figure 4.20 TOC content of soil against concentrations of (a) Cu, (b) Cr and (c) As in soil samples.

(a)



(b)



(c)

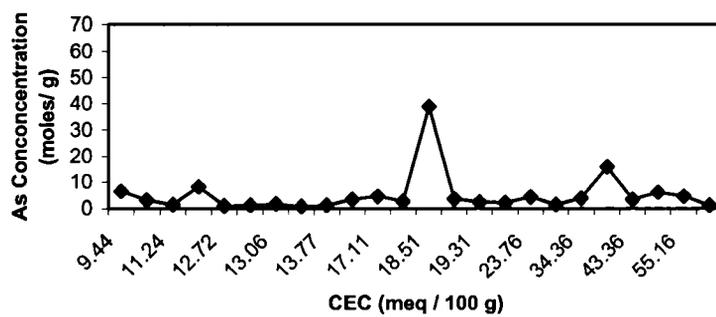
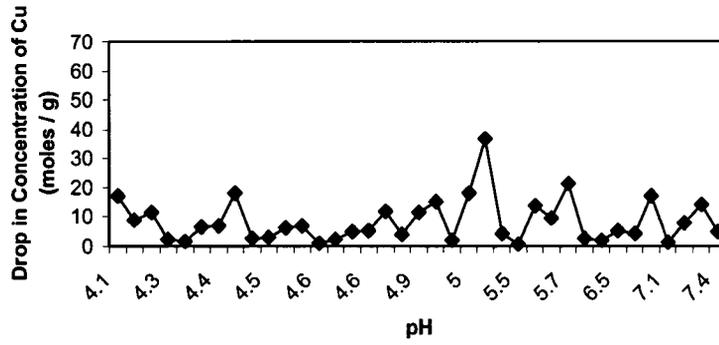
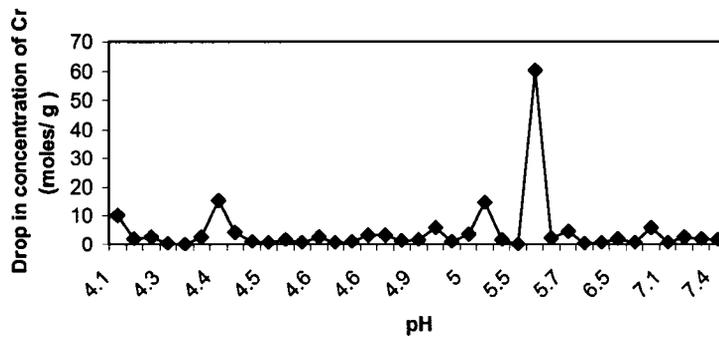


Figure 4.21 CEC against concentrations of (a) Cu, (b) Cr and (c) As in soil near the first yr pole.

(a)



(b)



(c)

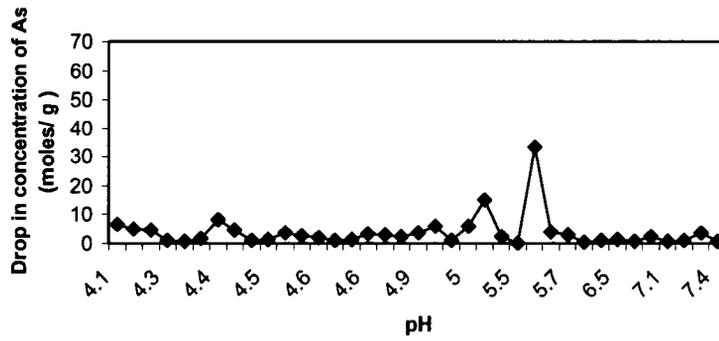
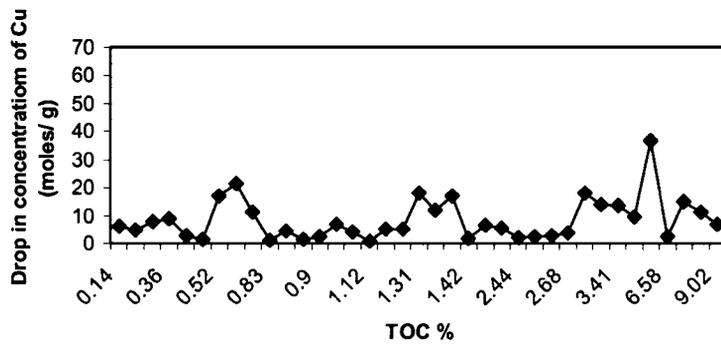
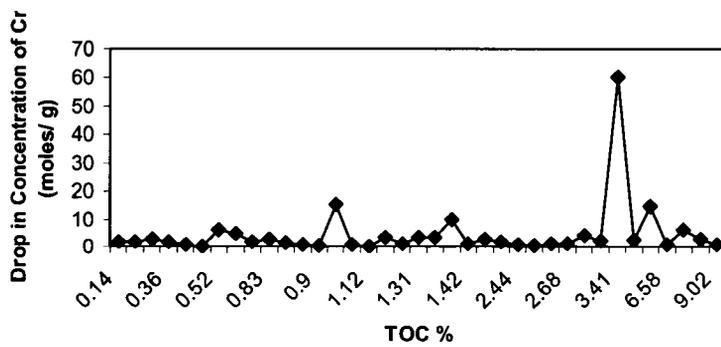


Figure 4.22 pH of soil against drop in concentrations of (a) Cu, (b) Cr and (c) As in soil

