THE DEVELOPMENT AND EVALUATION OF A RECYCLING METHODOLOGY FOR OUT OF SERVICE PENTACHLOROPHENOL-TREATED UTILITY POLES.

by

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List of Abbreviations and Acronyms

ACA – Ammonicial Copper Arsenate

ACQ – Amine Copper Quaternary00

ACZA – Ammonical Copper Zinc Arsenate

AWPA – American Wood Preservers Association

CA – Copper Azole

CCA – Chromated Copper Arsenate

Checking – The splitting of wood caused by drying.

CSA – Canadian Standards Association

CITW – Canadian Institute of Treated Wood

CuC – Copper Citrate

CuN – Copper Napthanate

CWPA – Canadian Wood Preserver's Association

Cylinder – The tubular pressure vessels used to pressure treat wood.

FPS – Forest Products Association

IRG – International Research Group on Wood Preserving

MSW – Municipal Solid Waste

MISA – Municipal/Industrial Strategy for Abatement

Na-PCP – Sodium Pentachlorophenate

PCP – Pentachlorophenol

Penetration – The depth to which preservative has entered the wood.

PMRA – Pesticide Management Review Agency

PIRI – Petroleum Industry Research Institute

RBCA – Risk Based Corrective Action

RCRA- Resource Conservation and Recovery Act

Retention – Amount of preservative left in a pole's treated zone, measured in kg/m^3.

SAS – Statistical Analysis System

TCLP – Toxicity Characteristic Leaching Procedure

Acknowledgements

I would like to thank the sponsor Stella-Jones Inc. for funding my research and giving me the time from my position with them to complete the required course work and thesis for this degree. Thanks as well to the personnel at the plants who helped me by taking their own initiative and asking less of me on a daily basis.

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From a family perspective, I wish to thank my two children, Emma and Alexander, for understanding why Daddy was always busy. Hopefully, I struck a good balance in splitting time between them, work and school.

Abstract

The objective was to develop a commercially viable method for removing pentachlorophenol (PCP) from out-of-service utility poles. The distribution of PCP within 30 year old poles was mapped with respect to depth and length. A comparison of gas chromatography versus X-ray fluorescence was performed and it was verified that no significant difference existed between the two analytical methods. Preliminary experiments led to the choice of 1N NaOH as an extraction solvent for the removal of PCP. The scale up of wood surface area to solution volume ratios began with sawdust and ended with full pole sections. Greater than 98% of the PCP was removed from all samples. Values obtained from the solvent detreatment process were below the hazardous waste criteria for residual PCP and the extraction process is under patent finalization.

1.0 Introduction

The wood preserving industry is at a turning point environmentally and must adapt in order to survive. For years, the Canadian Institute for Treated Wood (CITW) has successfully argued that treating wood saves trees and that less energy is used in the production of treated wood than in substitute long–lived products, such as steel and concrete. Still, the industry remains tarnished by the image of old run down production facilities with creosote stained soil and contaminated groundwater. Although preservatives must be toxic to wood destroying organisms a trend towards the use of more environmentally friendly products has been initiated by the wood preserving industry. This fact is unknown to the public, despite intensive regulation of the industry by Environment Canada under the Technical Recommendations Documents (TRDs) for both the design, operation and monitoring of plant employees and discharges. However, regulations only serve to protect and establish a level playing field for all competitors. The public now demands that the production and use of treated wood products be ecologically sound and both the development of more suitable preservatives and the recycling of existing treated wood products are an important aspect of this strategy.

There remains a continuing dilemma, however, about how to manage the disposal of wood that, despite being treated with toxic chemicals, has had little environmental impact during its service life. This is a particular problem with larger products like utility poles.

The wood preserving industry lacks a comprehensive recycling system for pentachlorophenol (PCP) treated utility poles regardless of the species of wood used to produce the poles. It is this inability to be recycled that gives an advantage to substitute products and threatens the continued use of PCP as a wood preservative, and the market share associated with its use (Murray, 2001). The only methods used extensively to deal with these poles revolve around their reuse, with the associated liability disclaimers, rather than around the ultimate removal of the actual liability source, which is both the PCP and its carrier oil (Cooper *et al.*, 1996; Konasewich *et al.*, 2001).

Pentachlorophenol has been the dominant pole preservative used in North America since the late 1960s (Stephens *et al.*, 2001). Most of the concerns over its use as a preservative relate to the presence of co-contaminants, such as lower chlorinated phenols, dioxins and furans that are produced during the PCP manufacturing process (Crosby, 1981). Though the PCP industry has improved the manufacturing process since the mid-1980s, all of the poles considered in the present study were treated prior to this change, in the mid to late 1970s. This fact explains the age of the references used in this presentation with respect to PCP chemistry.

Overall, the peer-reviewed literature is sparse on the details of wood preserving, as information is mostly contained in unpublished industry and company promotional and operational literature, or the specific standards imposed by the American Wood Preserver's Association (AWPA) and the Canadian Standards Association (CSA). The

author has worked in this industry for 16 years, and is currently a Vice President – Environment and Technology, and is responsible for writing the treatment methodologies and associated manuals for the largest wood preservation company in Canada, which is Stella-Jones Inc. (SJI), and its United States division, Stella-Jones Corporation (SJC).

The goal of the present research was to develop an effective PCP removal system from wood to allow for either reuse of the wood fibre as by-products or its disposal as non-hazardous waste. The sponsor of this project, SJI, will benefit from this research as follows:

1) Competitive advantage by being the first to bring a recycling system to wood preserving customers (Murray, 2001).
2) Ability to generate a new revenue stream for an industry which is in the decline phase of its product life cycles (Murray, 2001).
3) Being ready for the future, as bans on the land filling of treated wood are inevitable (Murray, 2001).
4) Long time frame in which they can offer this service on PCP treated material, even if substitute preservatives were to take over the bulk of the industry in the near future (Murray, 2001).

1.1 Objectives

The scientific objectives of this study were as follows:

i) To map the distribution of PCP with respect to length and depth, within out-of-service utility poles.

ii) To develop an economical method to remove PCP from out-of-service utility poles.

iii) To design a system for PCP removal from out-of-service utility poles that can be adapted for use at a full scale commercial operation.

Research involved mapping the distribution of PCP within out-of-service Red Pine (*Pinus resinosa*) poles relative to pole length and treatment depth. This information was used to develop a methodology for a chemical and physical removal system for PCP from these out-of-service Red Pine poles. Though bioremediation and straight chemical extraction were both considered, these concepts were eliminated from the project as being less financially viable alternatives.

The ideal situation was to develop a methodology that uses existing wood preserving plant equipment to "untreat" the utility pole by reversing the preservative penetration process through chemical and phase change reactions. A step by step scaling up of the concept of conversion of PCP to Sodium-PCP (Na-PCP), followed by vacuum extraction with a phase change, was performed on spent utility poles using sawdust sized particles up through pole peeler strips, pole slats of varying thicknesses, and finally to full pole

sections. Red Pine was selected due to its composition of intermediate sapwood, its ease of treatment and its dominance in the utility pole market (Stephens *et al.*, 2001).

1.2 Originality

Extensive review of the scientific literature and internal utility and telecommunication company reports has shown that no system exists to remove PCP from spent utility poles (Summers, 1995; Cooper *et al.*, 1996; Malecki, 1998; Environment Canada, 1998; Konasewich *et al.*, 2001; Morrell, 2004). The main contributions to scientific knowledge in this thesis are as follows:

1) Development of an economical and patentable method for removing PCP (pentachlorophenol) from out-of-service utility poles.

2) Mapping of the distribution of PCP within a utility pole with respect to pole length and preservative penetration depth.

3) Comparison of Gas Chromatography versus X-ray Florescence to determine if non-extraction methods with the latter instrument can be as effective on quantifying PCP in wood fibre.

4) Scale up of the PCP removal method from bench scale experiments to full poles in a pilot plant.

5) Design and construction of two pilot plants for PCP extraction and a specialized grinding apparatus for preparing wood samples for chemical extraction.

6) Preparation of a theoretical concept for the modifications required to a wood treating plant for a full scale PCP extraction operation.

7) Initial costing and the business plan for the process to go to full scale PCP extraction.

2.0 Literature Review

2.1 Background on the Wood Preserving Industry

Over time, the protection of wood against decay has involved drying, chemical treatment, water storage, or a combination of the above (Yang, 2001). Decay has always been positively correlated to high moisture and oxygen content, hence, there was a historical development of submergence and drying technologies for wood preservation in ancient Japanese and Egyptian cultures (Hingley *et al.*, 1983). The Romans were the first to record the susceptibility of wood to fungal and boring degradation in 72 AD (Richardson, 1993).

Wood preservation has been credited with enhancing the exploration of the earth by sea going vessels through improving hull and mast performance in tropical oceans. This was pioneered by Lord Cochrane in the 1800s (Richardson, 1993). Wood preservation has also been responsible for the expansion of the world's rail and power distribution networks (Richardson, 1993). Coal tar was the first mass produced preservative, invented in 1660 by Dr. J. Becker and later adopted by the British Royal Navy (Richardson, 1993). By 1842, Zinc Chloride, Mercuric Chloride, Copper Sulphate, Ferrous Sulphate with a Sulphide, and Creosote preservatives were all available commercially (Richardson, 1993).

The evolution of the utility pole (Figure 2.1) began with the telegraph in 1840 and its' growth phase was initiated with the first hydro-electric project in 1896 (Murray, 2001). Pentachlorophenol has been the dominant utility pole preservative used in North America since the early 1960's (Kosanovich, 1999; Stephens *et al.*, 2001). The lifespan of a treated pole averages 30 years in Canada (Konasewich *et al.*, 2001; Stephens *et al.*, 2001). This means that the majority of the poles removed from service in Canada within the next 30 years will be PCP treated (Cooper *et al.*, 1996). To date, no one has

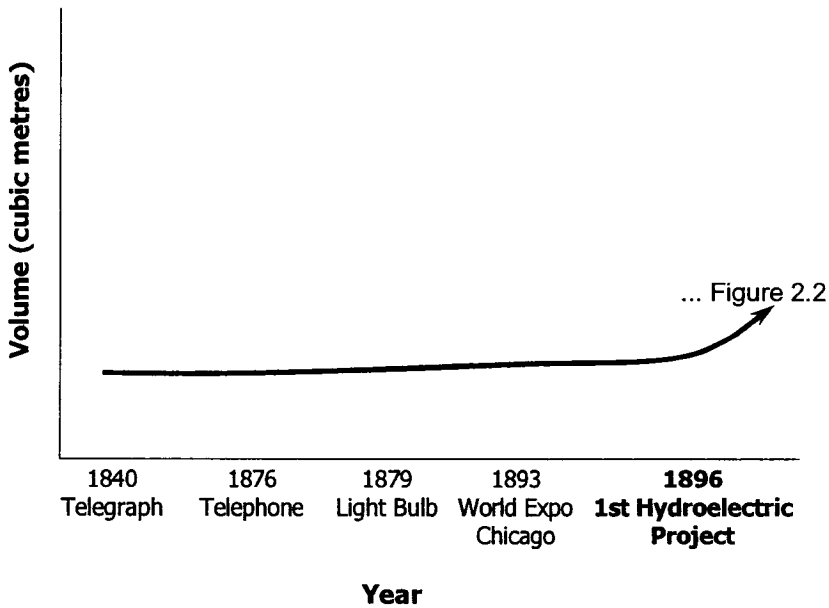

Figure 2.1. Milestone inventions leading to utility pole growth phase in North America (after Murray, 2001).

developed a preservative removal technology to handle out-of-service products. The one exception is Chromated Copper Arsenate (CCA) treated poles recycled by Stella, SPA of Italy (Kosanovich, 1999). The commercial downside of this particular process is the extensive grinding of the pole which is required to improve efficiency of the extraction solvent. Only the government regulation of pole disposal in landfills in Italy made this level of recycling a necessity for the treated pole producers (Kosanovich, 1999).

From a product life cycle perspective, the use of poles, is in the decline phase of the product life cycle (Murray, 2001). The exponential growth phase for treated poles began in the early 1900's, peaked in 1955, when the majority of our infrastructure was in place, and has been declining since that time period as noted in Figure 2.2 (Murray, 2001). A market based, forecast driven demand-function-technology analysis clearly shows that threats to the continued marketing of this product include the availability of substitute products, an increase in underground distribution networks and the growth in wireless telecommunications (Murray, 2001). The on-going demand for poles is expected to continue, due to the need to replace existing infrastructure, but reductions in new line construction will continue (Kosanovich, 1999). As a result, a successful wood treating company will require new technology to develop an additional revenue stream based on pole recycling (Murray, 2001).

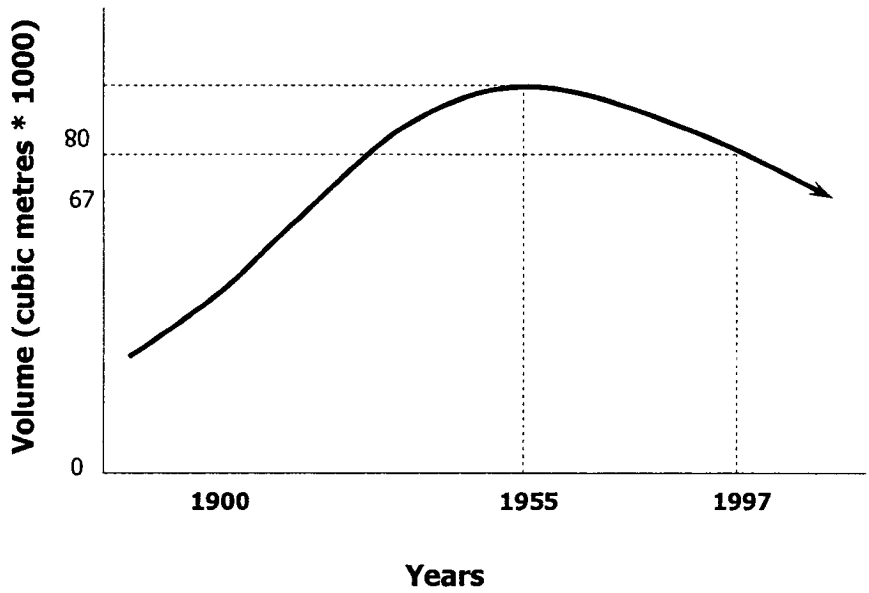

Figure 2.2. Utility pole product life cycle in North America peaking in 1955, equal to 800,000 poles (after Murray, 2001).

2.2 Recycling Issues

After the ice storm of 1998, that struck parts of Ontario, Quebec and the North Eastern United States, a major study was conducted by New York State Gas and Electric to look at the options available to deal with the large quantities of treated utility poles that will require disposal. The study was performed by the Treated Wood Disposal Task Forces Utilities Solid Waste Activities Group which was composed of members of all the

utilities impacted by the 1998 event (Malecki, 1998). This included Hydro-Quebec, Hydro-One, Bangor Hydro and Central Maine Power, all of which are customers of SJI.

The results of that study indicated that Utilities most commonly try to have old or damaged poles taken away for other unspecified uses, with or without disclaimers on their future use, while the balance are landfilled (Malecki, 1998). Other methods include: 1) mechanical removal of the treated portion to minimize landfill volumes and to re-use the untreated portion for various commodities, and 2) co-generation burning of poles at temperatures greater than 800°C. These two methods are used on less than 0.5% of the removed volume of poles (Konasewich *et al.*, 2001).

The mechanical properties and reuse applications for out-of-service poles was assessed using 456 utility poles by Cooper *et al.* (1996). They detailed the relative percentage of poles that could be re-used at 7.8%, landfilled at 9.9%, 2.3 m to 4 m stud lumber at 37.3%, posts at 20.3%, shingles at 14.7%, and firewood at 10% (Cooper *et al.*, 1996).

The major stumbling block with the disposal of PCP treated wood is the presence of chloride ions, which restricts incineration of the wood and its use as a fuel in cogeneration technologies, which is a common method of disposing of creosote treated wood (Malecki, 1998; Konasewich *et al.*, 2001). Chlorine is the second most electronegative element and, as such, has the capability of destroying large amounts of ozone when released into the atmosphere (Malecki, 1998). In addition, older PCP treated

products contain dioxins and furans, further restricting incineration as a disposal option (Crosby, 1981). Consequently, the only recycling technology used on a minimal commercial scale is the removal of the treated portion on high dollar value wood species through sawing or peeling to minimize landfill volumes (Malecki, 1998; Konasewich *et al.*, 2001). Pyrolysis and ethanol extraction have been proposed with PCP treated wood but have not been economically feasible (Ensyn Inc., 1998; Konasewich *et al.*, 2001).

The wood preserving industry considers it to be only a matter of time before the volume pressure on landfills results in the banning of treated wood from burial (CITW, 2004). From a marketing perspective, the lack of a "true" recycling system for treated wood has resulted in the move towards substitute products, such as steel and concrete (Murray, 2001). Recycling is becoming an issue for all of the utilities and frequently appears in their tender documents (BC Hydro, 2004; Maritime Electric, 2004). The supplier who addresses this issue for the utilities will gain a substantial competitive advantage (Murray, 2001).

In 2000, over 200,000 utility poles were removed from service in North America, and 85% of them were treated with PCP (Stephens *et al.*, 2001). The predominant species removed in Canada is Red Pine (*Pinus resinosa*), which accounts for 74% of the PCP treated poles (Stephens *et al.*, 2001). Red Pine is intermediate in sapwood depth, ease of penetration and cost, making it the species of preference for utility poles (Murray, 2001). The other two most common wood species are shallow sapwood, refractory, Douglas Fir

(*Pseudotsuga menziesii*) and very deep sapwood, easily treated, Southern Yellow Pine (*Pinus taeda*) (Stephens *et al.*, 2001). Untreated Western Red Cedar (*Thuja plicata*) has also been used in environmentally sensitive applications (Stephens *et al.*, 2001). The current life cycle for treated wood is summarized in Figure 2.3. Leaving the treated material for disposal by any one is dangerous, as this material often is burned in family homes. The desired life cycle for treated wood products is shown in Figure 2.4.

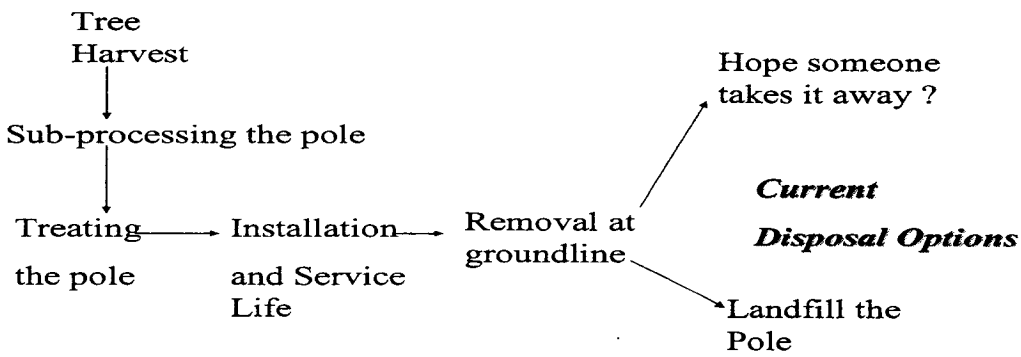

Figure 2.3. Nova Scotia Power's current approach to pole recycling, average service life is 30 years (adapted from Benedict, 2002).

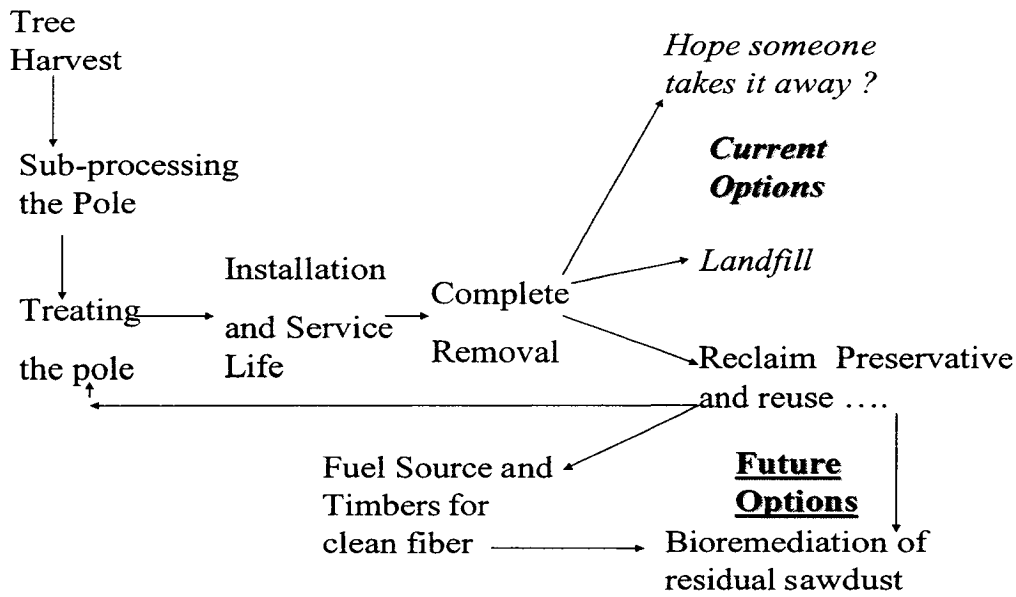

Figure 2.4. Future life cycle for treated poles.

The goal of this research is to develop a more appropriate life cycle for treated wood to protect the industry's market share, protect the environment and reduce the volume pressures on landfills. Criteria which affect the disposal impacts of treated wood and waste in landfills generally refers to the US based Resource Conservation and Recovery Act (RCRA) (Morrell, 2004). One aspect of disposal is the leaching of chemicals from treated wood. Data on this are collected using the Toxicity Characteristic Leaching Procedure (TCLP) which utilizes a buffered organic acid solution (acetic acid) to simulate contaminant leaching under the anaerobic decomposition conditions of a

municipal solid waste (MSW) landfill (Groot and Felton, 1995; Government of Canada, 2006).

2.3 Common Wood Preservative Formulations

To function as a wood preservative the treatment applied must be able to remove wood as a food source for decay organisms (Hack, 2000). This is normally accomplished through the chemical formulations used (CITW, 2002). Preservatives are generally not applied in order to protect a specific product from a specific decay threat, but rather they are all designed to be applicable in the harshest environments where insect, marine borers and fungal decomposition are all accounted for (Yang, 2001). The only variables required are changes in the loading rate and the applicable penetration depth for each wood species and product end use (AWPA, 2004).

Clearly, preservatives that address a specific end use are required and the financial incentives to pursue improved preservative technologies are twofold: 1) to decrease the remediation costs associated with soil and groundwater contaminated by leached chemical preservatives, and; 2) to reduce the over two billion dollars (US) per year that is spent replacing decayed wood in North America (Stephens *et al.*, 2001; Yang, 2001).

In Canada, the majority (about 80%) of treated wood in service is subject only to fungal decomposition (Stephens *et al.*, 2001; Murray, 2001). As well, many species of wood are

used in their untreated form since their low sapwood to heartwood ratios impart a natural decay resistance (Jin and Laks, 1994). Western Red Cedar (*Thuja plicata*) is the most common wood used in an untreated form in utility and dimensional structures. Locally, Tamarack (*Larix laricina*) has been used by farmers for years as fence posts and generally has three times the lifespan of other locally available species (Srinivasan *et al.*, 1999;Yang, 2001).

Current preservatives licensed in Canada by the Pesticide Management Review Agency (PMRA) for external residential or industrial uses are Creosote, (PCP), (ACA), Ammoniacal Copper Zinc Arsenate (ACZA), Chromated Copper Arsenate (CCA), Ammoniacal Copper Citrate (CuC), Ammoniacal Copper Quaternary (ACQ – ammonia), Amine Copper Quaternary (ACQ-amine), Copper Napthanante (CuN) and Copper Azole (CA) (CITW, 2004; PMRA, 2004). Borates are common additives for internal structures requiring termite and fungal protection and in the field treatment of transmission lines (CITW, 2004; PMRA, 2004). Field treatments are used on existing treated poles associated with high electrical capacity transmission lines as a means of increasing their service life (AWPA, 2004).

PCP and CCA are the two most often used preservatives for poles. Creosote, ACA and ACZA maintain market niches due to their ability to treat refractory species or their ability to improve mechanical properties of the wood (FPS, 1999). The balance of the formulations, particularly ACQ-amine and CA, are only now being used in commercial

quantities after the ban on CCA for residential applications took effect at the beginning of 2004 (CITW, 2004). ACQ-amine maintains 85% of the former CCA residential market, with CA replacing the balance (CITW, 2004; AWPA, 2004).

2.3.1 Future of Preservatives

The recent pressure on the industry brought about by concerns over CCA has resulted in an actual resurgence of the old organic preservatives, such as creosote, since the treated products can be incinerated or biodegraded (Rodriguez, 2000). Even the USEPA's review of PCP treated poles was very positive with respect to natural attenuation of any leachate leaving the installed structure (USEPA, 2004b,d). The waterborne preservatives have become regulatory targets due to the presence of arsenic and chromium, which do not degrade and which are more or less mobile depending on the redox state within their environment (CITW, 2003). In fact, the wood preserving industry is the largest importer of arsenic into North America (Stephens *et al.*, 2001). This has resulted in the banning of CCA for residential applications within North America beginning in 2004 (CITW, 2004).

Without understanding the realities of the market, the new generation of preservatives that were meant to replace CCA followed the same chemical track by simply replacing a portion of, or the entire, arsenic component (Murray, 2001; Ziabro, 2005; Mitchell, 2006). These new formulations, such as ACQ and CA, are already under attack due to their inability to chemically bind to wood fibres, resulting in excessive leaching of copper

components (Domtar, 1992). Unfortunately, this has not affected their adoption into wood treatment specifications despite excessive copper loss. The most promising new preservatives are organo-copper complexes which are now being placed into the testing programs of all major suppliers (Ziabro, 2005; Mitchell, 2006). This line of product development follows the work on lignin-copper complexes by Jin and Laks (1994).

The last few years have seen an increased environmental awareness of the use of chemicals in general, whether truly risk based or not (CITW, 2003). This has opened the door for the application of biotechnology procedures to the preservation of wood. To date, this line of research has not been successful due to the limited availability of biological sources of preservatives, a narrow spectrum of inhibition of wood destroying agents by these biological extracts, the high cost of obtaining bio-preservatives versus other types, an interdependence of co-factors affecting natural resistance, and an inconsistency in the natural production of useable biological materials based on growth location (Jin and Laks, 1994).

Given that three of the above issues can be overcome in northern climates, such as Canada, with respect to the predominance of fungal species in the decomposition of wood and the presence of many under utilized wood species, work will continue on biotechnology solutions (Ziabro, 2005; Mitchell., 2006). In addition, a marketing study done by Home Depot on wood preservatives has indicated that Canadian consumers are willing to pay a higher price for more "environmentally friendly" preservatives and that

the preservative accounts for only 5% of the current finished product cost (Murray 2001;Crowchuck, 2002).

2.4 Wood Structure

The generalized structure of wood, moving inwards from the outside, includes bark, phloem, vascular cambium, sapwood and heartwood (Haygreen and Bowyer, 1996; Hack, 2000). Bark is the outer covering of the tree which provides protection from extremes of temperature, drought, and mechanical injury (Hoadley, 1990).

Phloem, or inner bark, conducts food and chemicals manufactured in the leaves to regions of active growth and areas for storage (Haygreen and Bowyer, 1996). Vascular cambium is the thin tissue layer between the bark and the wood. This layer produces phloem cells toward the outside and wood cells (xylem) toward the inside (Bidwell, 1979). In temperate regions, growth occurs in this layer during spring and summer months (Hack, 2000).

Sapwood is the outermost, or youngest growth layer of wood and is actively involved in the transport of water and dissolved minerals from the roots of the tree to the leaves

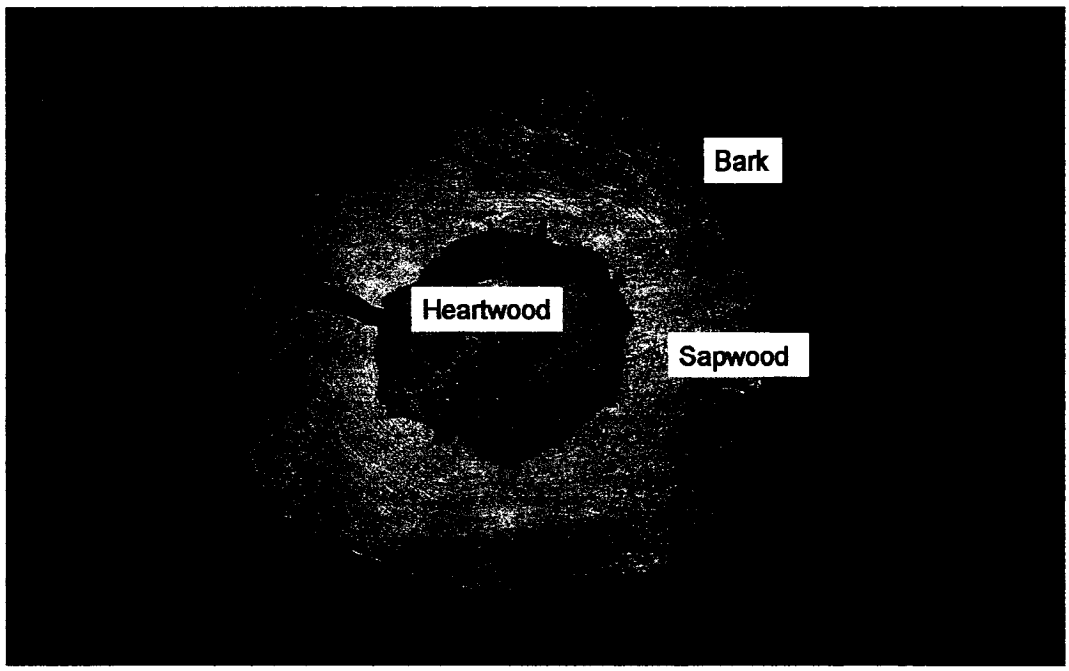

Figure 2.5 Representative cross section of Red Pine.

(Haygreen and Bowyer, 1996). Heartwood is the innermost, or oldest growth layer of wood and is formed as sapwood ages and becomes infiltrated by gums and resins (Bidwell,1979). Heartwood can usually be identified by its darker color. A cross section of a Red Pine (*Pinus resinosa*) tree can be found in Figure 2.5.

Wood dried to below the fiber saturation point is composed of cellulose, lignin, hemicelluloses and minor amounts of extraneous material (FPS, 1999). Cellulose accounts for 50% of wood by weight and is comprised of high molecular weight linear

polymer chains with at least one *B*-linked glucose monomer (Haygreen and Bowyer, 1996). These chains are arranged into fibrils that make up the cell wall (Bidwell, 1979). In softwood, lignin is the next most common component at 28% by weight, and it is concentrated in the cell walls as well as between cells where it acts as a cementing agent (Blanchette, 1991). Lignin is a three-dimensional phenylpropanol polymer that is not fully understood structurally despite the focus of the pulp and paper industry on its efficient removal (FPS, 1999).

Hemicelluloses are branched low molecular weight polymers composed of pentose and hexose sugar monomers (Blanchette, 1991). Relative quantities vary with species but generally occur in higher concentrations in preferred pulp species such as Black Spruce (Mullins and McKnight, 1981). Extraneous materials generally run between 5 and 30% of wood but are key components in imparting specific properties, such as color, density and decay resistance (Jin and Laks, 1994). Tannins and other polyphenolics are the key decay resistant materials (FPS, 1999; Grohs and Kunz, 1998). The natural decay resistance of the heartwood of certain species has been linked to tropolones, condensed tannins, stilbene, pyrethrum and flavanoids, most of which have similar fungal inhibiting properties to PCP (Grohs and Kunz, 1998).

The majority of softwood volume, or 90-95%, is composed of long slender vertically arranged cells call tracheids (Richardson, 1993). These tracheids are about 100 times greater in length than they are in diameter, with an average length of between 2.5 and 5

mm (Troya *et al.*, 1995; Haygreen and Bowyer, 1996). Tracheids have hollow centers (lumen), but are closed at the ends. Small passages called pits join tracheids to each other and to other types of wood cells (FPS, 1999).

Parenchyma cells are another common type of wood cell. Parenchyma cells are thin-walled food storage cells (Bidwell, 1979; Hoadley, 1990). Some parenchyma cells are aligned longitudinally (similar to tracheids), but most are aligned radially (horizontally) (Haygreen and Bowyer, 1996). The latter type of parenchyma cells are arranged in a linear pattern, called rays, which extend from the cambium layer (inside the bark), to the center of the heartwood (Troya *et al.*, 1995). Both longitudinal parenchyma and ray parenchyma provide avenues where fluids can pass (Hack, 2000). Parenchyma cells are usually connected together by pits at the ends, allowing flow from one parenchyma cell to another unless aspirated during growth, as mentioned above (Haygreen and Bowyer, 1996; Hack, 2000).

Pits are areas within wood cells where there is an absence of the secondary cell wall, leaving only the primary cell wall or pit membrane (FPS, 1999). Normally, pit placement in a cell matches the pit placement of the adjoining cell, except in hard to treat or refractory wood species (Hack, 2000). The thin membrane between the pits allows the penetration of fluids and gases between cells (FPS, 1999).

2.4.1 Preservative Penetration

Penetration of a preservative into wood is species dependent. Penetration of common utility pole wood species, from the easiest to penetrate to the hardest, are as follows: Southern Yellow Pine (*Pinus taeda*), Jack Pine (*P. banksiana*), Lodgepole Pine (*P. contorta*), Red Pine (*P. resinosa*), Scots Pine (*P. sylvestris*), Western Red Cedar (*Thuja plicata*) and Douglas Fir (*Pseudotsuga menziesii*) (Richardson, 1993; FPS, 1999; Hack, 2000). Penetration is dependent on cellular structure, particularly the pits which connect the tube-like cells. As the wood is converted from sapwood to heartwood these pits become blocked (Hack, 2000). Aspirated or offset pits, which occur during the growth of many softwood species inhibit preservative penetration (Haygreen and Bowyer, 1996). Fungal decay during the life span of the pole tends to reverse this process by increasing porosity in the wood cells even when treated (Cooper *et al*, 1996).

Preservative penetration in sapwood should occur relatively easily throughout the tracheids and ray cells by means of the pit passageways (Troya *et al.*, 1995). However, heartwood in most softwood species is difficult to penetrate with preservatives due to the presence of polyphenolic compounds, pit aspiration, or a change in alignment and tylosoids forming in resin canals (Haygreen and Bowyer, 1996; FPS, 1999). High density incisors were developed specifically to deal with the penetration of preservatives into the heartwood of dimensional material (Hack, 2000). These incisors create diamond shaped incisions into the heartwood to promote preservative penetration.

2.4.2 Fluid Flow During Treatment

When penetrating coniferous trees, preservative liquids move longitudinally through tracheid lumina, passing from one to the other through bordered pits (Usta, 2005). Both longitudinal and tangential flow is governed by bordered pits while horizontal flow paths are dictated by aligned ray cells (Hoadley, 1990). Since tracheid lumina provide an unobstructed pathway for flow, it follows that reductions in permeability are dictated by bordered pits which become offset during drying and blocked by the torus in the pit being moved outward or inward to block the pit aperature (Usta, 2005). The torus is a piece of the primary cell wall located in the center of the pit as illustrated in Figure 2.6 (FPS, 1999). Surface tension also plays a role in reducing permeability (Usta, 2005). Drying of the wood, while required to allow for preservative penetration, is the principal cause of reduced fluid flow in wood conditioned for treatment (Usta, 2005). It is the classic dilemma for the industry and is the primary reason why air drying is preferred to kiln drying (Murray, 2005a,b).

2.5 Wood Decay

In order for wood to biologically decay there must be unbound water, suitable temperatures, sufficient oxygen and a source of carbon for the decay organisms (AWPA, 2004). Microbial decay dominates in non-marine applications of treated wood in Canada,

and due to the lack of termite populations in Canada this would include all PCP pole installations (CSA, 2004). Both prokaryotes and eukaryotes are involved in wood decay but fungal decay dominates all other forms of wood deterioration (Murray, 2002). Wood cell walls consist primarily of cellulose, hemicellulose and lignin in the form of large biopolymers which are mainly attacked by bacteria and fungi in our Canadian climate (Haygreen and Bowyer, 1996).

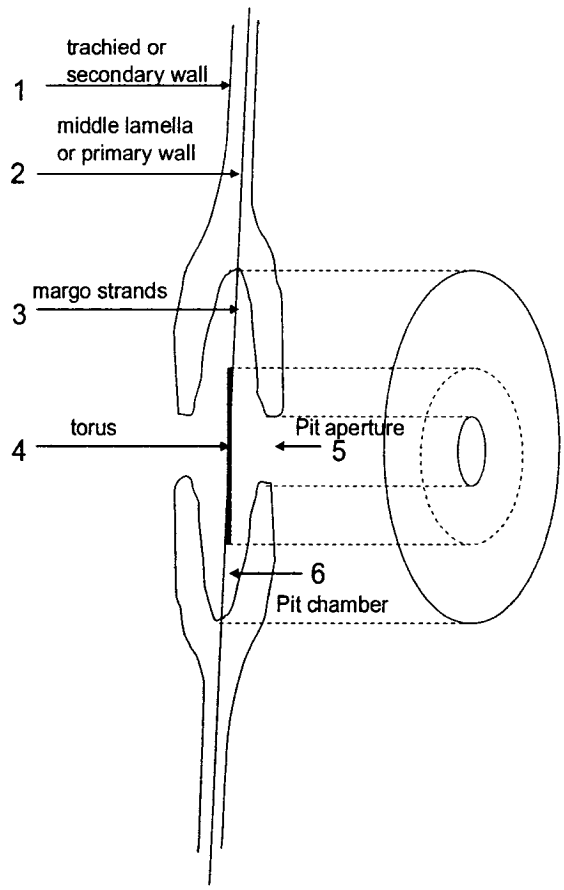

Figure 2.6. Representation of an early wood bordered pit with torus not yet aspirating the aperture (adapted from Usta, 2005).

Broadly, the types of fungal decay are labelled with the common terms white rot, brown rot and soft rot (Hack, 2000). Brown rot is the most important with respect to strength loss (FPS, 1999; AWPA, 2004). Bacteria are also important in wood decay, but more in terms of enhancing the ability of fungal hyphae to penetrate wood (Zabel and Morrell, 1992). The main function of wood preservatives is to render the wood unsuitable as a food source for these microorganisms, versus being pure toxicants designed to kill the organisms (Murray, 2002). Fungal damage to wood may be traced to three main causes: improper storage prior to milling, improper seasoning and storing after milling, and failure to account for the conditions within the end use environment (Mullins and McKnight, 1981; Green *et al.*, 1992).

2.5.1 Bacteria

Bacteria are prokaryotic organisms characterized by having their genetic material not enclosed in a nucleus (Tortora *et al.*, 2002). Bacterial species involved in wood decay vary widely and are responsible for the sour smell of wood (Zabel and Morrell, 1992). The principle role of bacteria in wood decomposition is water absorption, increasing wood permeability, cellulose decomposition and overall nutrient cycling within the decompositional micro and macro environments (Zabel and Morrell, 1992).

Terms recently used in describing wood deterioration include cavitation, erosion, and tunnelling, all of which are caused by key groups of bacteria which colonize the outer

surface of wood by means of extracellular slime secretion (Singh and Butcher, 1999). The slime secretion is an acid mucropolysaccharide which may also contain lignin peroxidase enzymes (Singh and Butcher, 1999). Vesicles within bacteria are known to carry cellulases and hemicellulases (Singh and Butcher, 1999). Oddly, both tunneling and erosion bacteria show remarkable tolerances to CCA, due to the outer membrane storage of metals (Zabel and Morrell, 1992). The presence of partially digested lignin and cellulose within the penetrated zones suggest that these vesicles release enzymes within the extracellular slime secretion (Singh and Butcher, 1999). Key groups of bacteria identified by Singh and Butcher, (1999) are as follows:

1) *Cytophagales* responsible for surface soft rot and capable of cellulose decomposition.

2) Gram-negative facultatively anerobic rods which may cause excess moisture Absorption by extracellular secretion of polymeric substances which protect cells from dessication.

3) Gram-negative aerobic rods and cocci, such as *Pseudomonas,* which are proposed as the initial invaders of wood stems and the precursors to more advanced decay by fungi.

4) Endospore-forming rods and cocci, such as *Bacillus polymyxa* that decompose the fibrils bordering pits in water saturated logs.