(a)



(b)



(c)

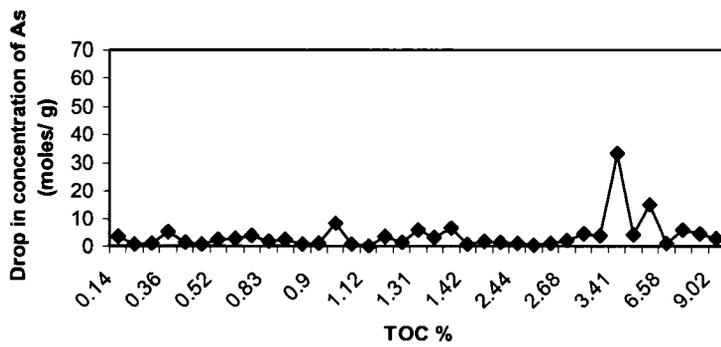
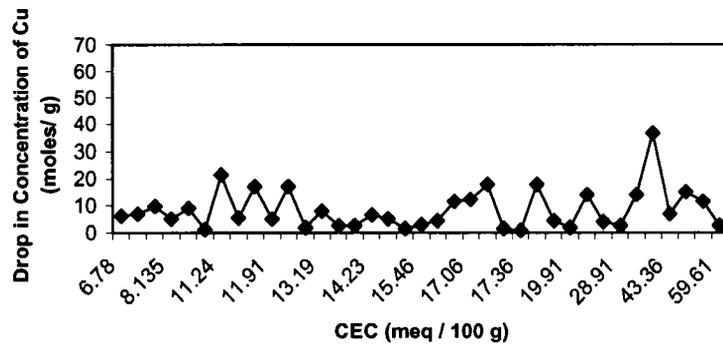
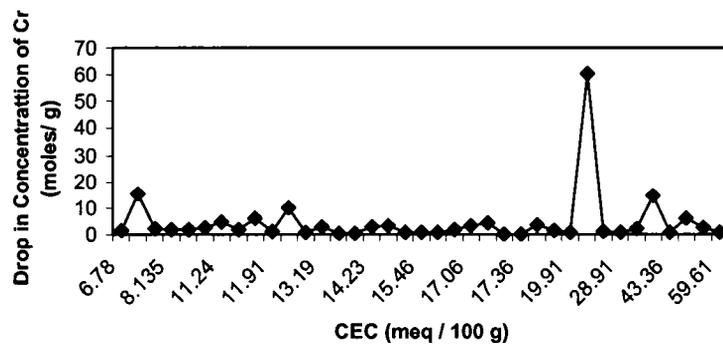


Figure 4.23 TOC of soil against drop in concentrations of (a) Cu, (b) Cr and (c) As in soil

(a)



(b)



(c)

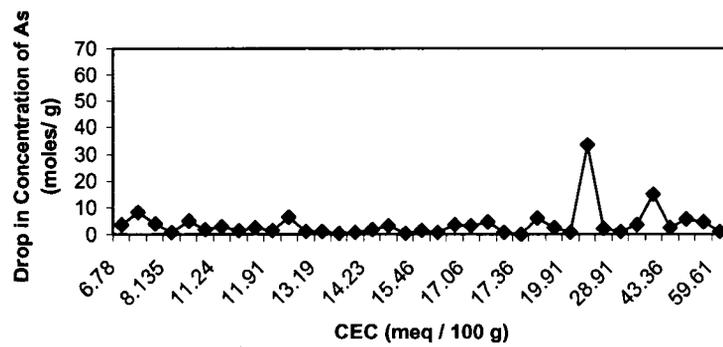


Figure 4.24 CEC against drop in concentrations of (a) Cu, (b) Cr and (c) As in soil

4.6 Remedial Measures

From section 4.4, there is a clear evidence of leaching going on near utility poles and hence remedial measures for leaching is discussed in this section. The remediation of contaminated soil around utility poles can be done by methods such as soil conditioning, phytoremediation and soil solidification/solidification. These methods are described in detail in the following paragraphs:

1. Soil conditioning refers to improving or modifying soil quality and texture in a particular area (Robert, 2003). Mixing of a conditioning agent such as soil organic matter to a soil can be done around utility poles. High organic soils may tend to retain more cations due to the presence of negatively charged carboxyl groups, in them (Lu, 2002) and hence more amounts of Cu, Cr and As can be retained very near to the poles.
2. Phyto remediation can be done to remove the Cu, Cr and As in contaminated soil near existing CCA treated poles. As absorbing Vetriver grass lawns (Srisatit.T, et. al., 2003) can be grown in a 0.6 m radius around each CCA treated pole. However, it can only remediate the top surface and a small amount of the soil beneath.
3. Soil solidification/Stabilization immobilizes contaminants within the soil medium instead of removing them. It reduces the mobility of contaminants in

the environment through chemical or physical treatment (Alpaslan, 2000). Chemical treatment like adding ferrous chloride to the soil can reduce mobile Cr (VI) into stable Cr (III). Portland cement with a combination of ferrous sulfate and lime (known as PFL) can be added to soil to reduce arsenic mobility by forming calcium arsenic minerals (Chattopadhyay, 2005). Physical treatment such as bottom barriers beneath the pole and side barriers in a 0.6 m radius around each CCA treated pole can prevent vertical and horizontal migration of contaminants.