5) Actinomycetes and related organisms that have been shown to have an effect on soft rot development and cellulose decomposition, such as *Coryneform humiferan*, *Micromonospora* and *Nocardia.* They are similar to fungi in their filamentous growth but are much smaller and are prokaryotic cells.

2.5.2 Soft Rot

The term soft rot is restricted to fungi that attack wet wood from the outside inward, penetrating very slowly (Haygreen and Bowyer, 1996). Though non-penetrating when compared to white and brown rot, these ascomycetes are capable of both staining the wood and eroding the cell walls (Haygreen and Bowyer, 1996). These take a much longer time to affect wood and primarily arise from improper wood storage (Hack, 2000). The widespread use of anti-sapstain chemicals on dimensional lumber was in response to controlling the appearance of soft rot impacted wood (FPS, 1999).

Type I soft rot organisms utilize carbohydrates within the cell wall and this type of rot is characterized by longitudinal boreholes which develop in the secondary wall (Haygreen and Bowyer, 1996). Type 2 soft rot fungi also use carbohydrates within the cell wall, but damage is characterized by secondary wall erosion from lumen surfaces and degradation of the cellulose. This is responsible for branch cleavage in living trees and creating pathways for white and brown rot in processed wood (Haygreen and Bowyer, 1996). Both of these fungi are classified as *Ascomycotina* and *Deuteromycotina*. Recently, soft rot has been shown to be caused by both white rot and brown rot fungi of the *Basidiomycetes* group (Schwarztz *et al.* 1999). Their wood destroying enzymes are listed below in the white and brown rot sections.

2.5.3 White Rot

White rot fungi attack the cellulose and lignin of the cell wall, resulting in large losses of mass but moderate strength losses (Hack, 2000). The name white rot is derived from the bleached to whitish color imparted to the wood (Haygreen and Bowyer, 1996). These fungi have actually been proposed as a pretreatment for hard to treat (refractory) wood species, such as Douglas Fir, to reduce treating cycle times by increasing wood permeability. Both white rot and brown rot fungi are caused by the *Basidiomycotina* subdivision (Zabel and Morrell, 1992). White rot fungi are broken down into those that selectively remove lignin from the wood prior to breaking down polysaccharides, and those that simultaneously degrade lignin and wood polysaccharides (Jennings and Lysek, 1999). The level of available nitrogen is inversely proportional to the rate of lignin decay (Jennings and Lysek, 1999). Over 94% of wood decaying fungal species in North America are white-rotters (Blanchette, 1991).

Typical degradation by white rot fungi involves attack on the middle lamella and cell corner regions (Datta *et al.*, 1991). The fungi colonize the anatomical paths of least resistance and quickly move to areas of high nutrient concentrations (Haygreen and Bowyer, 1996). Cell to cell movements are caused by both the excretion of extracellular oxidants and bacteria pre-colonization (Datta *et al.*, 1991). The complex structure of lignin has led to its decomposition being termed "enzymatic combustion", and this requires Manganese peroxidases, numerous extracellular lignin peroxidases, or phenol

peroxidases. Hydrogen peroxide (H_2O_2) is used by the ligninases as the electron acceptor while O_2 is used by the oxidases (Blanchette, 1991).

Lignin peroxidases and Mn-dependent peroxidases are produced by white rot fungi in response to nutrient limitation and are activated by H_2O_2 (Blanchette, 1991). The Fe in the two peroxidases is in the ferric, or resting state. H_2O_2 oxidizes the iron to form an enzyme complex called compound I, a ferryl-n-porphyrin cation radical which is highly reactive to a variety of reducing chemicals (Barr and Aust, 1994). This results in the formation of compound II and numerous free radicals (Barr and Aust, 1994). It then reacts with other reducing chemicals to return to compound I (Barr and Aust, 1994). The reaction for the Mn form of the enzyme is the same, as it simply replaces the Fe. Both elements go back and forth from either Fe^{+3} to Fe^{+2} or Mn^{+3} to Mn^{+2} (Barr and Aust, 1994; Datta *et al.*, 1991).

The two major enzymes thought to be responsible for the production of H_2O_2 are glucose oxidase and glyoxal oxidase (Blanchette, 1991). Both use their respective substrates to reduce O_2 to H_2O_2. Under nutrient limiting conditions it is hypothesized that H_2O_2 is released to react with glucose to form an extracellular oxidase termed glyoxal oxidase (Barr and Aust, 1994).

The other main factor is the required presence of free radicals produced by the decomposition of lignin to produce a sustainable reaction as long as lignin is present

(Blanchette, 1991). Lignin peroxidase is considered the main initiator of this free radical chain reaction. Veratryl alcohol (3,4-dimethoxybenzyl alcohol) is the main free radical produced. Quinones and quinine reductases are also produced during lignin breakdown, but their role is unclear (Barr and Aust, 1994).

2.5.4 Brown Rot

Brown rot fungi attack the hemicellulose and cellulose but leaves the lignin untouched, giving the most rapid strength loss (Haygreen and Bowyer, 1996). The name brown rot comes from the brownish to reddish color imparted during decay (Haygreen and Bowyer, 1996). Despite the fact that brown rot has the most deleterious effect on the billions of dollars of standing wood structures it is the least understood (Paszczyznski *et al.*, 1999). Most theories assume that this decay involves a Fenton type catalytic system that produces hydroxyl radicals which attack the cellulose and hemicellulose wood components (Paszczyznski *et al.*, 1999). Recent experimentation on *Gleophyllum trabeum (GT)* and *Postia placenta (PP),* which are two common wood preservative test fungi, has shown that the enzymes secreted by the hyphae are too large to penetrate fresh wood (Jensen *et al.*, 2001). Brown rot fungi, in general, are capable of secreting smaller extracellular oxidants that operate beyond the hyphae by diffusion through water (Jensen *et al.*, 2001).

The main mechanism of decay by the fungus GT involves a quinine redox cycle to generate extracellular Fe^{+2} and H_2O_2 (Jensen *et al.*, 2001). This reaction then proceeds with 2,5-dimethoxyhydroquinone, which oxidizes Fe^{+2} to Fe^{+3} to create a 2,5-dimethoxyhydroquinone radical that reversibly reacts with O_2 to yield 2,5-dimethoxy-1,4-dibenzo-quinone and the OOH radical (Jensen *et al.*, 2001). H_2O_2 is produced when OOH and its conjugate base, superoxide, return to its original oxidation state or when either of these oxyradicals is oxidized by the original Fe^{+2} (Halliwell and Gutteridge, 1999). Another possibility is that some of the semiquinones reduce the Fe^{+3} to Fe^{+2}. The end of the redox cycle involves the fungal mycelium reducing 2,5-dimethoxy-1,4-benzo-quinone back to 2,5-dimethoxyhydroquinone, while creating additional Fenton reagent (Jensen *et al.*, 2001).

The main decay mechanism of the fungus PP involves the secretion of small pore penetrating extracellular oxidants as small as 1.5 nm in size (Larsen and Green, 1992). These cause the initial cellulose-depolymerizing reactions that allow for the Fenton reaction detailed above (Larsen and Green, 1992). These extracellular enzymes are localized in the fibrillar elements of the sheath structure on the hyphal surface within the soluble sheath matrix (Jensen *et al.*, 2001). Extracellular polysaccharides may compose the sheath extensions and may be up to 25 μm in length (Larsen and Green, 1992).

It is now becoming clearer that bacteria, soft rot, white rot and brown rot fungi serve to enhance wood degradation in a stepwise fashion. Bacteria and soft rot fungi appear to

have much more of a role than has previously been recognized in creating pathways for entry of fungal hyphae (Jensen *et al.*, 2001).

Preservatives work by disrupting the production and secretion of enzymes by these fungi (Stephens *et al.*, 2001). Traditional drying and submergence techniques work by denying the decay organisms the required moisture and oxygen, respectively. Preservative chemicals must be used where these conditions are not sufficiently inhibitory. Poles that have been in service have all experienced some degree of decay or mechanical damage which has increased their permeability to fluids (Cooper *et al.*, 1996).

In more recent research, Yang (2001) isolated wood-inhabiting fungi from logs of three major Canadian hardwood species. The results revealed that most fungal species are not host specific and affect all of the hardwood species tested. The most frequently isolated decay fungi were in taxa from the phylum Basidiomycota. Other frequently isolated fungal species included; molds (*Alternaria alternata*, *Trichoderma* species, and *Mucor/Rhizopus* (Zygomycota) species), staining fungi (*Ophiostoma piceae* and *Ophiostoma piliferum*) and a bark saprophyte (*Nectria cinnabarina*). To date, no such research has been performed on popular softwood species (IRG, 2005).

2.5.5 Weathering Effects

Weathering is a general term that refers to the effect of climatic conditions on wood (FPS, 1999). Extreme heat or cold can make wood more brittle, leading to the expansion of any cracks, also called checks, present in the wood, thus exposing the whitewood beneath the treated wood outer shell (Cooper *et al*, 1996). Checks and cracks occur when wood dries (FPS, 1999). Excessive checking caused by too rapid drying under artificial conditions which can occur in kilns, are cause for rejection of wood under the CSA 080 pole specification (FPS, 1999). Checking if completely through the butt or tip of the pole can reduce the strength significantly (FPS, 1999)

Precipitation can cause excessive leaching of preservative, which reduces the wood's resistance to decay organisms (Hack, 2000). Water from precipitation events, coupled with cold and warm temperature cycles, often cause freeze and thaw induced widening of natural checks in the wood (Murray, 2005a). When white wood is subsequently exposed the decay organisms can have access to the unprotected carbon source (FPS, 1999).

Finally, wind and the potential for it to cause stresses on a pole beyond its modulus of elasticity can cause fractures which can then be penetrated by water or directly colonized by wood degrading organisms (Murray, 2005a). Wind may also result in other debris scarring the poles surface and the subsequent mechanisms enhancement of freeze-thaw or direct colonization as noted above due to exposure of untreated wood (FPS, 1999).

2.6 Specific Pole Preservatives and Treatment Processes

Generally, preservatives are broken down into two broad groupings, oil and water borne (Hack, 2000). The two most common pole preservatives are PCP, an oil borne compound, and CCA, a water borne chemical mixture (Stephens *et al.*, 2001). In treating solutions, PCP consists of 4 to 9% PCP solids dissolved in light petroleum oil, while CCA consists of 2 to 6% metal oxides of chromium (Cr), copper (Cu) and arsenic (As) as acids in water. Pentachlorophenol has been in service in Canada since the 1950s and CCA (poles) since the 1980s (Richardson, 1993; Hack, 2000).

Oil borne preservatives are applied using an empty cell process, while water borne preservatives use a full cell process (Hack, 2000). Empty cell processing involves the application of either an initial positive air pressure or atmospheric pressure, while filling the treatment container, which is known as a cylinder. These methodologies are referred to, respectively, as the Reuping process, which was patented in 1902, and the Lowry process patented in 1906 (Richardson, 1993). Full cell cycles involve the application of a vacuum prior to filling the treatment cylinder (Murray, 2002). This vacuum process is referred to as the Bethell process and it was patented in 1838 (Richardson, 1993).

In all cases, these pressure conditions are maintained by the controlled venting of the cylinder during filling with preservative, and the details of the processes are shown in Figures 2.7, 2.8 and 2.9 (Murray, 2005a). Empty cell processing is designed to limit the

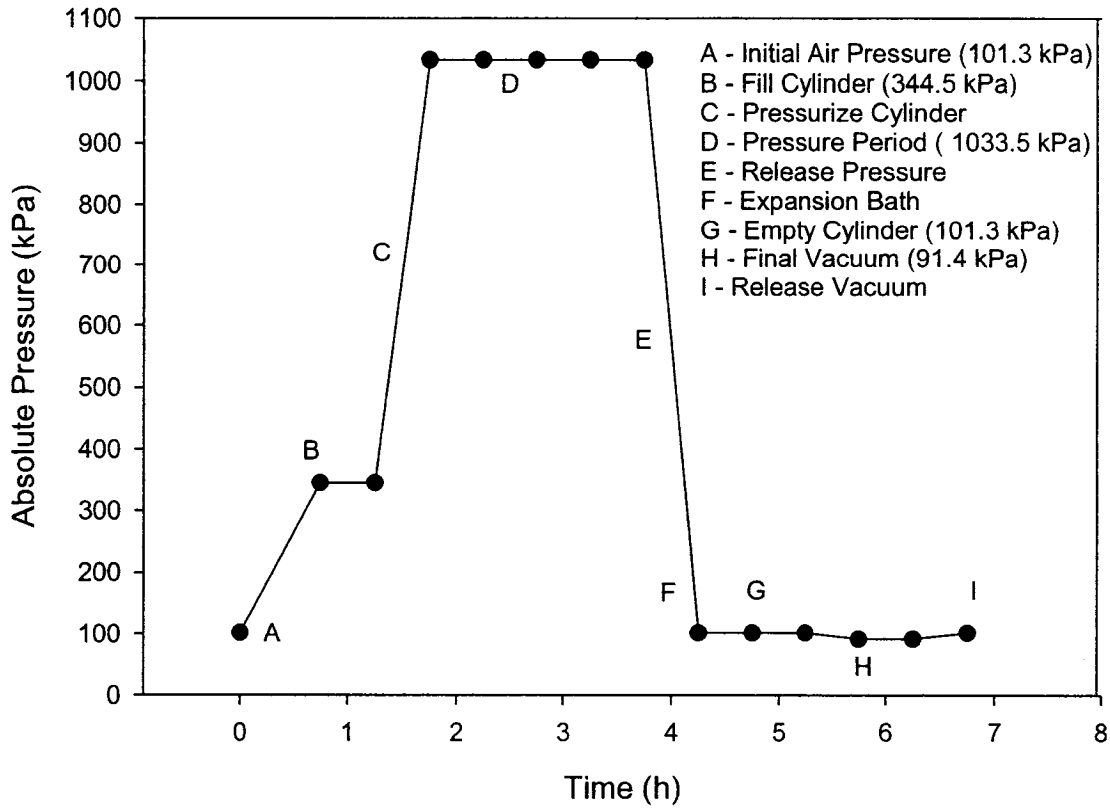

Figure 2.7. Reuping treatment process.

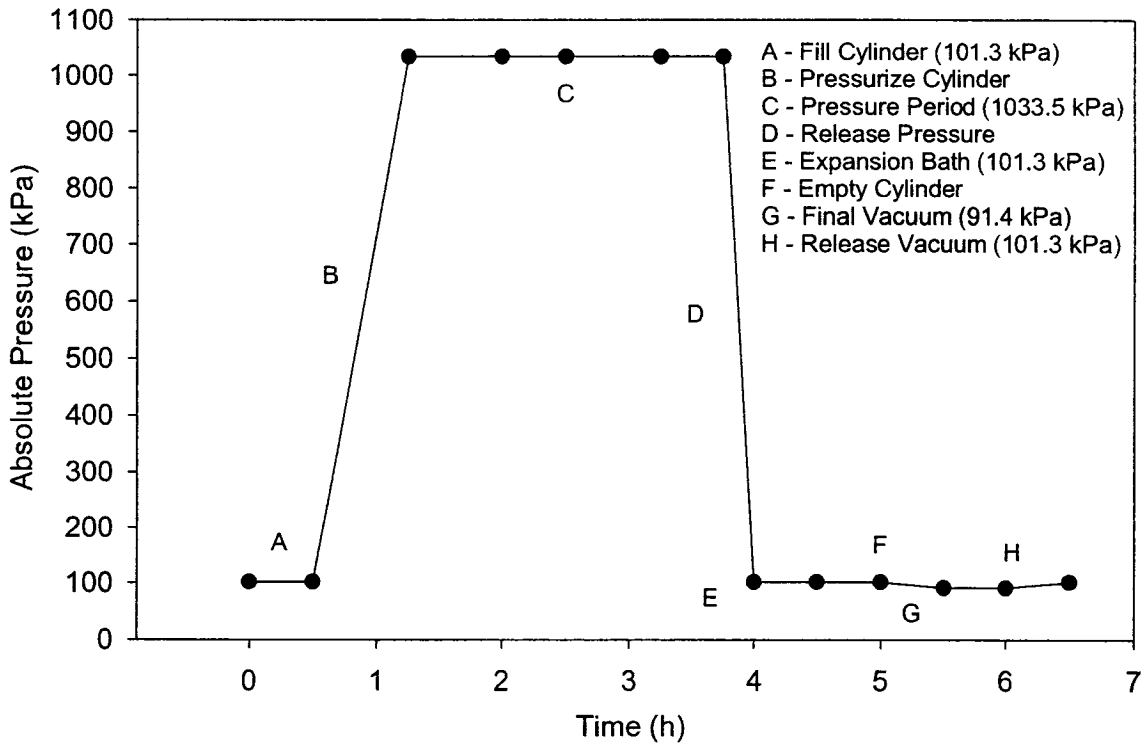

Figure 2.8 Lowry treatment process.

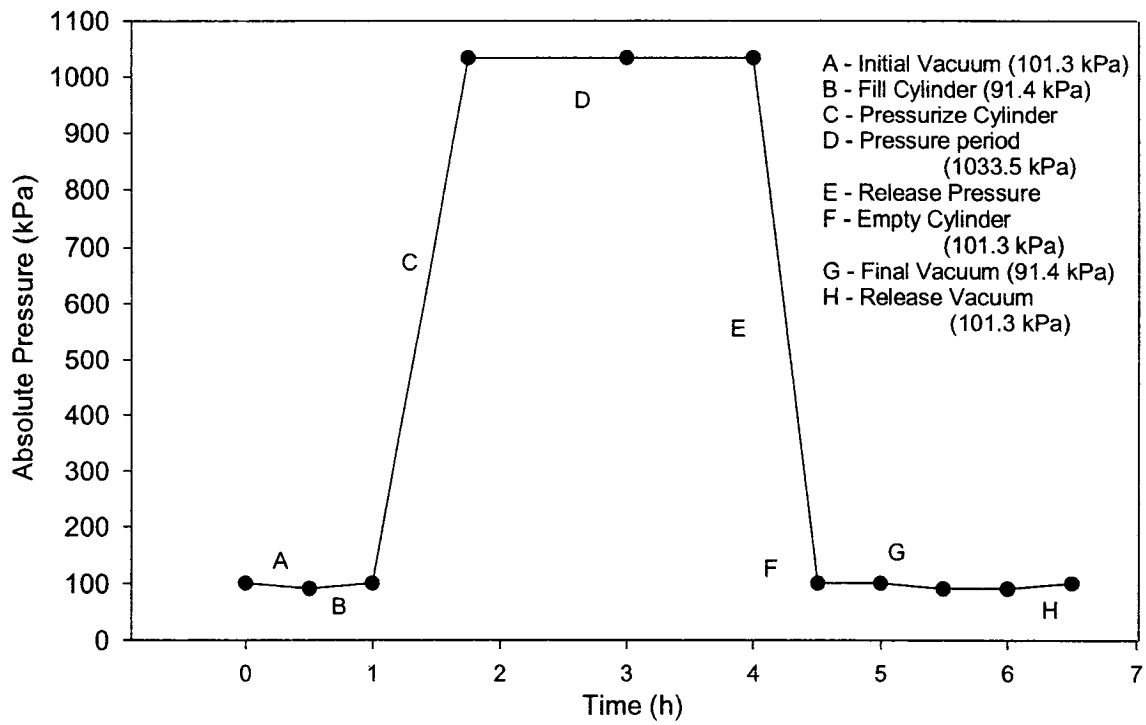

Figure 2.9 Bethell treatment process.

quantity of preservative to the outer portion of the wood cells, while full cell processing is designed to fill the wood cells entirely with preservative (Murray, 2005a). An understanding of the mechanisms of treatment is vital to developing any non-destructive chemical removal system. Non-destructive removal methods are the only ones that could provide technology at a low capital cost by allowing for both the use of existing treating plant equipment, reduced handling and transport, and for reuse of the wood fibre as full structural members or fuel (Murray, 2001). The Reuping process (Figure 2.7) with an initial air pressure is used for 99% of all PCP preservative treatments (Stephens *et al.*, 2001).

Post treatment stabilization systems are designed to reduce leaching and bleeding of preservative (Murray, 2001). Three main types of systems are employed, expansion baths, post pressure steaming and fixation. Expansion baths are where treated material is re-immersed in preservative at an increased temperature to improve final vacuum efficiency by reducing viscosity (Murray, 2001). Post pressure steaming has the same viscosity reducing effect as expansion baths but has the down side of producing more effluent water that requires treatment (Murray, 2001). Fixation involves a temperature and humidity treatment on CCA treated materials to reduce the Cr+6 to Cr+3 to induce an actual binding of the chemical to the wood fibre while chelating the Cu and As (Murray, 2001).

The main difference between the two pole preservatives, PCP and CCA, is that PCP is toxic to wood destroying organisms by virtue of the shape of the molecule, which consists of six carbon atoms, five chloride atoms and one oxygen-hydrogen alcohol grouping (Crosby, 1981). However, some micro-organisms are capable of metabolically cleaving the aromatic ring of PCP to leave carbon dioxide, chlorine and water (Miller, 2002; USEPA, 2004b). CCA consists of chromium trioxide, cupric oxide and arsenic pentoxide and is toxic by virtue of its chemical composition (FPS, 1999). The general toxicity of CCA is related to its individual metal components. Chromium, copper and arsenic will bio-accumulate and do not break down any further or cannot be metabolized to innocuous compounds (Kosanovich, 1999). CCA has been voluntarily removed from the residential lumber market as of 2004, and it is unlikely that its industrial applications will survive the inevitable public pressure, since the higher loading rates of this preservative are used in industrial structures (Ziabro, 2005).

2.7 Pole Preservative Comparison

PCP's positive points include its susceptibility to biological metabolism of the aromatic ring, which makes for ease of remediation, its decreased conductivity, its non-corrosive nature to hardware, its low solubility in water which limits migration, an efficacy proven over the past 40 years and no negative effect on mechanical properties of the treated wood (FPS, 1999). Negative points include its aromatic nature, bleeding from improperly treated wood, marked colour variations of the preservative and the migration

of PCP and its carrier oil down the pole once installed (FPS, 1999). The downward migration of oil by gravity over time is illustrated in Figure 2.10. As the less expensive CCA preservative is replaced in the market by 700% more expensive non-arsenic based formulations (ACQ and CA), the main PCP suppliers have announced a major manufacturing change to remove any co-contaminants, such as dioxins and furans (Penta Council, 2004). Though a common point of contention between CCA and PCP suppliers, dioxins and furans have never been conclusively determined to be a threat or proven to migrate out of treated poles (Lorber *et al.*, 2002).

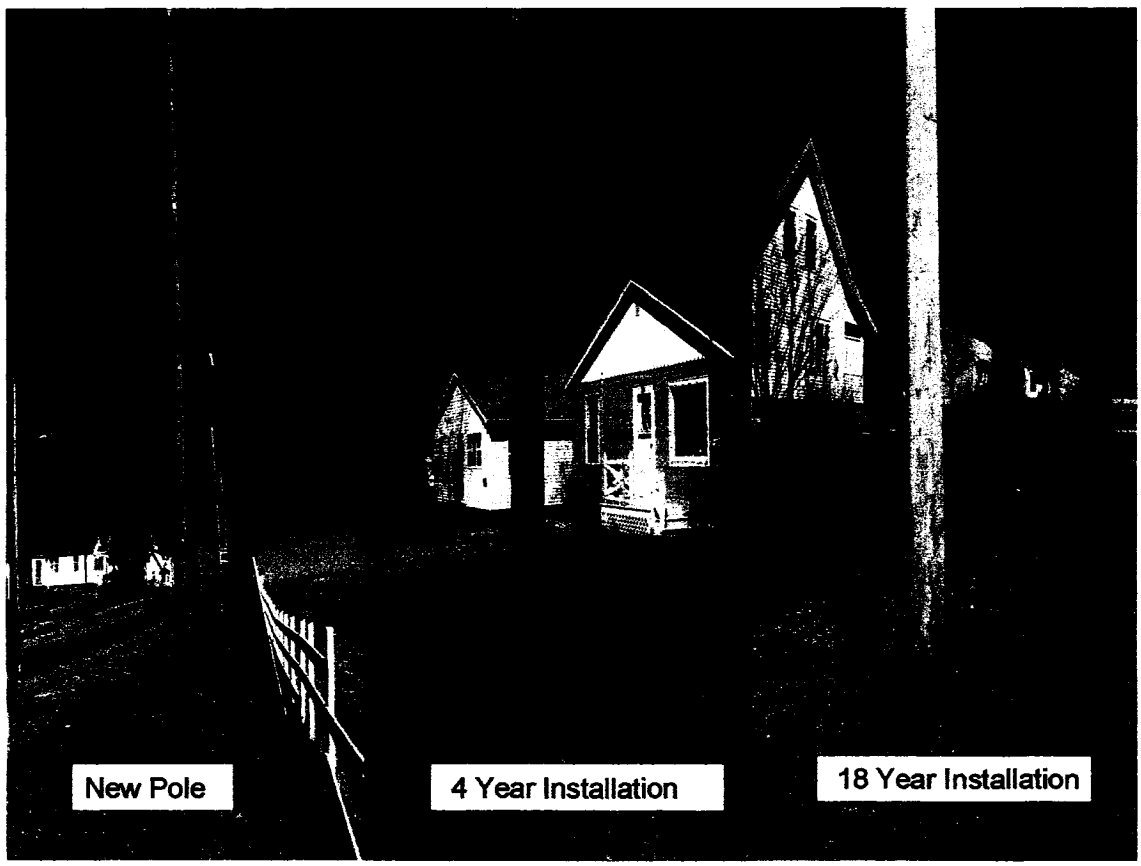

Figure 2.10. Migration of carrier oil in poles ranging from 0-18 years.

2.8 Pentachlorophenol

Pentachlorophenol is an aromatic alcohol that has been used as a broad spectrum biocide in many applications (Crosby, 1981). These include uses as an insecticide, bactericide, herbicide, algicide and mollusicide (Penta Council, 1999). Pentachlorophenol is an extremely effective biocide due to its ability to inhibit oxidative phosphorylation by making cell membranes more permeable to protons, thereby disrupting the proton pump associated with ATPase activity (USEPA, 2004b). This results in a change in the cell's electrical potential (Steiert *et al.*,1988). The structure of PCP is shown in Figure 2.11.

Pentachlorophenol was first produced in the United States in the early 1930's and has been used in Canada since the early 1950's (Hack, 2000). The highest reported usage of PCP is in the wood preservation industry, particularly for utility poles, fences and railway ties (McAllister *et al.*, 1996). In 2000, PCP consumption by the wood preserving industry in Canada was just over 2.03 million kg, 95% of which was used for utility poles, with the balance being used to treat cross arms, spar arms and railway car floors (Stephens *et al.*, 2001).

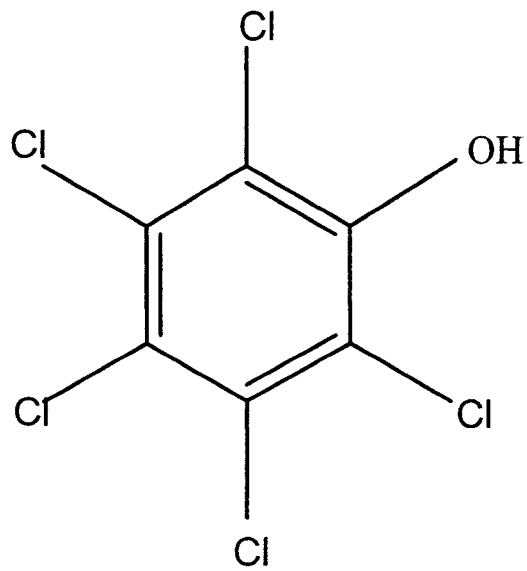

Figure 2.11. Pentachlorophenol structure.

In its raw form, PCP is crystalline and yellow to brown in color. It is used industrially either as large blocks of approximately 2,000 kg or bags of small pellets, each 1 to 2 g in weight. Manufacturing has improved over the years to reduce the presence of co-contaminants, such as dioxins and furans (Penta Council, 2003). There are two methods of production but only one is used in North America by the two suppliers of PCP, Vulcan Chemicals and KMG Bernuth (Hildebrant, 2005). North American producers use the chlorination of phenol in the presence of catalytic amounts of aluminium chloride and organic-chlorination promoters or stabilizers (Crosby, 1981). Though Vulcan was recently acquired in mid-2005 by KMG, they were both the primary suppliers to the Canadian market since PCP was introduced. In other parts of the world, hydrolysis of

hexachlorobenzene in the presence of either sodium hydroxide or sodium carbonate, or by exposing hexachlorobenzene to the catalysts calcium phosphate or silicate, is more widely used to manufacture PCP (Crosby, 1981). These reactions when performed in the presence of a separate organic hydrogen donor can reduce the percentage of chlorophenol isomers, dioxins and furans (Penta Council, 2002). Current legislation allows for a maximum concentration of 4 ppm of dioxins and furans with a total toxic equivalency value of 127,000 (Penta Council, 1999). Toxic equivalency values are the relative toxicity of each type of dioxin and furan, present in PCP, with respect to 2,3,7,8-dibenzo-p-dioxin. No 2,3,7,8-dibenzo-p-dioxin is allowed in commercial PCP (Penta Council, 1999).

Reactions are termed second order when they depend on the concentration of two reactants, and these reactions form dioxins and furans (Baird, 1999). The side reaction that produces dioxins is termed "second order chlorophenoxide" because the reaction rate depends on the square of this ion's concentration (Baird, 1999). Therefore, the rate of dioxin formation is dependent on the initial chlorophenoxide ion concentration and rate of increase. This is normally caused by higher temperatures or "forcing" reaction conditions (Crosby, 1981). The extent to which the chlorophenols and the resulting PCP becomes contaminated with dioxin can be minimized by controlling the concentration of the chlorophenoxides and the temperature during preparation (ATSDR, 1994; Baird, 1999). A diagram of the formation of a tetrachloro dioxin species is shown in Figure 2.12.

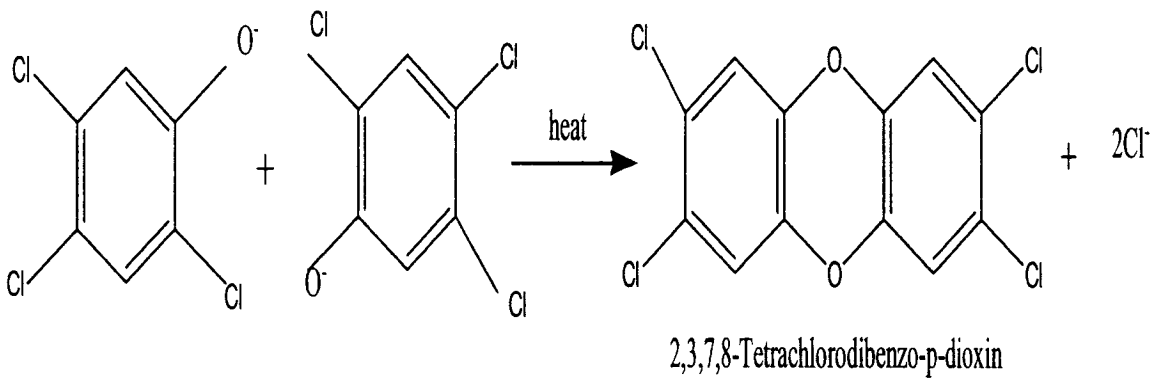

Figure 2.12. Formation of 2,3,7,8 Tetrachlorodibenzo-*p*-dioxin.

PCP is produced by the chlorination of phenol or by the hydrolysis of hexachlorobenzene (Crosby, 1981). Apart from those methods mentioned above, the industrial producers of PCP (Vulcan and KMG Bernuth) are intentionally reacting an organic hydrogen donor in the presence of extra chlorine, reducing the reaction temperature, and practicing post formation removal of impurities by distillation or extraction after production (Penta Council, 2004). The increased price, by a factor of 7, of the alternatives to CCA has allowed PCP producers to undertake additional measures to improve the quality of their PCP. They predict the total dioxin and furan content of technical PCP to drop from 4 ppm (no 2,3,7,8 isomer allowed) to below 0.001 ppm by 2007 (Hildebrant, 2005).

The sodium salt of PCP (Figure 2.13), sodium pentachlorophenate (NaPCP), is no longer used in North America as a preservative due to its high water solubility and uncontrolled spraying during application as an anti-sapstain treatment for dimensional lumber (Penta

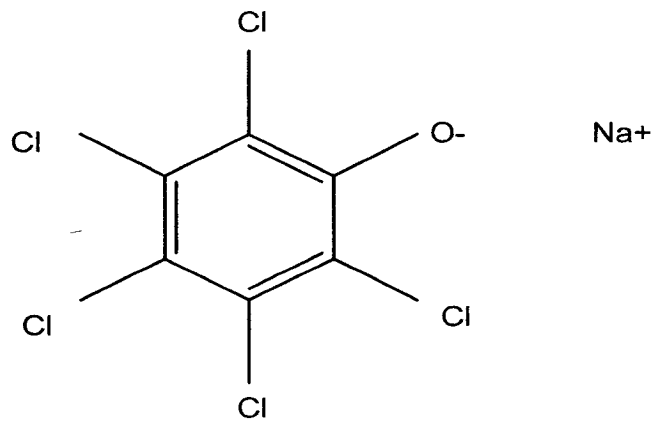

Figure 2.13. Na-PCP structure showing loss of alcohol group.

Council, 1999). This form cannot exist at a low pH as it transforms to PCP which not water soluble leading to precipitation reactions (Penta Council, 1999). Prior to 1985, technical grade PCP contained 85 to 90% PCP and other phenolic compounds, mostly tetra-chlorophenols, and predioxins and iso-predioxins. These are formed when two molecules of PCP, trichlorophenol, or tetrachlorophenol undergo condensation (McAllister *et al.,* 1996). Currently, technical grade PCP in Canada is 98% pure as per the manufacturer's labelling (Vulcan Chemicals Inc., 2004). The majority of the utility poles presently being removed from service should have a much higher percentage of co-contaminants, as they would have been treated from 1965 through 1980. These are the

age of the poles analyzed in the present study.

2.8.1 Mode of Preservative Action

Pentachlorophenol works by uncoupling oxidative phosphorylation, causing a reduction in the activity of adenosine triphosphate phosphohydrolases, transport mechanisms, and the inhibition of nitrification (Crosby, 1981; ATSDR, 1994). This is the same mechanism that inhibits all boring organisms, including aquatic organisms, even though PCP is not allowed for use in aquatic environments (AWPA, 2004).

The effect of PCP on terrestrial and marine borers is a reduction in calcium uptake which reduces the ability to molt (USEPA, 2004b). The carrier oil used also repels water and imparts a certain hydrophobic nature to the material, further inhibiting decay (ATSDR, 1994). Despite the ability of PCP to be biologically metabolized, its retention specifications within the standards for treated wood far exceed the threshold levels for biological decomposition (AWPA, 2004). These retentions have been specifically tested to accomplish a level of protection for all wood preservative and wood species combinations (AWPA, 2004). The method of determining preservative retentions is found in the AWPA standards. Changes in retention methodologies over time involve the use of smaller wood samples and accelerated growth chambers to bring preservatives to market more quickly (AWPA, 2004). A chart summarizing toxicological effects of PCP on various species is found in Table 2.1.

Table 2.1. Toxicity and environmental risk characterization.

Test Group	Test Basi	Test Type	Toxicity Value	Toxicity Category
avian species	acute oral	LD50	380-627 $mg \cdot kg^{-1}$	Moderately slightly toxic
avian species	sub-acute dietary	5-day LC50	3400-5581 ppm	Practically non-toxic
small mammals	acute oral	LD50	137-155 $mg \cdot kg^{-1}$	Moderately toxic
freshwater fish	acute	96-hr LC50	0.015-0.600 ppm	very highly toxic
freshwater invertebrates	acute	48-hr LC50	0.450 ppm	highly toxic
estuarine/marine fish	acute	96-hr LC50	0.240 ppm	highly toxic
estuarine/marine invertebrates	acute	96-hr LC50	0.048 ppm	very highly toxic
aquatic vascular plar	acute	EC50	0.250 ppm	none given
Aquaticnonvascular plants	acute	EC50	0.027-0.124 ppm	none given

*Adapted from U.S. Environmental Protection Agency, 2004b.

2.8.2 Environmental Chemistry and Toxicology

All chlorinated phenols are toxic with specific toxicity being directly proportional to their degree of chlorination (McAllister *et al.*, 1996). These chlorinated phenolics can enter the human body through dermal or inhalation exposure (Vulcan Chemicals Inc., 2004). The severity of toxic effects depends on the dosage received, the route of exposure, and the individual's characteristics, such as age and body weight (Mostaghimi, 2000). Since the body is able to metabolize these chemicals, worker exposure can be mitigated by removing the person from the exposure (Crosby, 1981). Pentachlorophenol is a suspected carcinogen and is highly embryotoxic, with symptoms of severe exposure beginning with chloracne (USEPA, 2004c). Eucaryotic organisms generally respond to PCP exposure by increasing the chemical's water solubility to promote excretion (USEPA, 2004f).

In mammals, pentachlorophenol will accumulate unless the species is able to efficiently conjugate PCP into excretable forms (ATSDR, 1994). Rats and humans are able to eliminate 75% of all PCP even in the unconjugated form through the urinary tract (USEPA, 2004f). PCP is strongly bound to creatine due to its effect on oxidative phosphorylation (ATSDR, 1994). Rapid dechlorination occurs in rats and is mediated by liver microsomal enzymes (Rao, 1976). The oxidative dechlorination products formed are tetrachloro-p-hydroquinone and trichloro-p-hydroquinone (USEPA, 2004f). In the

liver PCP is also conjugated to a glucuronide by bacterial *B*-glucuronidase. It is important to note that this reaction is inhibited by the prescence of quinines (Rao, 1976).

In rats, PCP is metabolized mostly to the dechlorination breakdown products, some pentachlorophenyl-beta-glucuronide and a small amount of chloranil in the urine, intestines and the liver (Rao, 1976). Oxidative dechlorination products may also be conjugated to sulphate to increase solubility (Crosby, 1981). When analyzing for PCP exposure in humans, monitoring creatine, a protein excreted by muscles into the blood, is vital to detecting exposure (USEPA, 2004f).

In fish, PCP is rapidly excreted after conjugates of PCP-glucuronide and PCP sulfate are formed. Major roles are played by the gall bladder and bile in PCP-glucuronide depurtation kinetics and by the gill in PCP-sulfate (pentachlorophenylsulfate) depurtation kinetics (USEPA, 2004f). Detoxification of PCP may also occur via methylation under reduced oxygen conditions following a spill (Rao, 1976). Fish can concentrate PCP in the gall bladder and excrete it mostly in the detoxified bound form identified as pentachlorophenylsulfate, which is formed through activity in the liver (ATSDR, 1994). The chemical composition and routes of excretion of PCP are shown in Figure 2.14 (Rao, 976). Invertebrates also accumulate PCP and metabolize it to PCP acetate, or dechlorinate it to tetrachlorophenol and tetrachlorohydroquinone or sulfate conjugates, such as pentachlorophenylsulfate (USEPA, 2004f).