Chapter 5

Conclusion and Further research

5.1 Conclusion

The average Cu, Cr and As contents in soil collected immediately adjacent to the utility poles were 9.04 ± 0.91 mmoles / g for Cu, 4.12 ± 0.44 mmoles / g for As, and 5.02 ± 0.52 mmoles/ g for Cr. The molar ratio of leaching of Cu, Cr and As into soil immediately adjacent to the utility poles, or Cu:As:Cr was 100:46:56. A similar trend of leaching of these elements from the suspended wooden log was also observed. The molar ratio of leaching of Cu, Cr and As from the suspended log or Cu:As:Cr was 100:44:57 which may indicate that leaching of preservatives is going on continuously over time.

The results also suggested that As was more mobile than Cr since the As concentration in the soil around the utility poles decreased more with distance than the Cr concentration.

It appears that soil background conditions in surface soils were reached at a distance of only 0.60 m from the utility poles because the background concentration and the concentration at 0.60 m were nearly similar.

The leaching of Cu, Cr and As from the utility poles was highest for 13-yr-old poles in service. This was due to the weathering effect of the pole, frequency and amount of rainfall in that area.

The leaching of Cu, Cr and As for 2-yr-old poles was low when compared to leaching for the 1 yr old poles. Possibly the reason is that the freshly treated utility poles might contain unfixed CCA at its early stage and received higher amounts of Cu, Cr and As treatment than necessary. Perhaps some “in shop” leaching of poles such as washing with water should be considered.

For 1-yr-old poles, As was leached more than Cr near the poles. This suggests that As may not be as well fixed with the timber and hence excess amount of As is leached from the poles. For 13-yr-old poles, Cr leached most near the pole. It may be that Cr in due course of time loses its fixation characteristics meaning it is more susceptible to leaching under weathered conditions.

In the province of Newfoundland and Labrador the leaching was mostly concentrated in the north or south direction due to the prevailing wind direction. As the amount of rainfall increased, leaching of Cu, Cr and As from the wooden log also increased. There was no evident trend available for the temperature effects on leaching. The pH effects on leaching also do not show any trend and one of the possible reasons is that the frequency and amount of rainfall may be the dominant factor in leaching of Cu,

Cr and As rather than soil pH. TOC and CEC effect on leaching also did not show any trend.

Currently there is a problem with leaching of preservatives from unlined landfills into ground water systems. With diminishing land resources for agriculture, water resources and forestry (Muezzinoglu, 2003) there will come a time when landfill space will be more limited and disposal of utility poles may be prohibited. This will lead scientists to search for an alternative to wooden utility poles. Wooden utility poles also cannot withstand high winds. The alternatives to wooden utility poles are steel and spun (centrifuged) and prestressed concrete poles. Concrete poles have low maintenance, need no chemical treatment and are corrosion resistant although they are very heavy (Canadian Precast/ prestressed concrete institute (CPCL)). Steel poles are 30 % lighter than wood (Oliver, 1997), have low maintenance and greater life expectancy when compared to wood, and require no chemical treatment but are not highly resistant to corrosion (Oliver, 1997). Since steel is a good conductor one disadvantage of steel is that if any malfunction situation arises in the pole the electricity can flow through the pole and can cause a fatality (Malcolm, 2000). As the Newfoundland and Labrador weather is wet and stormy (Environment Canada, 2006), the probability of a malfunction situation in the pole may be high and hence a concrete pole may be good for this environment.

5.2 Recommendations

The recommendations from the research are as follows:

1. There is a clear evidence of leaching going on near utility poles and As and Cr are carcinogens Health Canada's PMRA should suggest wood treaters voluntarily ban the use of CCA in the utility poles industry and used alternatives like Ammonical Cu Quaternary (ACQ) or Cu Azole for preservation.
2. Since there is clear evidence of leaching going on in more weathered utility poles, the disposal of CCA treated poles in unlined landfills can be a problem. This is also mentioned by Mulligan (Mulligan, 2003). This environmental problem can be reduced by disposing of CCA-treated poles in lined landfills to prevent leached Cu, Cr and As from entering the groundwater. The current Robin Hood Bay landfill near St John's is not lined and will not stop leaching of contaminants into the ground water or the ocean.
3. CCA treated poles can be pyrolysed at low temperatures with no oxidation agents. After pyrolysis CCA rich charcoal is grounded and separated using densities of Cu, Cr and As in centrifuges and filters (Jarden, 2004).
4. Bioremediation of CCA using *Bacillus licheniformis* can convert CCA into a water-soluble form and allows CCA to be removed easily. Oxalic acid extraction on poles was also used for the extraction of CCA from the wood and then discarded in the landfills (Jarden, 2004).
5. The use of decay-resistant timber such as chestnut or tropical woods in the utility pole industry can be considered. These woods requires less preservative

applications and hence decrease the amount of preservatives going to waste disposal

6. Finally, Timber can be substituted by other materials, which can be reused and have a longer life such as include steel structures or concrete. As the Newfoundland and Labrador climate is wet and windy utility poles made of spun (centrifuged) or prestressed concrete can be considered.

5.3 Further research

Phytoremediation using Vetiver type grass on CCA contaminated soils can be tested at the lab scale. Since As is more mobile in soil than Cu and Cr, in future soil below the ground level can also be tested for any transportation of contaminants into the ground. Bioremediation using Bacillus strain on CCA contaminated soil can be done in the lab. Different types of clay minerals present in the soil can also be tested to determine if they may be able to retain the Cu, Cr and As and prevent their migration. Some quantitative evaluation on the leaching amount from each pole once disposed to landfill will help in asserting long-term leach ability of discarded utility poles in the landfills.