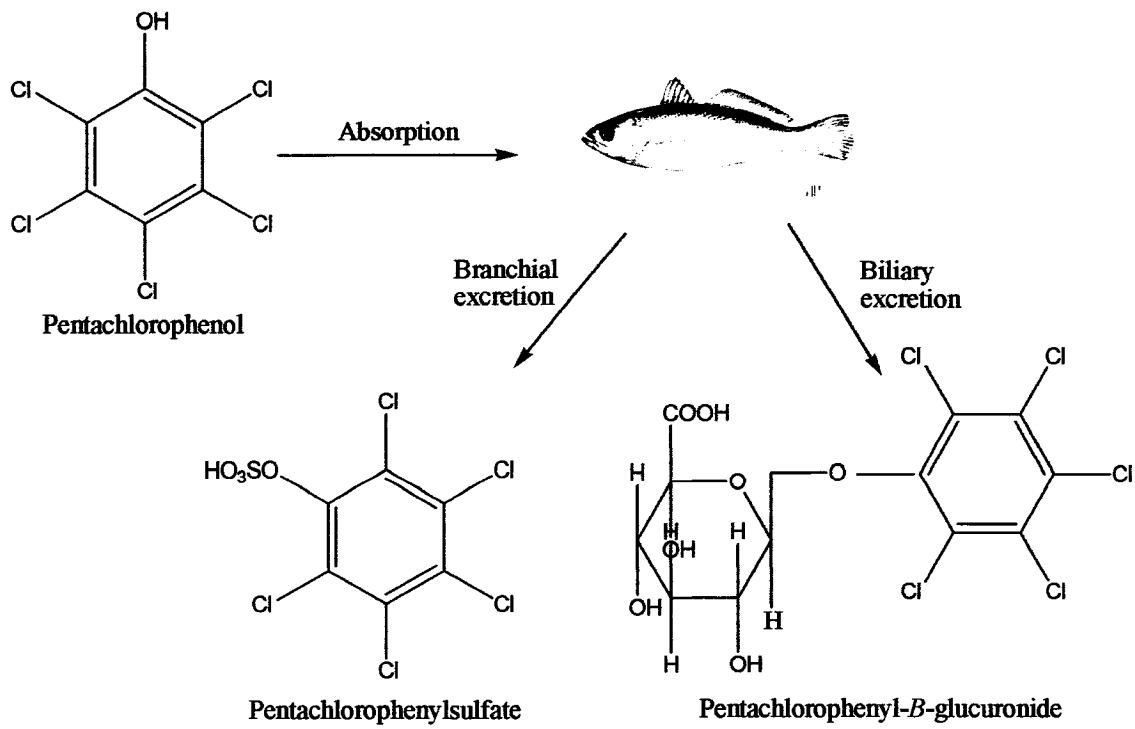

Figure 2.14. PCP detoxification pathways for fish.

Generally, you would expect that pentachlorophenol (PCP) would become concentrated in the limited fatty tissues associated with muscles, as its effect is to uncouple oxidative phosphorylation (Mostaghimi, 2000). The increased sensitivity of salmon to PCP when compared to trout indicates that the fat portion is important, as salmon have a higher fat content than trout (Arsenault, 1976). Several papers indicate that PCP's biological concentration factor (BCF) is highly overstated, since in a natural aquatic environment PCP is in a dissociated or partially dissociated state (Palla and Dion, 1986). There is an apparent partition coefficient of approximately 80 for PCP in trout, as calculated by

Neely's equation (Palla and Dion, 1986). Other papers support the higher partition coefficient as defined by the equation:

$$K_{ow} = \frac{[PCP]octanol}{[PCP]water}$$

The partition coefficient (K_{ow}) is used extensively to describe a compound's lipophillic or hydrophobic properties and is therefore a valuable parameter in the quantitative structural activity relationship (QSAR) studies that have been developed for pharmaceutical, environmental, biochemical and toxicological sciences (Breindl *et al.*, 1997).

2.9 Environmental Fate

Routes of PCP entry into the environment are numerous and can best be illustrated by Figure 2.15. Most high concentrations are present at old manufacturing sites where operational and disposal systems were either inadequate or entirely lacking (Murray, 2001). When entering the terrestrial environment PCP is readily decomposed by existing soil microorganisms and is subject to photodecomposition by ultraviolet light (Crosby, 1981). A variety of microorganisms are capable of degrading PCP and other chlorinated .phenols, but how completely and efficiently depends on the environmental conditions (Miller, 2002).

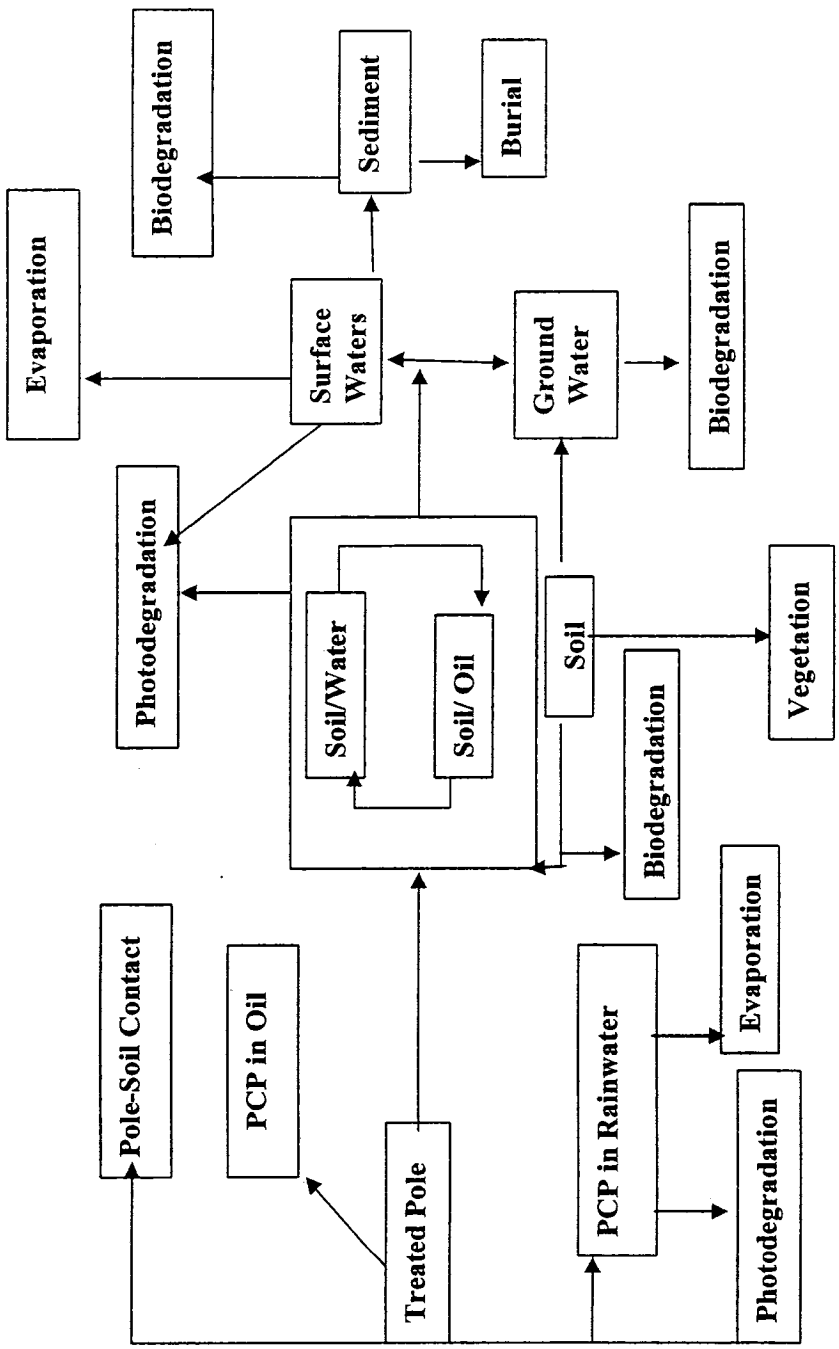

Figure 2.15: Environmental fate of PCP

Fresh water aquatic impacts and fates are important due to the ban on PCP use in marine environments (AWPA, 2004). Impacts to fresh water would relate to migration of the preservative from treated poles. Overall, pH is the controlling issue with respect to mobility of PCP in groundwater, wood and soil (USEPA, 2004e). The pKa of PCP is 4.9 while the pKa of phenol is 10 (USEPA, 2004e). This pKa decrease is shown progressively through the various isomers of mono, di, tri and tetra chlorophenolics (USEPA, 2004e). A single chlorine will reduce the pKa of phenol to 8.5, as in 2-chlorophenol and the addition of extra chlorine will progressively reduce the pKa until you reach the pKa of PCP (USEPA, 2004e). This is caused by an electron withdrawing effect which is dependent on both the number and position of the attached chlorine (USEPA, 2004e). The net result is an increase in bond resonance caused by induction (USEPA, 2004e). Electron withdrawal increases the double bond character of a carbonyl by redistributing the π electrons into a more highly shared arrangement (Baird, 1999). This will increase the bond force constant. The halogen substituted aromatic ring has an electron withdrawing effect for chlorine and essentially no effect for fluorine (Baird, 1999). Differences between the two are attributed to fluorine's higher electronegativity (Baird, 1999).

The solubility of PCP increases with pH. At a low pH, below the pKa, the solubility of PCP is fairly constant but begins to increase as the pH increases to the level of the pKa value, due to an increase in ionic species (Huang *et al.*, 2000). Theoretically, the total solubilityshould double when the pH equals the pKa and tends to level off at a pH of 9

(Huang *et al.*, 2000). In water at a pH of 6-8, which is common for discharge water from industrial facilities, the predominant form of PCP would be anionic as this is above the pKa value (Huang *et al.*, 2000).

2.9.1 Surface Water, Soil and Groundwater Impacts

For PCP found in soil pores and groundwater at pHs above 6, the phenolate ion dominates and has the highest mobility, which can be substantial in the absence of degradation (USEPA, 2004e). Despite this fact both aerobic and anaerobic PCP degradation is generally rapid enough to minimize groundwater and contacted soil contamination (USEPA, 2004e). The first stage metabolites of degradation, tetra and trichlophenols, will continue to degrade and, even under anaerobic conditions with increasing soil depth, will have half lives of less than two months (USEPA, 2004e). These are US data, and our climate may induce an increase in this half life, however, there is a lack of soil contamination at the base of in service utility poles (PMRA, 2005). Initial leaching is dependent on the type of carrier oil or co-solvent used and is always highest during the first year of installation (USEPA, 2004e). This degradation is one key to making PCP a viable preservative in the long term.

The main issue with PCP is the gravitationally induced migration of carrier oil, which causes an accumulation of oil at the base of the pole (Murray, 2005a). Factors which affect this process are wood type, lignin content, age, organic carbon content, type of

carrier oil, wood moisture at time of treatment, rainfall, pH of incident water, temperature and sunlight exposure (USEPA, 2004e). Of most importance is the moisture content of wood at the time of treatment, which influences whether leaching or bleeding will dominate (Murray, 2005a). Bleeding releases much more PCP and carrier oil into the environment adjacent to the pole (Fortune-Phillips, 2003).

Frequently, leaching and bleeding are confused. Leaching is the dissolution of a chemical from the surface of the pole by the solvent action of incident water (Murray, 2005a). Bleeding is the expelling of oil and chemical caused by the equalization of moisture gradients from the inner portion of the wood to the exterior or treated portion of the wood (Murray, 2005a). This is caused by steep moisture gradients associated with too rapid kiln drying or steam conditioning so that only the outer portion of the wood is dry while the inner portion remains completely saturated (Hack, 2000). In these cases, treating companies are trying to force preservative into the applicable CSA or AWPA assay zone without thought to the inevitable equalization (Murray, 2002). Treating during winter months aggravates this as the center core of the pole may remain frozen (Murray, 2002).

As the pole attempts to dry, inner moisture physically expels preservative in significant quantities, proportional to the moisture gradient and preservative loading rate (Murray, 2002). It is vital that the specific wood treating plant use properly conditioned wood when using oil based preservatives. The USEPA concluded that treated poles in service

do not pose a threat due to natural degradation of the preservative unless large numbers are stored in a single area (USEPA, 2004e,f). Modelling of the release of preservatives from poles does correspond well with data collected from actual samples, likely due to natural degradation of the preservative within the surrounding soil (USEPA, 2004e,f).

2.9.2 Volatilization, Photo-Degradation and Phyto-Remediation

Volatilization of PCP is a function of temperature, water solubility, vapour pressure, solution mixing depth and molar concentration (USEPA, 2004e). Volatilization can be reduced by increasing the surface tension through the use of neoprene or other suitable surface tension enhancement or anti-foaming surface coverings during boiling (Murray, 2005a). Temperature control is the most obvious way of reducing the rate of volatilization without surface tension adjustments (Murray, 2005a). Dilution and lowering of the pH are also acceptable, and in Europe, UV lights are used to photodegrade the PCP while undergoing evaporation (Warrington, 1996). This is primarily an operational concern with respect to odour at treating plants when dealing with elevated operational treating temperatures.

Currently, the wood preserving industry in Canada is not allowed to evaporate its effluent to the atmosphere unless it is with the use of a boiling under vacuum (BUV) system equipped with a condenser to intercept the vapours rather than directly emit them to the atmosphere (Stephens *et al.*, 2001). This BUV method is used for reducing the moisture

content of wood and to lower the water content in PCP treating solutions as a regular quality control issue (Murray, 2005a).

Photodecomposition of PCP is readily achieved with light at a wavelength of 300 nm when not in wood (Crosby, 1981; Cooper *et al.*, 1996). The decomposition involves the replacement of chloride with hydroxl groups until dichloromaleic acid is produced, which is readily converted to CO_2 and HCl (Crosby, 1981). Initial samples of wood analyzed for total chlorophenolics reveal only the tetra and penta forms, supporting the theory that photodecomposition is not common within wood (Cooper *et al.*, 1996). Photodecomposition may also proceed by photoreduction of parent molecules at carbons 2 and 4 (Ray *et al.*, 2002). The two products produced are 2-dehydro-2,3,4,5,6-pentachlorocyclohexanone (II) and 2,3,4,5,6-pentachlorocyclohexanaone (IV) (Ray *et al.*, 2002).

Uptake of PCP by plants is not a common control or remediation system, though solar aquatics or standard wetland systems are designed to work at least partly by plant uptake (Droste, 1997). Studies done on PCP contaminated soils at one SJI location showed very limited remediation success with the use of plants (Grant, 2001). In wetlands or solar aquatics, the main function of plants is as filtration systems and points of attachment for degrading organisms (Means and Hinchee, 1999).

2.9.3 Effluent and Solid Wastes from the Wood Treatment Process

Waste water from treating facilities is closely monitored for all preservatives in use at the facility. Each facility is issued with permits for discharge and solid waste generation (NSDOE, 2004). The majority of water is generated from the wood itself and steam injection for post treatment conditioning (Hack, 2000).

The most common method for dealing with PCP impacted water is to allow for physical separation of the oil from the water, to re-cycle the oil back to the treating tanks and to flocculate and then filtrate the balance through activated carbon (Murray, 2005a). The precipitate and carbon become solid wastes requiring disposal at a secure landfill and the water is either discharged or reused in waterborne treatment or boiler feedwater systems (Murray, 2005a). Thermal oxidation is the next most common method to treat PCP contaminated water, but has high capital and operational costs (Biothermica, 2001). In the author's opinion, solar aquatics is a promising methodology for reducing the concentration of effluent contamination while having the additional benefit of allowing for both photo- and biodegradation.

Pyrolysis of PCP waste has been promoted as a disposal method, but the temperatures required must exceed those that produce dioxins and furans. The production of dioxins can occur at temperatures as low as 200°C (Crosby, 1981; Biothermica, 2001). If commercial pentachlorophenol (containing tetra and pentachlorophenol) is burned at low

temperatures several dioxins could theoretically be produced from tetra-tetra, tetra-penta and penta-penta reactions (Crosby, 1981). Octochloro-dibenzo-p-dioxin (OCDD) has been stated in the literature to be the most common dioxin formed from hexachlorobenzene by the production of an intermediate decachlorophenyl ether (II), which on cleavage in the presence of HCl gives PCP and hexachlorobenzene (Arsenault, 1976). This formation may take place by the loss of two molecules of HCl from two molecule of PCP (Ensyn, 1998). The ether then formed can lose a second molecule of HCl to give OCDD (Ensyn, 1998).

2.10 Biodegradation

The importance of biological transformations of PCP within the soil is the basis on which PCP treated poles have been assessed to have low impact by the USEPA (USEPA, 2004e,f). The requirements for biological metabolism are summarized in Figure 2.16. Of prime importance is the presence of a consortium of organisms capable of producing the required enzymes that will degrade the target compounds (Baker and Herson, 1994). Each organism must have an energy source and an electron acceptor since the degrading organisms gain their energy from redox reactions (Baker and Herson, 1994). Moisture and pH must be appropriate, along with additional nutrients and temperatures appropriate for the degrading organism (McAllister *et al.*, 1996). Absence of toxicity or too high a concentration of target chemicals, subsequent removal of metabolites through the

consortium, and the absence of competitive organisms will all serve to accelerate the rate of biological metabolism (Baker and Herson, 1994).

The recognition of the need for a biological consortium stems from the specific catalysts or enzymes supplied by each micro-organism (McGrath and Singleton, 2000). Numerous organisms are required to prevent enzyme repression by metabolites, as shown in Figure 2.17. Two key concepts are the requirements for a specific electron acceptor and any single microbial species is extremely limited in what it can transform (Eweis, 1996).

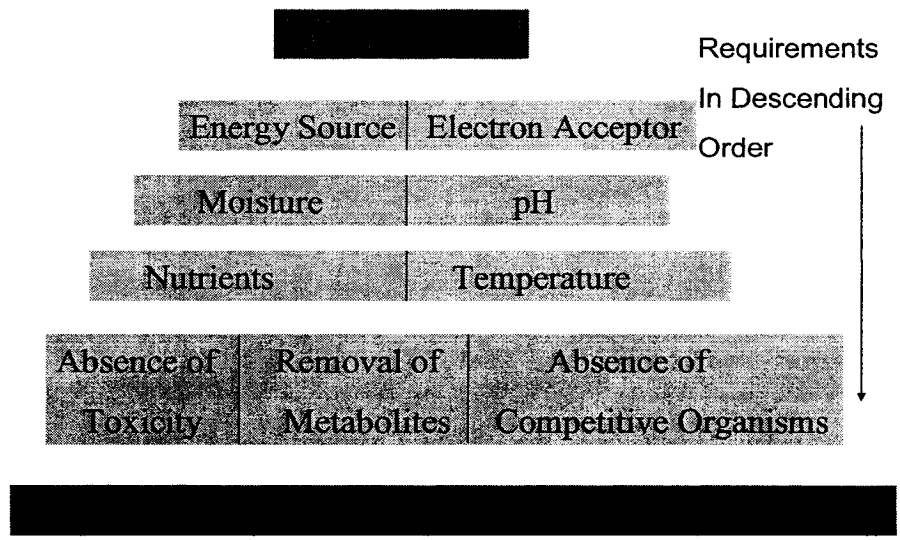

Figure 2.16. Requirements for biological metabolism of PCP.

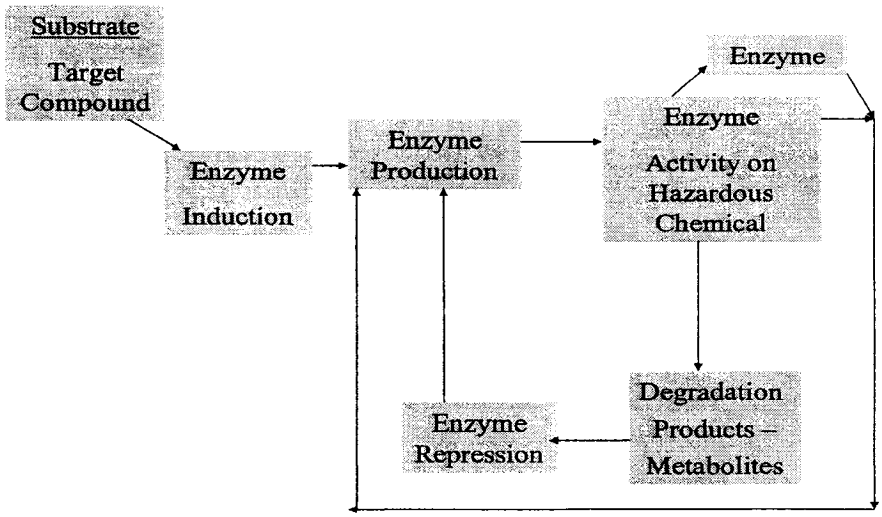

Figure 2.17. Lack of a microbial consortium will cause enzyme repression by metabolites.

2.10.1 Biodegradation of PCP

Biodegradation of PCP can occur by oxidative displacement of chlorine, reductive dechlorination, and reductive dehydrochlorination (van Eekert *et al.*, 1999; Gerritse *et al.*, 1996). The type of degradation that occurs depends on the redox conditions at the PCP impacted area (USEPA, 2004e,f).

Oxidative displacement of chlorine is an aerobic dechlorination method that can occur as a result of either direct metabolism or aerobic cometabolism (Baker and Herson, 1994).

In either case, an oxygen molecule replaces a chlorine molecule which is then excreted as inorganic chloride (Fetzner, 1998). Direct metabolism is not as common since there is typically no energy gain for microorganisms from oxidizing the carbon-chlorine bond (Fetzner, 1998). Therefore, the most common oxidative dechlorination is the result of aerobic cometabolism (Haggblom, 1992). During aerobic cometabolism the microorganism typically gains nothing metabolically from the dechlorination process since the chlorinated molecule is not the target substrate (Haggblom, 1992).

This method of dechlorination is common with both fungi and methanotrophic bacteria (Paszczynski and Crawford, 1995). These organisms utilize monoxygenase enzyme systems to incorporate oxygen atoms into the chlorinated compound (Paszczynski and Crawford, 1995). In order to induce the metabolic activity of the methane monooxygenase system of methanogenic bacteria, nitrogen-deficient conditions should be present (Fetzner, 1998).

Overall, oxidative displacement of chlorine occurs in an aerobic environment with high redox potentials and is the desired design for a bioremediation/degradation pathway above the water table (Baker and Herson, 1994). This reaction is catalyzed by mono- or dioxygenases which incorporate one or two atoms of oxygen into the molecule, respectively (Fetzner, 1998). This is possible with either fungi or bacteria but is most effective with a combination of the two, and is a common process with mono and di-

chlorophenolics; while tri-chlorophenolics can follow either pathway (Paszczynski and Crawford, 1995).

Reductive dechlorination can occur with PCP under both aerobic and anaerobic conditions, depending on the oxygen level at the time of reaction (Fetzner, 1998). This is a two-electron transfer reaction that involves the release of the chloride in ionic form and its replacement by hydrogen (Sims *et al.*, 1991). Though some authors claim that it is more efficient, this appears only to occur on synthesized contaminated material and often results in undesirable metabolites (Sims *et al.*, 1991). This was one of the key drivers for the development of air sparging equipment, either ambient or ozone based, with fluctuating groundwater aquifer systems (Baker and Herson, 1994).

The reductive dechlorination of PCP involves the addition of hydrogen atoms and the resulting loss of chlorine (Haggblom, 1992). Degradation of chlorinated aromatic compounds generally occurs through this process (Baker and Herson, 1994). During this process hydrogen acts as an electron donor (Sims *et al.*, 1991). One hydrogen is used to replace the chlorine that is excreted while a second hydrogen ion is stripped of its electrons and excreted with the chloride ion (Sims *et al.*, 1991). This is common during anaerobic cometabolism when a microorganism metabolizing other substrates produces soluble exogenous enzymes capable of catalyzing reductive dechlorination of the PCP molecule (Fetzner, 1998). Iron and nitrate reducers commonly carry out this method of dechlorination (Fetzner, 1998). The availability of dissolved hydrogen becomes the

limiting factor with this method of dechlorination (Baker and Herson, 1994). It is most common on tetra- and pentachlorophenolics (USEPA, 2004e,f).

Whether reductive or oxidative dechlorination predominates is dependent on the microbial consortium being utilized (McAllister *et al.*, 1996). Microorganisms are also not restricted to the use of one or the other methods. An example occurs with *Phanerochaete chrysosporium* which has been reported to degrade 2,4,6-trichlorophenol via oxidation, reductive dechlorination and methylation (Hammel, 1995). McAllister *et al.* (1996) reported that *Flavobaterium* species (ATCC 39723) initiates PCP degradation with oxygenolytic enzymes but the bacteria then uses reductive dechlorination to further break down the intermediates produced from the initial oxidation reactions (Fetzner, 1998).

Reductive dehydrochlorination is typically abiotic and is most often catalyzed by the presence of bases (Fetzner, 1998). During dehydrochlorination, one hydrogen and one chlorine atom are simultaneously eliminated from the PCP molecule resulting in the formation of a double bond between the two neighboring carbon atoms (van Eekert *et al.*, 1999). The formation of intermediates can be of environmental concern since the breakdown products may be more toxic than the parent molecule (Fetzner, 1998). Since this metabolic reaction does not involve metabolically catalyzed reactions where intermediates are subject to further breakdown, the dechlorination process may cease after only the first reaction, thereby resulting in the accumulation of toxic intermediates

(Fetzner, 1998). Although typically abiotic, it has been suggested that concurrent metabolic activities may actually catalyze dehydrochlorination reactions (Löffler *et al.*, 1997). Overall, aerobic organisms are more efficient at the degradation of PCP when compared to anaerobic cells (Farone *et al.*, 2000). Species of bacteria known to degrade PCP include: *Flavobacterium* sp., *Rhodococcus chlorophenolicus*, other *Rhodococcus* sp., *Arthrobacter* sp., *Mycobacterium* sp., *Sphingomonas* sp. and *Pseudomonas* sp. (McAllister *et al.*, 1996). During biodegradation, enzymes act as chemical catalysts in the oxidation and reduction reactions that constitute microbial activity. Hydrocarbon substrates are oxidized to carbon dioxide, thereby providing the necessary energy and molecules to grow and reproduce (Harris, 2000). The target hydrocarbon ends up as part of the degrader's cellular biomass. The degradation components become carbon dioxide and water (Harris, 2000). The initial steps in degradation involve the loss of chloride ion, then the eventual cleaving of the aromatic ring (Erikson *et al.*, 2000).

Fungi generally do not utilize PCP directly as a source of carbon and energy (Baker and Herson, 1994). Fungal enzymes normally are present in the soil to degrade cellulose and hemicellulose (Paszczyznski *et al.*, 1999). Their use in degradation normally revolves around their ability to degrade the carrier oil compounds (Nam and Kukor, 2000). Most bioremediation companies promote the use of mixed cultures of bacteria and fungi or a two step process (Harris, 2000).

2.11 Analytical Methods for PCP in Wood

The development of penetration and retention standards for treated wood all over the world led to the development of various analytical methods to ensure that the wood had the required quantity of preservative within a specified assay zone. This zone is dependent on species and preservative (CSA, 2004; AWPA, 2004). Since 2000 Red Pine treated with PCP requires a retention of 7.2 kg/m^3 and 65 mm of penetration or 85% of the sapwood (CSA, 2004). Prior to this period retentions of 6.4 kg/m^3 and 65 mm of penetration or 85% of the sapwood was required to meet specification (Murray, 2001). Retention refers to the concentration of preservative in the specified assay zone or penetration depth, which in Red Pine is 2.54 mm to 40.6 mm (CSA, 2004).

Determination of retention has evolved from extraction and combustion methodologies designed to remove the matrix interference from wood. Current systems for on-site quality control rely on X-ray fluorescence to determine the concentration of chloride and relate this back to the concentration of pentachlorophenol present (Murray, 2002). In order for this method to be accurate tetra- and pentachlorophenol must dominate and the dry wood density must be determined accurately (Murray, 2002).

Advantages of measurements with X-ray sources are the ability to operate in air, low detection limits, low specimen damage and little or no sample preparation (KanngieBer, 2003). A fundamental parameter method is used for the quantification procedure using a

Monte Carlo simulation to describe the theoretical relationship between weight fractions and net X-ray intensities for mono-energetic excitation radiation (KanngieBer, 2003). Most microanalytical techniques cannot be considered as accurate methods of analysis as their application relies on the use of certified reference materials which are usually not available (Adams *et al.*, 1998).

In wood preserving applications, due to limited species and preservative combinations, standards are supplied by the manufacturer and spiked samples are frequently circulated within the customer-supplier labs and third party inspections of treated material are common place (Murray, 2002). Despite an intense matrix effect, the physical basis of the interaction of X-rays with matter is fully understood and the physical constants governing the interaction and radiation absorption are well known, so it is possible to correct for deviations (Adams *et al.*, 1998).

Necemer *et al.* (2003) studied Cl and S contents in forage as determined by X-ray fluorescence (XRF) and compared this method to atomic absorption (AA), inductively coupled argon plasma (ICP) and potentiometric methods. The results for Cl and S obtained by all techniques, except for one of the potentiometric methods, were more or less compatible (within 5 to 10% accuracy). When homogenization of plant tissue was performed more statistically reliable results were obtained (Necemer *et al.*, 2003). All wood samples are ground and mixed thoroughly prior to X-ray analysis (Murray, 2002).

Third party analytical results may use gas or liquid chromatography for correlation of results but the lack of variation between X-ray fluorescence and chromatography, along with high concentrations of PCP in the treated wood, have almost exclusively moved this analysis to X-ray fluorescence (Ziabro, 2005; Hildebrant, 2005). The main research apparatus used by the two largest producers of wood preservative are X-ray fluorescence instruments (Ziabro, 2005; Hildebrant, 2005).

The Oxford Lab-X 3500 machine used in this project is the newer generation of machine which uses electricity to produce radiation at the desired wavelengths versus an actual radioactive source. The Oxford works with electrons bombarding a tube of palladium to provide the excitation X-rays (Oxford Instruments, 2005), which requires less regulation as the radioactivity is triggered by induced electrical potential not natural radioactive decay (Murray, 2005a). This machine is capable of causing Cl, Cr, Cu, As or Zn to emit energy and the wavelength tells the machine what is present, while the intensity is related to concentration (Murray, 2005a).

2.12 Pole Usage and Distribution Line Design Criteria

Poles in service are subject to three types of loading; static, nominal and ultimate breaking load (Murray, 2005a). Static loads are simply the weight imparted downward by all of the equipment attached to the pole, such as wires, transformers, insulators, cross arms, lights and telecommunications cables. Normally, a pole when used in a straight

line configuration on level ground has no net horizontal force vectors. Nominal loads are phenomena such as wind on the cross section of all attached objects, all types of precipitation and perhaps a fallen object. When these nominal loads build, as often happens during an ice storm, a single pole may break which can cause a domino effect as the ultimate horizontal breaking load is exceeded (Murray, 2005a). Poles not installed in straight lines may have alternative bracing, such as guide wires, in order to increase the ability to withstand a large nominal load (Murray, 2005a).

Current design criteria call for anti-cascading poles at regular intervals on high usage lines to prevent the damage which occurred in 1998 (Hydro Quebec, 2005). The sponsor for the present research (SJI) provides line design services using a program combining PLS Pole software graphics with a three dimensional finite stress model developed by SJI and first used by Nova Scotia Power in 2001. An illustration of this computer model's capability is shown in Figure 2.18 and 2.19. Any specific point on the pole can be analyzed for loading, species, material and ultimate pole selection and positioning of attached components (Murray, 2005a).

Poles fall under the most stringent guidelines for quality of any "tree" length material (Murray, 2005b). The pole must have less than a total of 20 cm of knots within a 30 cm vertical section with no individual knot exceeding 8.8 cm in diameter (CSA, 2004). In addition, poles must have no sweep, gouges deeper than 1" or knots clustered in the same

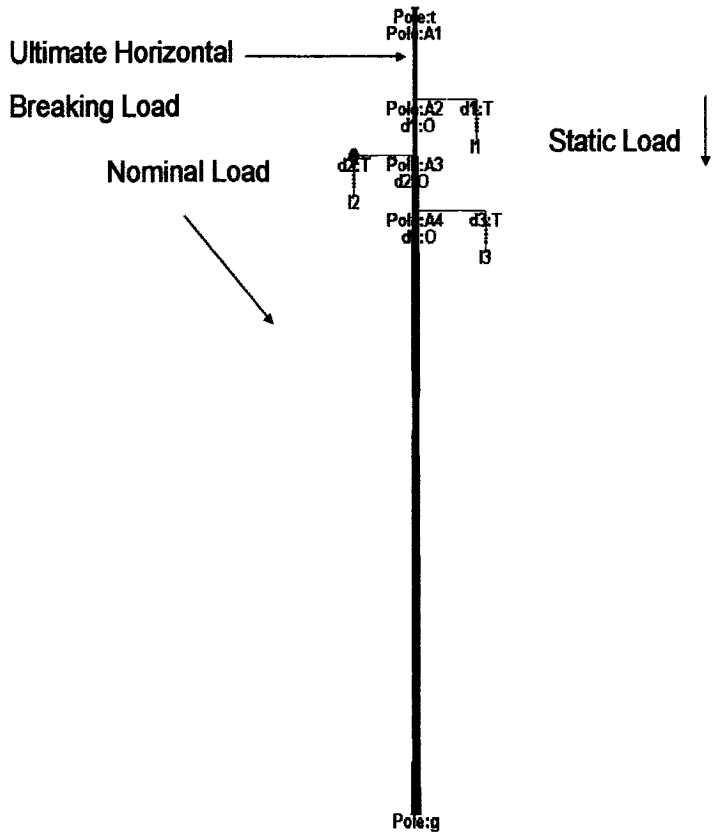

Figure 2.18. Illustration of the use of computer software in designing a distribution pole.

plane of the pole as with a whirl of branches (CSA, 2004). The only other wood product that exceeds these criteria are "clear" grade cross arms.

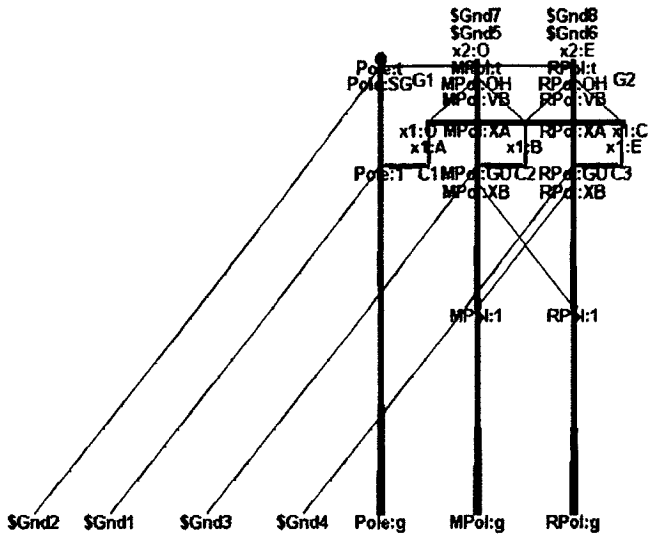

Figure 2.19. Illustration of the use of computer software to design a more complex transmission structure.

2.13 Wood Preserving Plant Layout and Key Equipment for PCP.

All wood preserving plants require at minimum a pressure cylinder, heating source, working tank, storage tank, mix tank, effluent tank, chemical delivery platforms, containment for all of the above, service pump, pressure pump, vacuum pump and air compressor (Murray, 2005c). These systems are controlled via an automation system run by a programmable logic controller or straight computer program.

Untreated wood (or whitewood) is loaded onto some type of rail or roller system conveyor after processing for each customer. Processing mostly involves cutting to length, drilling, branding and sometimes angled tops. Once in the cylinder, the wood (or charge) is given initial air pressure to fill the wood cells with air (ranges from 138-500 kPa) and the cylinder is filled with preservative at 90°C using controlled venting to maintain pressure in the wood cells. A desired fluid pressure is reached (usually in the 1000 kPa range) and maintained for several hours depending on the wood species. A pumping out of the cylinder then occurs and a gross retention of preservative is determined. If this is within an acceptable range after the air pressure has expelled the preservative, a vacuum is applied in order to remove any additional free preservative product (FPS, 1999). At the end of this process there is a net retention of preservative which experience will tell the operator whether the charge is likely to pass or fail penetration and retention of preservative. A final steaming is performed to clean off the wood with a short terminal vacuum (Murray, 2005c). The wood is then bored as per CSA specifications and a pass or fail determined based on penetration and retention of preservative within a specified zone (FPS, 1999). Wood treatment in SJI's experience still remains as much of an art as a science, which is especially due to the variability of wood.

Each component in the system serves the following purpose (FPS, 1999; Murray, 2005c):

1) Pressure cylinder – A long cylindrical tube which contains the wood and preservative mixture and is designed and certified under the Pressure Vessels Act to be able to handle pressures of up to 2500 kPa.

2) Heat Source – Normally some type of steam boiler system which allows for maintenance of elevated temperatures within the tanks and cylinder and to provide heat for post pressure steaming and to dry the wood by boiling it in preservative.

3) Working Tank – Kept at 7-9% PCP in light carrier oil (P-9); this is the tank used to empty and fill the cylinder in day to day operations. Topped up by the mix tank it requires a minimum volume to fill the cylinder minus the volume of the wood.

4) Storage Tank – This keeps the solvent or P9 carrier oil and feeds this product into the mix tank where it is combined with large blocks of PCP to obtain the required strength.

5) Mix Tank – A smaller tank where the PCP is dissolved in the P9. The mixing of this product is the most hazardous area in the plant, with respect to chemical exposure, so special protective equipment is worn at all times.

6) Effluent Tank – Tank where the oil water emulsions and steam condensate are sent for treatment in the water treatment facility.

7) Chemical Delivery Platform – Designed under the local provincial Fire Code to hold the volume of any chemical delivery container plus an additional percentage volume unique to each province. May range from tanker truck to railcar in containment volume.

8) Containment – Under new regulations implemented at the end of 2005, all plants must have primary, secondary and tertiary containment on all process and delivery platforms.

9) Service Pump – Normally a high capacity (5,000 Lh^{-1}) pump used to empty and fill the cylinders between the cylinder and work tank.

10) Vacuum Pump – Used to create vacuum in the cylinder of 101 kPa to pull excess preservative from the poles or to remove water vapour if drying activity is occurring.

11) Pressure Pump – Used to apply and maintain pressures within the cylinder of 1000 kPa, the cycling of which is used to determine when the maximum amount of preservative has been absorbed.

12) Air Compressor – Used to provide air pressure within the wood cells to provide the maximum expulsion of excess PCP after fluid pressure release.

This equipment can also be used to untreat PCP-treated wood products, as demonstrated by the research presented here. The research presented here is purely applied in nature in order to meet the requirements of the sponsor, who will be using this technology on a commercial scale within the next two years.

3.0 Materials and Methods

To achieve the goal of a "true" pentachlorophenol (PCP) extraction system for out-of-service utility poles the problem was attacked systematically. The first step was to map the distribution of PCP at various lengths and depths within out-of-service utility poles and compare this to newly treated and untreated control poles. This information was vital in determining the direction in which the research would progress. A simultaneous study was also conducted to compare GC-MS (gas chromatography with mass spectrometry detection) analysis of chlorophenolics to the readings for total chloride obtained by X-ray fluorescence from the same wood samples. This was done to verify that X-ray technology could be used for analytical purposes, as this method is quicker, less costly and does not require the extraction of the chlorophenolics from the wood. The repeatability of X-ray fluorescence results and the detection limit for the machine were also determined.

The poles studied had all been treated in the late 1970s, but not at the same time or from the same plant, so the physical characteristics which would affect chemical permeability could only be assessed visually. Microscopic methods were not required as significant weathering and physical splitting (known as checking) had occurred which were visible to the naked eye.

The second step of the research was to determine if the residual PCP in out-of-service poles could be converted to sodium-PCP (Na-PCP), the water soluble salt of PCP which can easily be removed from the poles. It was important to determine not only if this conversion was possible, but also at what ratio of surface area to volume was required to ensure a high probability of contact between PCP and the extractant, sodium hydroxide (NaOH), in order for the reaction to occur. An understanding of treatment processes and permeability was vital to ensure that minimal processing would be required. If unsuccessful, alternative solvents would be required. The advantage of NaOH conversion is that a simple pH change would return the Na-PCP back to PCP, which could then possibly be re-used.

A 1 N NaOH solution was used to facilitate rapid development of a patented industrial process and to facilitate the calculation of the re-conversion of Na-PCP back to PCP. Two lower solution strengths were also tried (0.5 N NaOH and 0.75 N NaOH) but the results were much less effective. Future refinements of the process developed can be performed, as is done with all industrial processes when they first come on-line, once the system reaches full commercial production. This process is a routine part of SJI's statistically based quality improvement process.

The third step of the research was to take the above laboratory results and scale the extraction procedure up to a full production system with minimal production costs. This procedure was highly dependent on the results of step two and the scaling up exercise

was performed with a view to using existing wood treatment plant equipment and wood processing capabilities. This equipment ranges from remanufacture sawmills, to pole peelers designed to remove bark and create a smooth pole, to chippers for the processing of "hog fuel" used in wood burning heating activities, and finally to full size production cylinders that range from 20 m to 50 m in length.

Prior to the initiation of this project an enormous amount of work was required in presenting the value of this project to several utility companies to secure a supply of these out-of-service poles for experimentation, construction of the two small pilot plants used in the experimentation from high pressure pipe, and their subsequent certification by the Nova Scotia Department of Labour, sizing the various pumps required, selection of pressure relief valves and ensuring all processes took similar processing times as in a full production environment. All control valves, gauges and gaskets, and control systems had to be built from raw materials according to the company's experience and specifications.