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APPENDIX A

TABLE A.1 Pole number, transmission lines number, soil metal concentration values of Cu, Cr and As, pH, TOC, CEC values for the soil and pole age for 37 surface sample sites taken from 0 cm away from poles.

Sample	TL	Cu (mmoles/g)	Cr (mmoles/g)	As (mmoles/g)	CEC (meq/100 g)	pH	TOC (%)	Age
P 1-32	227	3596	1212	1298	11.75	4.4	0.71	Nov 6 2001
P 1-33	227	4546	1632	2504	24.36	5.5	1.33	Nov 1 2001
P 1-31 (E)	227	12405	3755	3227	19.26	5	2.22	Nov 7 2001
P 1-31(W)	227	2384	1338	1019	27.96	5.1	1.07	Nov 7 2001
P 1-31(N)	227	12273	2278	3924	20.16	5.0	1.07	Nov 7 2001
P 1-31(S)	227	19781	4466	6494	22.41	5.3	1.56	Nov 7 2001
P 1-19	227	18459	4976	4518	15.36	4.6	2.67	Oct 26 2001
P 1-18	227	10525	2952	4403	0	5.8	2.96	Oct 26 2001
P 1-17	227	8552	1800	3293	53.91	4.8	10.15	Nov 7 2001
P 1-16	227	14827	2732	3768	49.86	7.3	5.01	Nov 7 2001
P 1-12	227	460	1774	1545	22.71	4.7	2.11	Oct 26 2001
P 1-11	227	11346	2578	4453	35.46	4.3	9.53	Oct 25 2001
P 1-10	227	15378	6369	5881	46.86	5.2	6.51	Oct 25 2001
P 1-9	227	2934	1213	1292	57.51	4.6	7.62	Oct 25 2001
P 1-8	227	37505	15502	15709	40.56	5.0	4.52	Nov 13 2001
P 1-5	227	4188	1489	2265	0	5.0	3.09	Nov 11 2001
P 1-4 (E)	227	6301	1981	3587	5.88	4.8	0.21	Nov 11 2001
P1-4 (W)	227	3131	886	1629	16.11	4.7	0.22	Nov 11 2001
P 1-4 N	227	1690	700	801	10.83	4.7	0.22	Nov 11 2001
P 1-4	227	9046	2239	5007	10.49	4.5	0.21	Nov 11 2001
ES	225	5306	3516	3332	20.61	4.7	1.41	June 2000
CR	225	2328	1186	1027	8.31	6.5	2.20	June 2000
P 19 R	225	4791	1341	812	8.76	6.5	1.30	June 2000
P 19 C	225	851	208	209	17.46	5.3	1.18	June 2000
P 19 L (E)	225	4954	1666	694	5.49	7.6	0.22	June 2000
P 19 L (W)	225	3895	1421	919	20.16	7.1	1.10	June-2000
P 19 L (N)	225	17304	6124	2481	12.56	6.4	0.66	June 2000
P 19 L (S)	225	8058	2695	1065	19.11	6.8	0.30	June 2000
P121	259	22441	5194	3189	6.54	6.3	0.43	1989
P 122 E	259	3828	4606	4570	15.21	4.2	0.70	1989
P 122 W	259	7313	15900	8511	6.15	4.6	0.64	1989
P 87	259	21279	11825	8251	7.23	4.2	1.89	1989
P 20 (E)	225	5368	1330	1518	8.69	4.9	0.91	June 2000
P 20 (W)	225	7042	2906	1826	10.91	4.8	0.88	June 2000
P 26	225	3245	1053	641	9.08	5.8	1.64	June 2000
P 27	225	6071	2101	1375	15.96	6.4	1.74	June 2000
P 101	259	28897	65517	38929	18.51	4.9	2.97	1989

TABLE A.2 Pole number, transmission lines number, Distance, soil metal concentration values of Cu, Cr and As, pH, TOC, CEC values for the soil and pole age for 37 surface sample sites taken from 30 cm away from poles.

Sample	TL	Cu (mmoles/g)	Cr (mmoles/g)	As (mmoles/g)	CEC (meq/100 g)	pH	TOC (%)	Age
P 1-32	227	1247	756	427	12.86	4.3	1.12	Nov 6 2001
P 1-33	227	198	133	62	17.31	4.6	0.69	Nov 1 2001
P 1-31(E)	227	479	493	126	16.86	4.6	1.5	Nov 7 2001
P 1-31(W)	227	543	471	191	15.21	4.8	1.58	Nov 7 2001
P 1-31 (N)	227	920	568	301	14.21	4.7	0.31	Nov 7 2001
P 1-31(S)	227	1846	911	565	17.61	4.9	1.37	Nov 7 2001
P 1-19	227	591	838	59	21.21	4.2	3.58	Oct 26 2001
P 1-18	227	892	674	384	0	6.1	4.27	Oct 26 2001
P 1-17	227	1694	985	728	44.91	4.5	12.50	Nov 7 2001
P 1-16	227	896	722	141	34.56	7.1	2.97	Nov 7 2001
P 1-12	227	1993	908	528	35.46	4.5	2.47	Oct 26 2001
P 1-11	227	38	0	4	69.06	4.1	8.50	Oct 25 2001
P 1-10	227	471	410	123	47.46	5.2	6.64	Oct 25 2001
P 1-9	227	575	609	258	71.31	4.7	6.33	Oct 25 2001
P 1-8	227	921	761	672	41.31	5.1	4.70	Nov 13 2001
P 1-5	227	312	344	90	30.96	4.9	1.74	Nov 11 2001
P 1-4 (E)	227	173	393	24	6.02	4.4	0	Nov 11 2001
P1-4 (W)	227	350	142	185	15.51	4.5	0.67	Nov 11 2001
P1-4 N	227	185	565	30	32.61	4.2	0.32	Nov 11 2001
P 1-4	227	233	384	58	12.39	4.3	0.43	Nov 11 2001
ES	225	210	164	72	13.85	4.6	1.19	June 2000
CR	225	378	557	50	16.86	6.6	1.73	June 2000
P 19 R	225	664	574	115	23.31	6.8	1.51	June 2000
P 19 C	225	308	233	95	18.96	5.4	1.39	June 2000
P 19 L (E)	225	81	12	16	6.12	7.5	0.22	June 2000
P 19 L (W)	225	2515	769	403	9.62	7.0	0.86	June 2000
P 19 L (N)	225	216	93	39	11.28	7.8	0.64	June 2000
P 19 L (S)	225	86	19	13	9.72	7.3	0.20	June 2000
P 121	259	1129	605	314	21.51	6.2	0.88	1989
P 122 E	259	2826	1949	2764	8.15	4.4	0.89	1989
P 122 W	259	491	493	332	6.99	4.5	0.83	1989
P 87	259	4312	1819	1770	14.46	4.0	1.25	1989
P 20 (E)	225	436	297	75	15.51	4.4	1.50	June 2000
P 20 (W)	225	615	228	64	14.61	4.3	2.08	June 2000
P 26	225	719	588	292	13.97	6.0	3.04	June 2000
P 27	225	765	289	64	9.69	6.6	1.36	June-2000
P 101	259	15163	5241	5507	30.9	6.0	3.89	1989

TABLE A.3 Pole Number, transmission lines number, soil metal concentration values of Cu, Cr and As, pH, TOC, CEC values for the soil, pole age for 37 sample sites taken from 60 cm and 3 samples taken from 7 m away from the poles.

Sample	TL	Dis	Cu (mmoles/g)	Cr (mmole s/g)	As (mmoles/g)	CEC (meq/100 g)	pH	TOC (%)	Age
P 1-32	227	60	631	655	112	16.71	4.3	0.88	Nov 6 2001
P 1-33	227	60	264	401	126	16.26	5.7	0.59	Nov 1 2001
P 1-31(E)	227	60	278	202	74	15.06	4.5	0.43	Nov 7 2001
P 1-31(W)	227	60	456	321	142	16.56	5	1.62	Nov 7 2001
P 1-31(N)	227	60	178	48	48	14.25	5.1	1.05	Nov 7 2001
P 1-31(S)	227	60	378	394	32	13.32	4.7	1.01	Nov 7 2001
P 1-19	227	60	475	747	43	14.76	4.3	2.53	Oct 26 2001
P 1-18	227	60	297	465	69	23.76	5.0	3.30	Oct 26 2001
P 1-17	227	60	533	592	156	31.26	4.2	4.41	Nov 7 2001
P 1-16	227	60	515	818	81	18.66	7.3	0.89	Nov 7 2001
P 1-12	227	60	398	451	62	28.56	4.4	2.86	Oct 26 2001
P 1-11	227	60	333	386	61	60.96	4.3	6.25	Oct 25 2001
P 1-10	227	60	311	354	66	63.51	4.2	6.59	Oct 25 2001
P 1-9	227	60	356	1228	124	50.01	4.4	5.79	Oct 25 2001
P 1-8	227	60	416	460	315	33.51	5.2	3.73	Nov 13 2001
P 1-5	227	60	282	420	86	35.91	4.9	3.20	Nov 11 2001
P1-4 (E)	227	60	272	586	66	8.45	4.2	0.21	Nov 11 2001
P1-4 (W)	227	60	661	450	340	14.76	4.2	0.22	Nov 11 2001
P 1-4 N	227	60	224	612	38	8.1	4.4	0.66	Nov 11 2001
P 1-4	227	60	293	533	49	8.67	4.0	0.43	Nov 11 2001
ES	227	60	275	180	66	8.90	4.6	1.04	June 2000
CR	225	60	389	278	68	12.99	6.4	3.40	June 2000
P 19 E	225	60	241	225	56	14.91	6.9	0.20	June 2000
P 19 C	225	60	580	356	175	15.66	5.9	0.79	June 2000
P 19 L (E)	225	60	231	92	125	12.81	7.1	0	June 2000
P 19 L (W)	225	60	1783	712	286	13.61	7.1	0.65	June 2000
P 19 L (N)	225	60	243	75	58	10.08	6.9	0.27	June 2000
P 19 L (S)	225	60	118	42	30	10.74	7.5	0.20	June 2000
P 121	259	60	157	92	22	5.67	4.5	0.45	1989
P 122 E	259	60	2070	1244	1917	10.22	5.1	0.89	1989
P 122 W	259	60	495	353	167	9.95	4.3	1.50	1989
P 87	259	60	298	331	83	15.21	4.1	1.09	1989
P 20 (E)	225	60	773	307	435	11.54	4.5	1.36	June 2000
P 20 (W)	225	60	458	157	28	17.16	4.2	2.29	June 2000
P 26	225	60	417	330	122	17.01	6.1	2.68	June 2000
P 27	225	60	826	341	78	8.07	6.7	2.23	June 2000
P 101	259	60	3203	1624	947	12.72	5.7	3.38	1989
P 19 (BG)	225	7 M	182	65	54	7.53	7.5	1.11	June 2000
P1-31(BG)	227	7M	293	467	323	29.91	5.6	5.00	Nov 7 2001
P 1-4 4(BG)	227	7M	386	484	0	7.32	4.9	1.00	Nov 11 2001