3.1 Pole Mapping Experiment

The mapping of the distribution of PCP (all chlorinated phenolics) in out-of-service poles relative to pole length and preservative penetration depth was accomplished by analyzing chipped wood samples using GC-MS and X-ray fluorescence. This information was required to determine the cost effective break point between using chemical extraction or biological remediation of any remaining PCP and any issues related to chemical

extraction. The method of sample preparation was designed to reduce the problems inherent with the variability of wood within the circumference of a pole, which is due to the fact that wood is a naturally grown material.

3.1.1 Poles Used in the Experiment

Full length out of service utility poles, about 30 years old, were dug out of the ground and delivered to Stella-Jones Inc. (SJI Truro, Nova Scotia) to be used in this study. The initial test set of 8 poles was identified with the letters A through H and the brand on each pole was recorded to determine the year, class and length of each test pole (brand: year treated/length in feet/class; pole A: 73/25/4, pole B: 70/35/4, pole C: 70/35/4, pole D: 76/35/4, pole F: 81/35/4, pole G: 77/35/4). The class of a pole is a designation of the maximum horizontal breaking load that the pole can take. For a class 4 pole this is 907 kg. The dimensions of a pole depend on the species of wood used in order to ensure that this maximum horizontal breaking load is uniform within that class, based on the pole's wood fibre strength. Also, visual observations of each pole were made. Imperial measurements still dominate in this industry, so pole contracts still refer to length in feet. For this study all conversions to metric units have been made but the standard used in the industry is still imperial.

Pole F was removed from the study in May 2002 due to its younger age (treated in 1981) and preservation method inconsistencies relative to the remaining poles. This pole was

approximately 10 years newer than the remaining poles and therefore was not exposed to the same weathering elements for the same period of time, or to the same quality of PCP preservative. It also appeared to have been treated with both creosote and PCP.

Pole A was removed from the study in June 2002 due to length inconsistencies with the remaining poles. Pole A was 7.6 m long, whereas the remaining poles were 10.7 m long. This length variation would pose problems when trying to relate preservative migration data between pole A and the remaining poles.

Two additional poles were added to the study in June 2002 for comparison purposes. One was an untreated pole and the other was a newly treated pole. These were labelled as poles U and T, respectively.

Pole U- This pole was untreated and was used as a control sample. This pole had a metal clip at the butt with the following identification: 02413 SJ 35-4. In addition this pole was branded as follows: SJ/2002/RPP/35/4. The rest of the pole was a uniform weathered grey color indicating that it had been air-seasoned (dried) sufficiently for treatment. It was brought directly from a storage yard where neither wood preservation nor the storage of treated wood takes place.

Pole T- This pole was a newly penta-treated pole which had not been in service. It was identified with a metal clip at the butt with the following identification: 05412 SJ 35-4.

In addition this pole was branded as follows: SJ/2002/RPP/35/4. The pole was a uniform light brown/beige color with no visible preservative migration. There was one defect in the pole where a chunk of the pole was missing where the tree appeared to have suffered damage. This defect did not extend into the wedges and this pole was chosen because it had suffered after treatment damage which made the pole non-saleable.

3.1.2 Blocks Removed from the Poles

One meter sections were marked off along the total length of each pole with equal amounts of wood left at the butt and the tip of the pole. For example, if the pole was 10.70 m long then 0.35 m would be left at the tip and butt and 1.0 m sections would be marked off starting from the 0.35 m point. This allowed the sections to be evenly spaced along the length of the pole. One block was removed from each marked section of the pole. Each block section was 10 cm wide so marks were made 5 cm on either side of the 1.0 meter marks, as shown in Figure 3.1. Each of the blocks was cut using a chain saw as shown in Figure 3.2. To identify each section, the pole sections were numbered from the tip to the butt starting with the letter of that pole followed by the number of the pole section, with number one starting at the tip of the pole as illustrated in Figure 3.3.

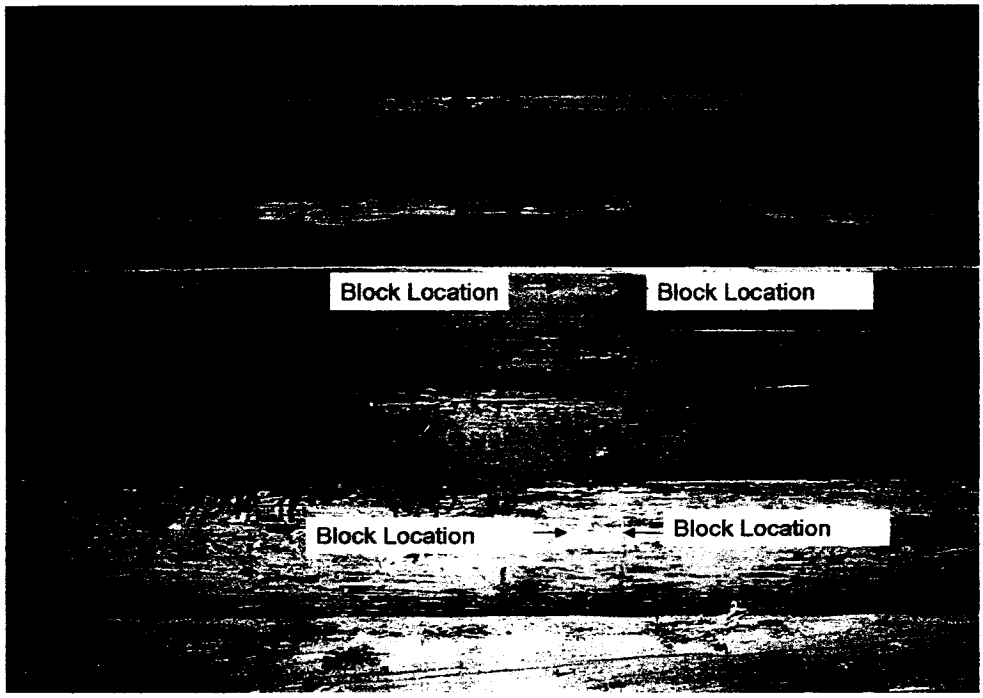

Figure 3.1. Layout and marking of out-of-service poles.

Figure 3.2. Cutting of first block starting at the butt end of the pole.

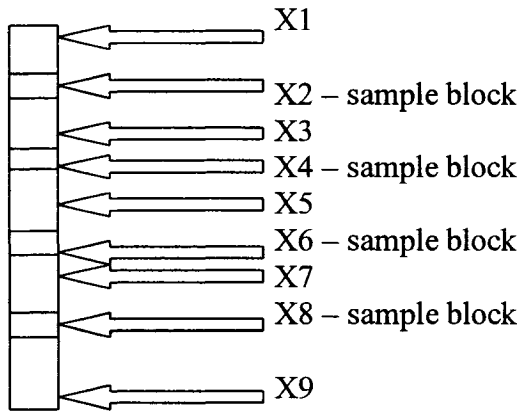

Figure 3.3. Labelling scheme used for test poles (X is the pole identification letter which is followed by the block number, all sample blocks have even numbers).

3.1.3 Rings Removed from the Blocks

Concentric rings were marked on each of the cut blocks in 1.5 cm deep intervals beginning at the outside edge of the block and moving in towards the center of the pole to a maximum depth of 4.5 cm. This maximum depth was chosen as it represented the maximum preservative penetration on any of the poles as verified by a standard PCP check solution and subsequent laboratory analysis. The 4.5 cm depth also corresponded to the sapwood-heartwood boundary in 98% of the samples as the poles were at the lower diameter and length scale for poles. This resulted in three sets of rings representing three different depth ranges (1) 0 to 1.5 cm, (2) 1.5 to 3.0 cm and (3) 3.0 to 4.5 cm. The blocks were cut into the appropriate ring sections using a bandsaw and the samples were labelled

with the block ID number and the depth range ie. A2 0-1.5 (pole A, block number 2, ring depth 0-1.5cm). This process is illustrated in Figure 3.4. Given the variability of wood with respect to sapwood and heartwood ratios this was agreed to be the best method to provide the most representative sample at a given depth. All poles vary in sapwood to heartwood ratio based on several factors, ranging from nutrient availability during wood growth to orientation of the tree towards the sun (FPS, 1999). This is the reason for the ring sampling but there will be some overlap and sapwood/heartwood mix due to natural variability.

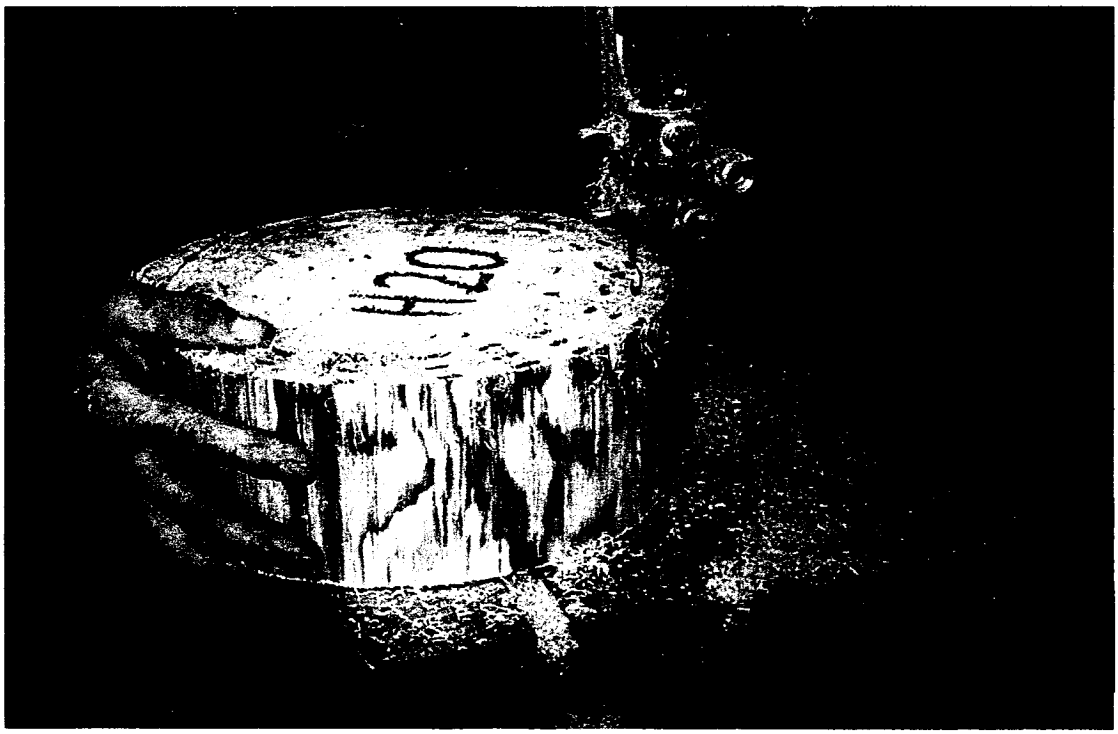

Figure 3.4. Sample of rings being cut prior to grinding.

3.1.4 Preparation of Wood Samples for Analysis

Two sample preparation methods were employed, with the second method evolving from the first, since a more efficient method of grinding was required due to excessive damage to the blades on the Waring blenders.

3.1.4.1 Sample Preparation Method A

Each of the wood ring samples was chopped into thin slivers about 10 cm long x 1.5 cm wide x 5 mm thick with a hatchet. These slivers were then chipped, 10 to 12 slivers at a time, in a 1 L stainless steel Waring blender (7011S blender model number 31BL92) alternating between medium speed and high speed for 2-3 minutes. The chipped samples were collected in large Ziploc bags and shaken to form a homogeneous mixture. The blender units were cleaned between samples with a laboratory detergent (Contrad 70), then rinsed four times with distilled water followed by four methanol rinses. Each of the chipped samples were then emptied into a large covered bucket and further mixed before being ground in a Wiley mill (Model N 0.3). Samples were ground in the Wiley mill to pass through a 2 mm mesh screen. These ground samples were stored in 1 L closed plastic containers at 4°C until needed.

3.1.4.2 Sample Preparation Method B

Each of the wood ring samples was chopped into pieces approximately 10 cm long x 2.5 cm wide by 1.5 cm thick with a hatchet. These pieces were ground using the grinder assembly shown below in Figure 3.5 with the resulting sample shown in Figure 3.6. The grinder assembly consisted of a router fitted with a "need type" tip. The router was mounted onto an enclosed pipe which was attached to a ShopVac. Each piece of the sample was held with vice grips and manually fed into the grinder assembly through the access window. The sawdust and wood shavings were collected in a ShopVac then sieved to remove any pieces larger than 2 mm. Samples were stored in 1 L closed plastic containers at 4°C until needed. All accessible parts of the grinder assembly and ShopVac were vacuumed between samples and rinsed with acetone to prevent contamination between the samples. This system was employed on 75% of the samples as it was much more robust than the Waring blenders. The continued need to replace blades on the blender unit was the driver behind the development of the new grinding apparatus. Again this was constructed specifically for this project through trial and error.

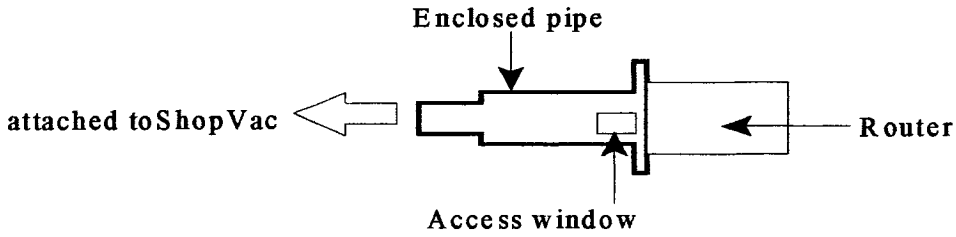

Figure 3.5. Schematic of grinder assembly designed by author.

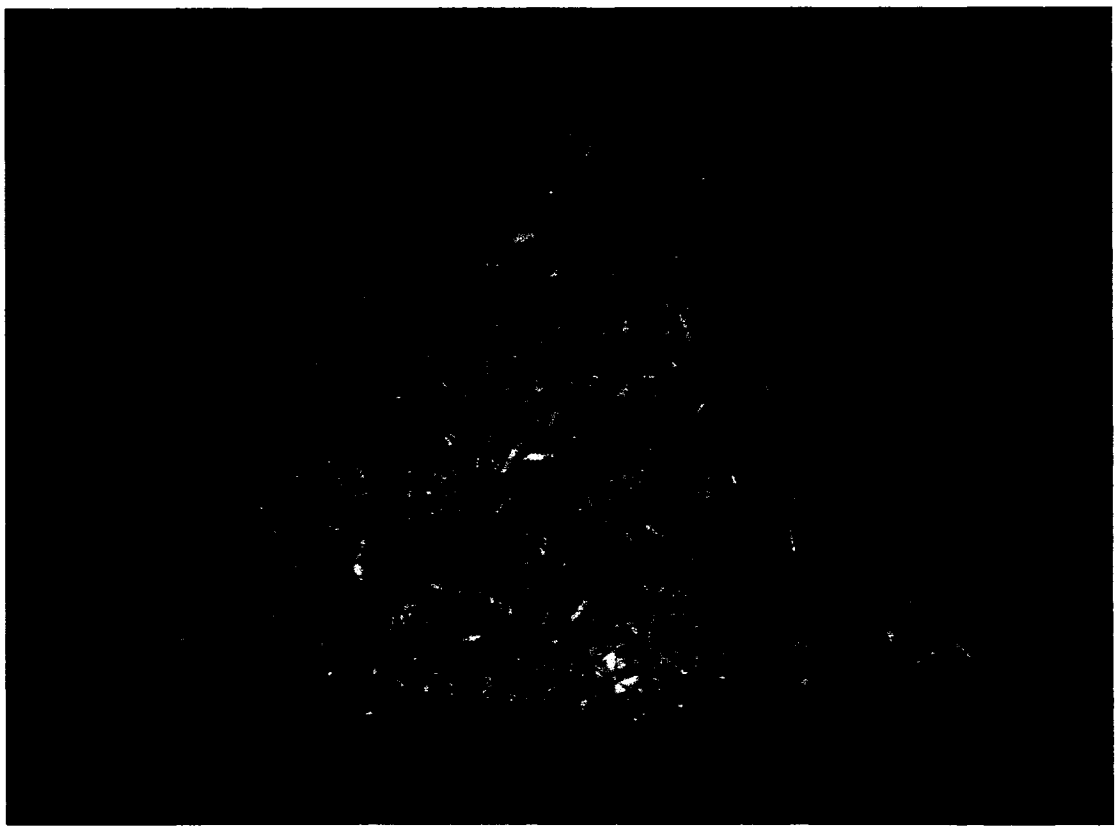

Figure 3.6. Typical homogeneous ground pole section.

3.1.5 Sample Identification

In order to eliminate bias during analysis, all samples were identified with a laboratory code number. The first half of the code consisted of the letter identifying the pole the sample was taken from and the second half of the code was a number generated using a random numbers table. This insured that the samples were analyzed in a completely random manner and without bias.

Pole C was chosen at random to be the initial test pole to be used in a preliminary test. Each ground sample from this pole was analyzed in triplicate in order to determine the degree of variation within a sample. If the variation was found to be sufficiently small, only one sub-sample from each of the remaining poles samples would need to be analyzed. As such, the samples from pole C were further labelled with a letter A through C to identify the replicate number. For example, sample C2 0-1.5 A represents the first replicate (rep A) of a sample taken from block 2 from pole C at a depth of 0-1.5 cm.

3.1.6 Chlorophenol Analysis

Two methods were used to determine PCP (chlorinated product) concentrations in the wood samples. These were soxhlet extraction followed by GC-MS and direct X-ray fluorescence of unextracted samples.

3.1.6.1 Soxhlet Extraction

The wood samples were extracted using a modification of United States Environmental Protection Agency (USEPA) method 3540C for soxhlet extraction (Miller, 2002). Ten grams of ≤ 2 mm mesh wood were mixed with 10 g anhydrous sodium sulfate and placed in a 33 mm x 80 mm cellulose extraction thimble (Whatman # 2800338). Samples were placed in a soxhlet extraction apparatus (Figure 3.7) and extracted for 24 h at 4-6 cycles per h with acidified 1:1 hexane: acetone (HPLC grade solvents, Caledon Lab, Georgetown, Ontario). The hexane: acetone solution was acidified with 1M sulfuric acid to an approximate pH of 2. After the extraction was complete the extracts were dried

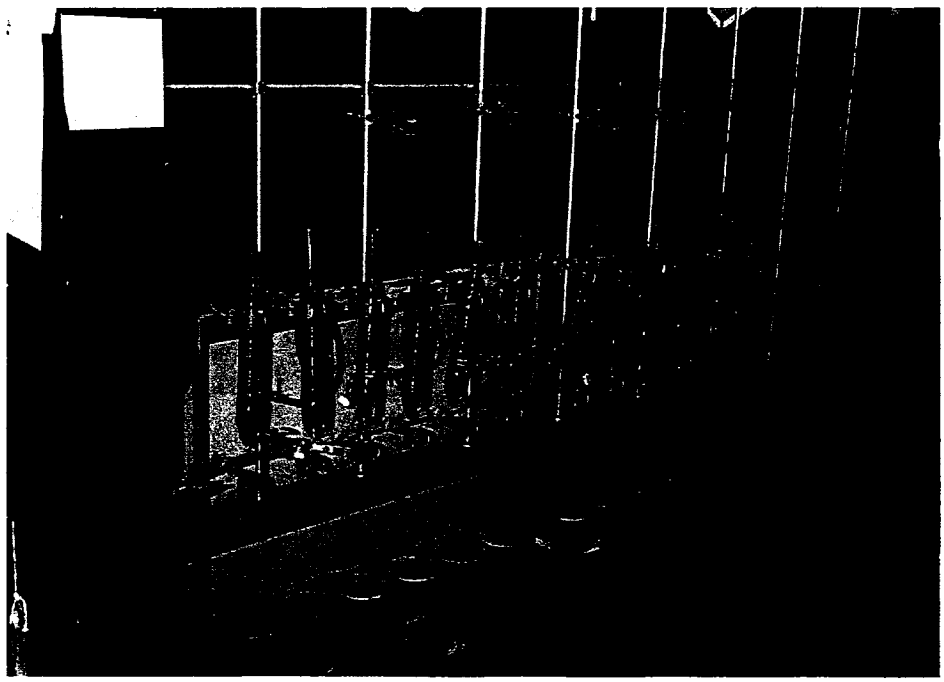

Figure 3.7. Soxhlet extraction units used to prepare extracts.

down to approximately 1 mL using rotary evaporation (Büchi models RE 121 and R-124). Samples were evaporated under vacuum at a water bath temperature of approximately 32°C (Figure 3.8).