Appendix B

Table B.1 Date of rainfall, Time of sample collection, Amount of Cu, Cr and As leached, Amount of precipitation and average temperature during rainfall for a freshly treated CCA wooden log.

Date	Yr	Time of Recording	Cu ($\mu\text{mol/L}$)	Cr ($\mu\text{mol/L}$)	As ($\mu\text{mol/L}$)	Environment Canada (Precipitation) mm	Tempratures from Environment Canada ($^{\circ}\text{C}$)
3-Sep	2004	4:00 PM	3.40	1.29	1.50	0.1	13.3
23-Sep	2004	11:30 PM	2.11	1.71	1.17	0.2	5.7
26-Aug	2004	6:10 PM	5.20	1.83	2.02	0.6	12
2-Sep	2004	2:30 PM	5.10	2.85	2.48	0.7	13.7
15-Oct	2002	6:55 PM	0.81	0.53	0.41	0.8	9.8
30-Apr	2004	12:00 PM	2.55	2.09	1.60	1	3
1-Sep	2004	1:15 PM	6.84	3.42	2.86	1.5	19.6
10-Jun	2004	3:15 PM	5.39	1.85	1.67	1.8	8.2
30-May	2004	11:00 AM	2.61	3.45	2.52	3.4	5.1
22-Aug	2004	9:00 AM	12.50	3.66	4.11	4.2	18.8
19-May	2004	11:10 AM	2.70	1.33	1.49	4.4	8.2
28-Oct	2002	7:00 PM	33.39	31.54	14.02	5	6.1
7-Jun	2004	11:15 AM	3.09	0.98	1.35	5.7	4.9
3-Jun	2004	11:30 AM	3.18	1.76	1.19	6.8	6.5
7-Oct	2002	7:00 PM	0.76	0.17	0.21	8	15.1
1-Jun	2004	10:25 AM	1.81	1.04	1.21	8	4
25-Aug	2004	11:00 AM	0.85	5.83	1.55	8.8	19.9
6-Sep	2002	6:15 PM	1.97	0.49	0.57	9.4	18.1
10-Oct	2002	7:30 PM	2.05	0.84	1.51	9.6	6
9-Sep	2002	7:15 PM	1.53	0.42	0.38	10.6	9.4
13-Jul	2004	8:30 AM	6.96	1.22	2.22	10.8	14.5
12-Sep	2002	6:00 PM	0.97	0.17	0.20	11	12
5-Oct	2002	2:45 PM	1.19	0.23	0.24	12.8	8.2
18-Jul	2005	11:00 AM	3.52	1.74	0.73	13	14
21-Oct	2002	11:00 AM	1.15	0.45	0.53	14	6.1
3-Jul	2005	4:30 PM	2.45	1.59	0.42	14.4	14.4
23-Jun	2004	11:50 AM	5.17	1.41	2.08	15	8.6
19-Aug	2004	10:45 AM	13.13	2.42	3.12	15.2	16.8
29-May	2004	6:10 PM	14.33	4.54	2.67	15.4	3.1
22-Sep	2004	5:00 PM	4.09	3.24	2.70	15.5	13
25-Jul	2005	12:30 PM	3.39	2.42	0.80	15.6	17.5
17-Sep	2002	7:25 PM	1.40	0.28	0.30	16.2	17
6-Jul	2004	11:00 AM	6.52	1.20	1.68	16.8	11.5
27-Oct	2002	4:00 PM	0.52	0.16	0.21	17.5	3.5
16-May	2004	5:30 PM	9.54	2.56	1.66	18.4	6.3
11-Sep	2004	6:00 PM	11.06	7.39	5.39	18.4	18.8
30-Sep	2002	7:50 PM	1.84	0.25	0.49	21	10.4

Date	Yr	Time of Recording	Cu ($\mu\text{mol/L}$)	Cr ($\mu\text{mol/L}$)	As ($\mu\text{mol/L}$)	Environment Canada (Precipitation) (mm)	Temperatures from Environment Canada ($^{\circ}\text{C}$)
5-Sep	2004	5:45 PM	149.29	77.69	55.81	22.8	8.8
8-Jun	2005	4:00 AM	3.70	3.40	0.71	23	11.7
31-Aug	2004	2:00 PM	29.42	13.65	8.87	30.6	11.5
26-Jul	2004	5:00 PM	16.69	9.85	5.61	32.2	16.1
14-Jun	2005	10:00 PM	3.17	3.02	0.65	34	9
5-Sep	2002	7:30 PM	4.68	2.35	1.82	36.4	16.6
28-Jun	2005	4:30 PM	4.57	3.81	1.72	42.6	9.2
30-Sep	2004	1:45 PM	9.29	7.15	4.14	45.5	13.6
20-Sep	2004	6:00 PM	60.79	46.15	50.47	100.9	13
27-Apr	2004	10:45 AM	13.32	11.19	6.89	S.M	ND
28-Apr	2004	10:45 PM	5.20	3.78	2.30	S.M	ND
14-Jan	2005	7:35 PM	5.17	2.58	1.25	S.M	ND
10-Feb	2005	9:00 AM	2.63	5.48	2.60	S.M	ND
12-Feb	2005	4:00 PM	1.59	3.52	1.05	S.M	ND
26-May	2005	6:00 PM	2.99	1.49	1.52	S.M	ND
3-May	2004	3:00 PM	0	0.10	0	Trace	4.2
14-Jun	2004	7:45 PM	4.41	1.69	1.51	Trace	4.4
6-Sep	2004	3:30 PM	4.13	2.96	2.62	Trace	11.7
12-Sep	2004	5:15 PM	3.03	2.38	1.54	Trace	9.4
9-Jun	2005	6:00 PM	2.68	1.61	0.92	Trace	5.8

Table B.2. Date of rainfall, time of sample collection, Amount of Cu, Cr and As leached, Amount of precipitation and average temperature during rainfall for a freshly treated CCA wooden log.

Date	Yr	Time of Recording	Cu (µmol/L)	Cr (µmol/ L)	As (µmol/ L)	Environment Canada (Precipitation) (mm)	Temperatures from Environment Canada (°C)
5-Sep	2002	7:30 PM	4.68	2.35	1.82	36.4	16.6
6-Sep	2002	6:15 PM	1.97	0.49	0.57	9.4	18.1
9-Sep	2002	7:15 PM	1.53	0.41	0.38	10.6	9.4
12-Sep	2002	6:00 PM	0.97	0.17	0.20	11	12
17-Sep	2002	7:25 PM	1.40	0.28	0.30	16.2	17
30-Sep	2002	7:50 PM	1.84	0.25	0.49	21	10.4
5-Oct	2002	2:45 PM	1.19	0.23	0.24	12.8	8.2
7-Oct	2002	7:00 PM	0.76	0.17	0.21	8	15.1
10-Oct	2002	7:30 PM	2.05	0.84	1.51	9.6	6
15-Oct	2002	6:55 PM	0.81	0.53	0.41	0.8	9.8
21-Oct	2002	11:00 AM	1.15	0.45	0.53	14	6.1
27-Oct	2002	4:00 PM	0.52	0.16	0.21	17.5	3.5
28-Oct	2002	7:00 PM	33.39	31.54	14.02	5	6.1
27-Apr	2004	10:45 AM	13.32	11.19	6.89	S.M	ND
28-Apr	2004	10:45 PM	5.20	3.78	2.30	S.M	ND
30-Apr	2004	12:00 PM	2.55	2.09	1.60	1	3
3-May	2004	3:00 PM	0	0.10	.0	Trace	4.2
16-May	2004	5:30 PM	9.54	2.56	1.66	18.4	6.3
19-May	2004	11:10 AM	2.70	1.33	1.49	4.4	8.2
29-May	2004	6:10 PM	14.33	4.54	2.67	15.4	3.1
30-May	2004	11:00 AM	2.61	3.45	2.52	3.4	5.1
1-Jun	2004	10:25 AM	1.81	1.04	1.21	8	4
3-Jun	2004	11:30 AM	3.18	1.76	1.19	6.8	6.5
7-Jun	2004	11:15 AM	3.09	0.97	1.35	5.7	4.9
10-Jun	2004	3:15 PM	5.39	1.85	1.67	1.8	8.2
14-Jun	2004	7:45 PM	4.41	1.69	1.51	Trace	4.4
23-Jun	2004	11:50 AM	5.17	1.41	2.08	15	8.6
6-Jul	2004	11:00 AM	6.52	1.20	1.68	16.8	11.5
13-Jul	2004	8:30 AM	6.96	1.22	2.22	10.8	14.5
26-Jul	2004	5:00 PM	16.69	9.85	5.61	32.2	16.1
19-Aug	2004	10:45 AM	13.13	2.42	3.12	15.2	16.8
22-Aug	2004	9:00 AM	12.50	3.66	4.11	4.2	18.8
25-Aug	2004	11:00 AM	0.85	5.83	1.55	8.8	19.9
26-Aug	2004	6:10 PM	5.20	1.83	2.02	0.6	12
31-Aug	2004	2:00 PM	29.42	13.65	8.87	30.6	11.5
1-Sep	2004	1:15 PM	6.84	3.42	2.86	1.5	19.6
2-Sep	2004	2:30 PM	5.10	2.85	2.48	0.7	13.7
3-Sep	2004	4:00 PM	3.40	1.29	1.50	0.1	13.3

Date	Yr	Time of Recording	Cu ($\mu\text{mol/L}$)	Cr ($\mu\text{mol/L}$)	As ($\mu\text{mol/L}$)	Environment Canada Precipitation (mm)	Temperatures From Environment Canada ($^{\circ}\text{C}$)
5-Sep	2004	5:45 PM	149.29	77.69	55.81	22.8	8.8
6-Sep	2004	3:30 PM	4.13	2.96	2.62	Trace	11.7
11-Sep	2004	6:00 PM	11.06	7.39	5.39	18.4	18.8
12-Sep	2004	5:15 PM	3.03	2.38	1.54	Trace	9.4
20-Sep	2004	6:00 PM	60.79	46.15	50.47	100.9	13
22-Sep	2004	5:00 PM	4.09	3.24	2.70	15.5	13
23-Sep	2004	11:30 PM	2.10	1.70	1.16	0.2	5.7
30-Sep	2004	1:45 PM	9.29	7.15	4.14	45.5	13.6
14-Jan	2005	7:35 PM	5.17	2.58	1.25	S.M	ND
10-Feb	2005	9:00 AM	2.63	5.48	2.60	S.M	ND
12-Feb	2005	4:00 PM	1.59	3.52	1.05	S.M	ND
26-May	2005	6:00 PM	2.99	1.49	1.52	S.M	ND
8-Jun	2005	4:00 AM	3.70	3.39	0.71	23	11.7
9-Jun	2005	6:00 PM	2.68	1.61	0.92	Trace	5.8
14-Jun	2005	10:00 PM	3.17	3.02	0.65	34	9
28-Jun	2005	4:30 PM	4.57	3.81	1.74	42.6	9.2
3-Jul	2005	4:30 PM	2.45	1.59	0.43	14.4	14.4
18-Jul	2005	11:00 AM	3.52	1.74	0.73	13	14
25-Jul	2005	12:30 PM	3.39	2.42	0.80	15.6	17.5

Appendix C

Table C.1 Average values of pH, TOC and CEC for each pole

Pole	T.L	pH	TOC %	CEC (meq/100 g)
32	227	4.3	0.71	13.77
31	227	4.9	1.52	18.65
33	227	5.3	0.87	19.31
19	227	4.4	2.93	17.11
18	227	5.6	3.5	23.76
17	227	4.5	9.03	43.36
16	227	7.2	2.96	34.36
12	227	4.5	2.48	28.91
11	227	4.2	8.09	55.16
10	227	4.9	6.58	52.61
9	227	4.6	6.58	59.61
8	227	5.1	4.31	38.46
4	227	4.4	0.37	18.28
5	227	4.9	2.68	22.29
Edward Street	225	4.6	1.21	14.45
19	225	6.9	0.67	13.05
26	225	6.0	2.45	13.35
20	225	4.5	1.50	13.06
27	225	6.5	1.78	11.24
Canal Road	225	6.5	2.44	12.72
121	259	5.7	0.59	11.24
122	259	4.5	0.91	9.44
101	259	5.5	3.41	18.51
87	259	4.12	1.41	12.3

APPENDIX D

Table D.1 Pole number, Transmission lines number, Drop in Cu, Cr and As concentration values from 0 to 30 cm, CEC, pH, TOC values for the soil and pole age for 37 sample sites.

Sample	TL	Cu (mmoles/ g)	Cr (mmoles/ g)	As (mmoles/ g)	CEC (meq/ 100g)	pH	TOC (%)
P 19 C	225	542	0	114	17.36	5.5	1.12
P 122 R	259	1002	2657	1806	11.19	4.6	0.83
P 19 L (L)	225	1380	651	516	14.46	7.1	0.87
P 1-4 N	227	1505	135	771	17.18	4.4	0.40
P 1-31(L)	227	1841	867	827	19.91	5.0	1.42
C R	225	1950	630	976	12.72	6.5	2.44
P 1-32	227	2349	457	871	13.77	4.3	0.90
P 1-9	227	2358	604	1034	59.61	4.6	6.58
P 26	225	2526	465	349	13.35	6.0	2.45
P 1-12	227	2611	866	1016	28.91	4.5	2.48
P1-4 (L)	227	2781	744	1444	15.46	4.5	0.37
P 1-5	227	3876	1145	2174	22.29	4.9	2.68
P 19 R	225	4127	767	697	15.66	6.7	1.00
P 1-33	227	4348	1498	2440	19.31	5.3	0.87
P 19 L (R)	225	4874	1654	677	8.135	7.4	0.15
P 20 (R)	225	4932	1033	1443	11.91	4.6	1.26
E S	225	5095	3353	3259	14.45	4.6	1.21
P 27	225	5306	1813	1310	11.24	6.5	1.78
P 1-4 (R)	227	6128	1589	3562	6.78	4.5	0.14
P 20 (L)	225	6427	2678	1762	14.23	4.4	1.75
P 122 L	259	6822	15407	8179	7.695	4.4	0.99
P 1-17	227	6858	815	2564	43.36	4.5	9.02
P 19 L (S)	225	7972	2676	1052	13.19	7.2	0.24
P 1-4	227	8813	1856	4949	10.52	4.2	0.36
P 1-18	227	9633	2278	4019	7.92	5.6	3.51
P 1-11	227	11307	2579	4449	55.16	4.2	8.09
P 1-31 (N)	227	11352	1710	3623	16.21	4.9	0.81
P 1-31 (R)	227	11925	3262	3100	17.06	4.7	1.39
P 101	259	13734	60276	33422	20.71	5.5	3.41
P 1-16	227	13931	2009	3627	34.36	7.2	2.96
P 1-10	227	14907	5958	5758	52.61	4.9	6.58
P 87	259	16966	10006	6481	12.3	4.1	1.41
P 19 L (N)	225	17088	6031	2443	11.31	7.0	0.52
P 1-19	227	17867	4138	4459	17.11	4.4	2.93
P 1-31(S)	227	17934	3554	5929	17.78	5.0	1.31
P121	259	21312	4590	2875	11.24	5.7	0.59
P 1-8	227	36583	14740	15037	38.46	5.1	4.31