Samples were transferred quantitatively to 15 mL amber vials (Supelco # 27003) using aliquots of hexane:acetone to rinse the flasks. The samples were dried under nitrogen using an N-EVAP Organomation Analytical Evaporator to a final volume of approximately 1 mL. Samples were then capped and shipped to the Research and Productivity Council (RPC) laboratory in Fredericton, New Brunswick Canada to be analyzed for the Municipal and Industrial Strategy for Abatement (MISA) analytical test

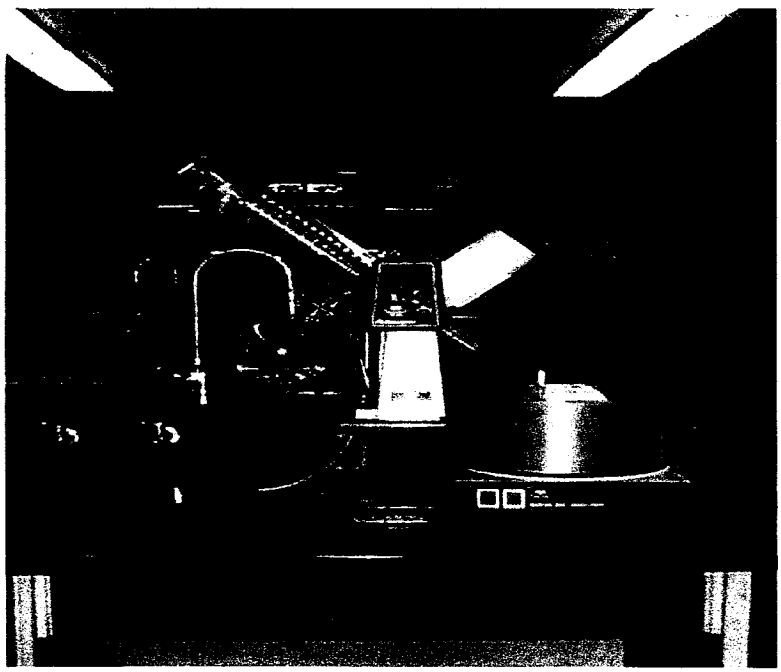

Figure 3.8. Roto-evaporation units used to remove solvent.

group consisting of 20 acid extractable phenolics as per the Atlantic Partnership in Risk-Based Corrective Action (RBCA) Implementation (PIRI) guidelines.

The Atlantic PIRI committee has a mandate to establish RBCA as the approach used to manage contaminated properties in Atlantic Canada. Upon receipt the extract pH was confirmed to be below 2, a hexane extraction was performed then evaporated under nitrogen, derivitized with diazomethane and analyzed by GC-MS. The MISA chemical group consists of the following analytes:

4-chloro-3-methylphenol	4-nitrophenol
2-chlorophenol	pentachlorophenol
2-cresol	phenol
3-cresol	2,3,4,5-tetrachlorophenol
4-cresol	2,3,4,6-tetrachlorophenol
2,4-dichlorophenol	2,3,5,6-tetrachlorophenol
2,6-dichlorophenol	2,3,4-trichlorophenol
2,4-dimethylphenol	2,3,5-trichlorophenol
4,6-dinitro-2-cresol	2,4,5-trichlorophenol
2,4-dinitrophenol	2,4,6-trichlorophenol

3.1.6.2 X-Ray Fluorescence

Ground wood samples were analyzed on-site for pentachlorophenol directly using an Oxford Lab-X3500 bench-top X-ray fluorescence analyzer as shown in Figure 3.9 (Oxford Instruments Industrial Analysis Group, Wyndyke Furlong, Abingdon, Oxfordshire, England. OX14 1UK). The instrument was calibrated before use with standardized samples supplied by the manufacturer. Each pole sample was analyzed five times using a different sub sample for each analysis. For each sample the Oxford sample cup was filled to the top with < 2 mm mesh sawdust. This allowed the sample to be compacted slightly when the sample lid was placed on the holder. This compaction was necessary to maintain a constant sample volume throughout the analysis. The sample holder with the ground penta-treated wood sample was weighed and placed into the Oxford Lab-X 3500 and analyzed for % penta content (please note: due to the method of detection this number includes penta as well as any other chlorinated products present in the sample). The % penta was then converted to percentage chloride ion to account for the predominantly penta but some tetra chlorophenolics were present. Comparison was performed on split samples analyzed by the RPC labs (GC-MS) and with the Oxford X-ray fluorescence instrument to determine the correlation of chloride ion concentrations, also printed by the Oxford unit, with the GC-MS data. This was necessary to see if all samples could be analyzed using X-ray fluorescence rather than the more costly GC-MS.

Figure 3.9. Oxford Lab-X 3500 X-ray fluorescence instrument.

Matrix interferences with X-ray fluorescence are reported to exist when samples are not properly homogenized (Necemer *et al.*, 2003). Due to this, preliminary experiments were required to check the repeatability of the sample data. These included multiple readings without removing the sample, readings of samples introduced with different orientations and readings of sub-samples from the same ground ring sample volume. The results from this experiment were statistically compared using a simple one way analysis of variance followed by a Tukey's means test.

3.1.6.3 Statistical Analysis of Chemical Analysis Comparison Data

Data sets obtained from the analysis of pole C on the GC-MS and Oxford Lab-X 3500 X-ray Fluorescence were statistically analysed to determine if there was a significant difference between the two methods of chemical analysis. The Univariate Procedure in the Statistical Analysis System computer software (SAS) (version 12) was used to test the assumptions of an analysis of variance. If the assumptions were met the GLM analysis of variance procedure was performed to test the significance of the model.

3.1.6.4 Detection Limit Experiment

It was important to determine the detection limit for Cl on the X-ray fluorescence instrument by analyzing untreated pole sections (pole U) at various depths using 6 replicates of randomly selected samples U4 (1.5-3 cm), U6 (0-1.5 cm), and U10 (3-4.5 cm). Oxford claims that the Cl detection limit for this machine varies from 10-50 ppm. The literature states that Red Pine sawdust can contain up to 0.005 Cl (%wt) (ECN, 2005).

Additional detection limit experiments were performed using a dilution series based on treated wood sawdust being mixed with progressively higher quantities of untreated sawdust until the machine's actual detection limit was reached, given the matrix interference factors for wood. Five dilution series were developed with five replications

each to determine the machine's practical detection limit. Samples of untreated sawdust were also sent for chloride ion analysis by RPC labs to determine background levels and for comparison to X-ray fluorescence readings. Total chlorophenolic leachate tests were used as the final check on the amount of chlorophenolics removed. This is dictated by the Government of Canada with respect to the transport of dangerous goods and the export and import of recyclable materials regulations (Canadian Government, 2006).

3.1.7 Data Analysis for Pole Mapping

The data that resulted from the analysis of the poles were subjected to statistical analysis using the Statistical Analysis System computer software (SAS) (version 12). The Univariate Procedure was used to obtain the summary and descriptive statistics for each pole data set. This procedure verifies whether the assumptions of an analysis of variance are met, such as whether data are normally distributed. For visual interpretation of the pole mapping, the data were graphed using Sigma Plot (version 8).

The data from the poles were statistically analyzed using Repeated Measures. Repeated Measures is the usual statistical procedure for analyzing experiments where the samples are not independent of one another (Littell *et al.*, 1998). In the present experiment the PCP concentrations from the various pole lengths are not independent, due to the fact that PCP tends to migrate downwards when the pole is in service. Consequently, the chemical level at one sample location is affected by the chemical level in the samples above it. As

well, PCP concentrations at the various wood depths taken at each length are not independent, due to the fact that the preservative migrates from the surface of the wood inwards, and the penetration at a given specific depth is affected by the overlying layers of wood.

Experiments analyzed with Repeated Measures are a type of factorial experiment. The Proc Mixed procedure in SAS was used to analyze these data as recommended by Littell *et al.* (1998). This procedure first models the variance and correlation structure of the repeated measures and optimises the model by selecting the proper covariance structure. The p-value that is produced from Repeated Measures analysis for the present experiment indicates whether there is a significant difference in preservative levels among the various pole lengths or depths. When significant differences are noted an LSMeans test was used to identify which of the lengths or depths differed from one another. LSMeans are basically an estimation of the measured means, but are developed from pooling the data. For example, in the present experiment the data for each of the three depths sampled for a given pole length would be pooled when testing for differences among lengths. As well, the data for all the pole lengths would be pooled for a given sample depth when testing for differences among depths.

If Repeated Measures analysis showed a significant effect of pole length or preservative penetration depth, linear regression analysis was then used to characterize these trends (Montgomery, 1997). All data were tested for normality and constant variance using the

Univariate Procedure in SAS prior to other testing. In the results section for this experiment pole length is identified in statistical tables as Block and the depth variable is identified as Ring.

3.2 Experiment to Determine Optimum Solvent Extraction System

This experiment involved optimizing extraction duration, surface area to volume ratio or size of treated wood exposed to the solvent, solution temperature, viscosity, solvent type, solvent strength and the ability to separate preservative solution from the extracting solution for reuse in the treatment cylinders. Sodium hydroxide (NaOH) was selected as the preferred solvent due to its ability to react with PCP to form Na-PCP. This conversion was verified by layering PCP treating solution on top of water and gradually adding NaOH to determine if PCP would come out of the carrier oil in response to the pH change. In addition, the ability of the resulting precipitate to return to PCP was assessed through pH adjustment with hydrochloric acid (HCl) and subsequent analysis in fresh pole oil. Samples of oil were analyzed before and after the addition of the NaOH.

3.2.1 Solvent Optimization

It was shown early in the research that NaOH was a suitable solvent at the 1 N concentration. Experiments were also conducted using 0.5 N and 0.75 N NaOH. Nine replicate extractions for each solution strength were performed and the results indicated

that 1 N was the concentration of choice. Results from this preliminary research are reported in Section 4.3.

3.3 Assessment of the Time and Depth Possible for Conversion of PCP to Na-PCP

An assessment was made of the time required and the depth of wood that was extractable for conversion of PCP to the water soluble salt Na-PCP, as well as the system's ability of a nearly instantaneous phase change of the solution to expel the converted preservative from the wood. This experiment involved the gradual phasing up of the size of wood being reacted with 1N NaOH from sawdust through to the processing of full pole sections. This was the point at which the study switched from the laboratory to the use of small scale treatment systems or pilot plants. Once the scaling up began, 2 L to 23 L to 1500 L pilot plant wood treatment units were employed, as outlined below. To focus on the equipment available at a typically equipped treating plant within SJI, the following sizes of treated wood were employed in this experiment:

a) Sawdust sized particles (< 2 mm) were produced by the grinding and blending systems outlined above in order to mimic the milling and grinding systems that are available to resaw material for odd sized industrial or consumer items. This consists of a large band resaw, blower and chipper apparatus to facilitate movement of sawdust from the resaw mill to the blower system for expulsion from the building. An illustration of the steps in the extraction of PCP from treated sawdust sized particles is shown in Figures

3.10, 3.11 and 3.12. Larger sized pieces of treated wood were extracted using the pilot wood treatment plants (Figures 3.13, 3.14 and 3.15).

b) Wood strips were produced using two reclaimed PCP-treated poles that were originally treated in 1972 and branded as 35/4s, which were the same types of poles as those used for the mapping experiment. The poles were run through the facility's pole peeler and samples were taken at 1 m intervals from depths of 0 to10 mm, 11 to 20 mm, 21 to 30 mm, 31 to 40 mm, and 41-50 mm. Stopping at 50 mm was a machine operation issue as pole became too brittle if ground further. The resulting pole peeler strips, ranging in size from 1 to 3 mm thick, 10 to 30 mm wide, and 150 to 300 mm long were the sizes employed. All samples were collected in plastic bags directly from the peeler waste chute and numbered A through E with the length and depth reported for each. This equipment was selected as each SJI plant is equipped with a pole peeler designed to remove bark and provide a smooth surface on harvested material (Figure 3.16 and 3.17).

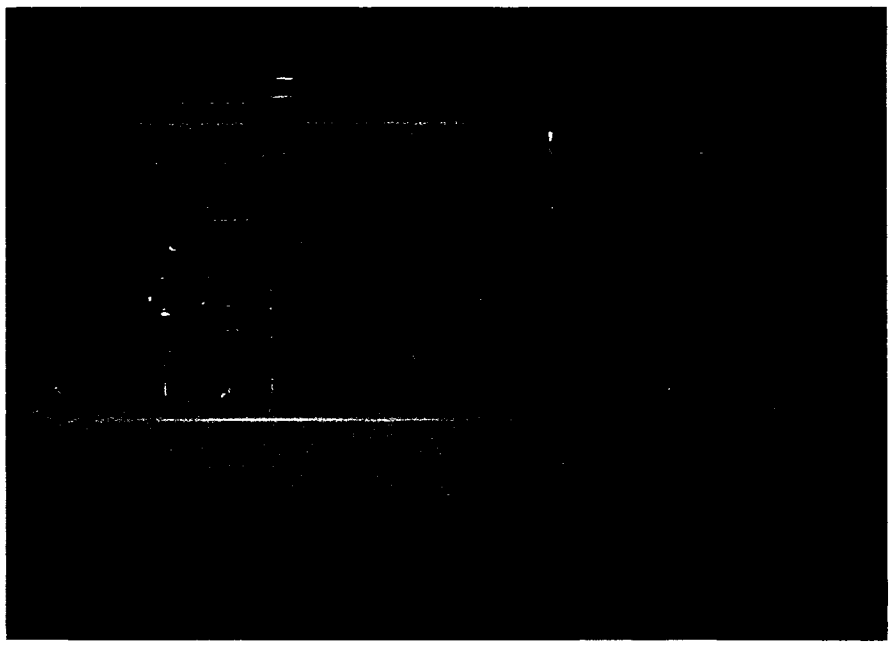

Figure 3.10. Apparatus for agitating sawdust with 1 N NaOH for 4 hours.

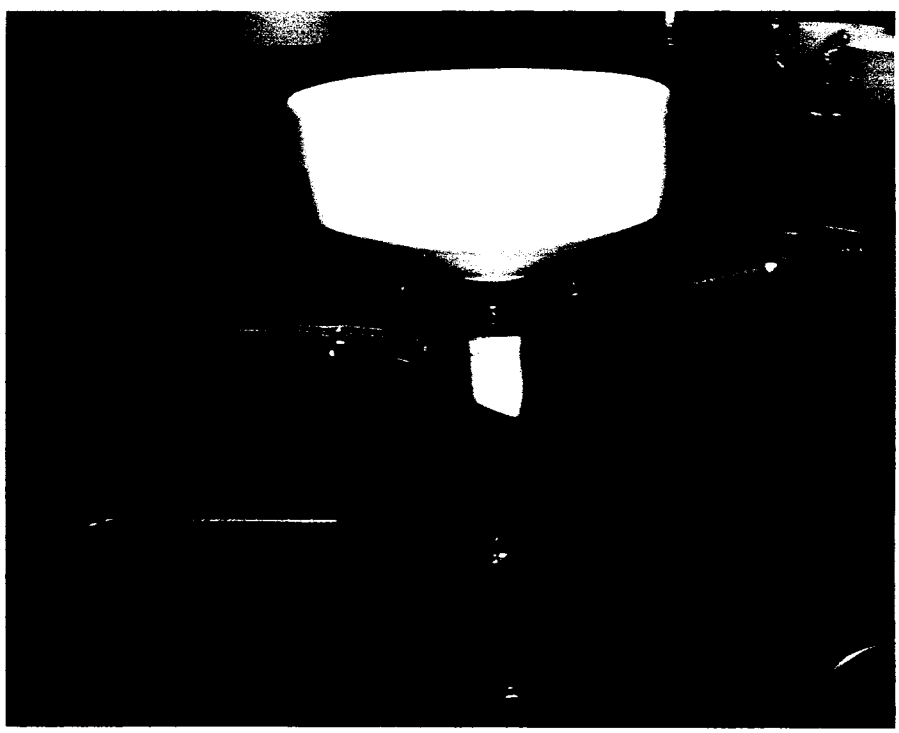

Figure 3.11. Vacuum filtration of sawdust sized particles.

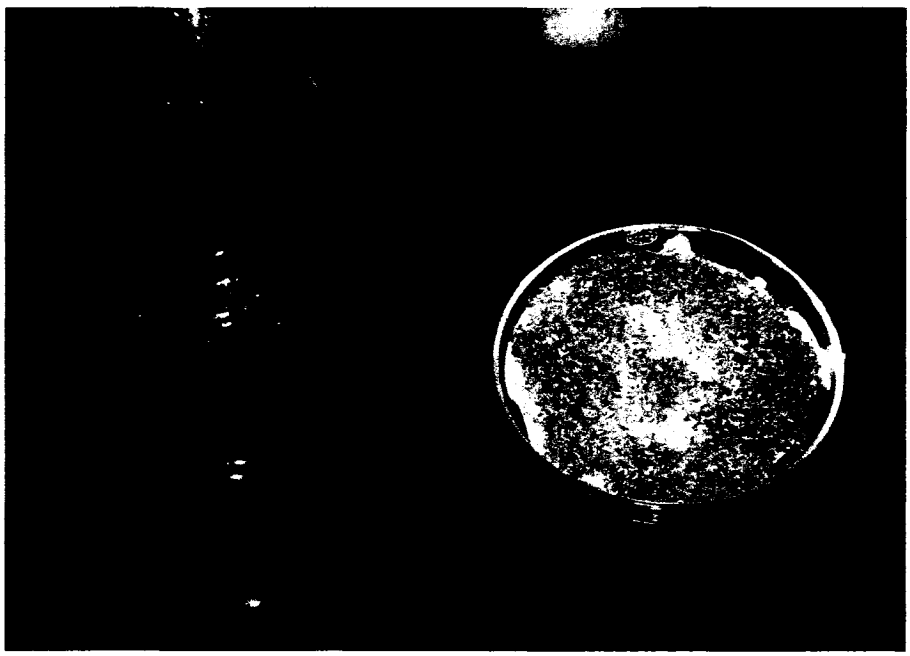

Figure 3.12. Extract and resulting clean sawdust.

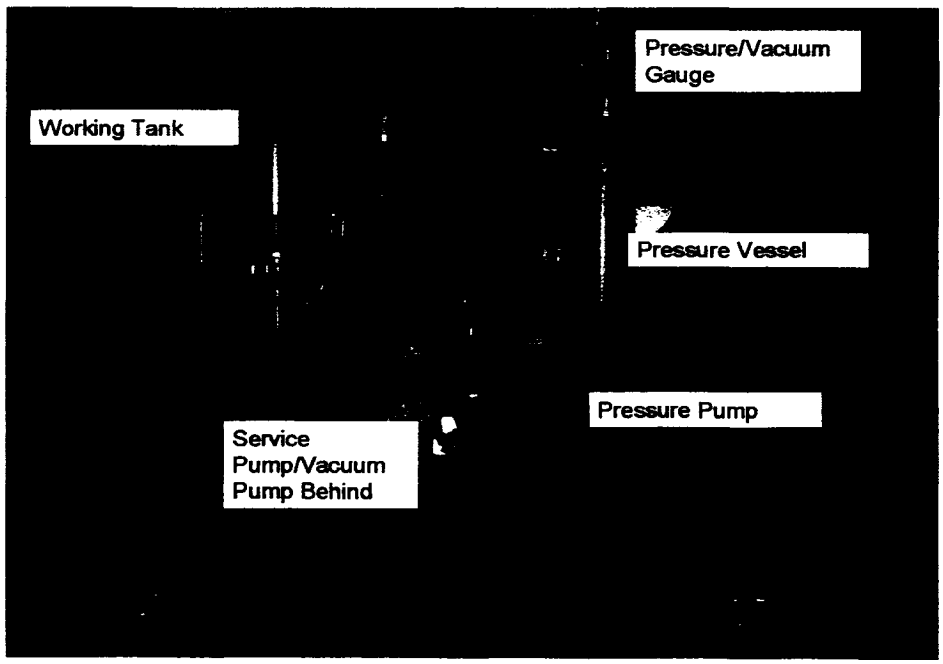

Figure 3.13. Smallest pilot plant with a 2 L treatment chamber designed for this project by the author and used to extract peeler strips (see notes overleaf).

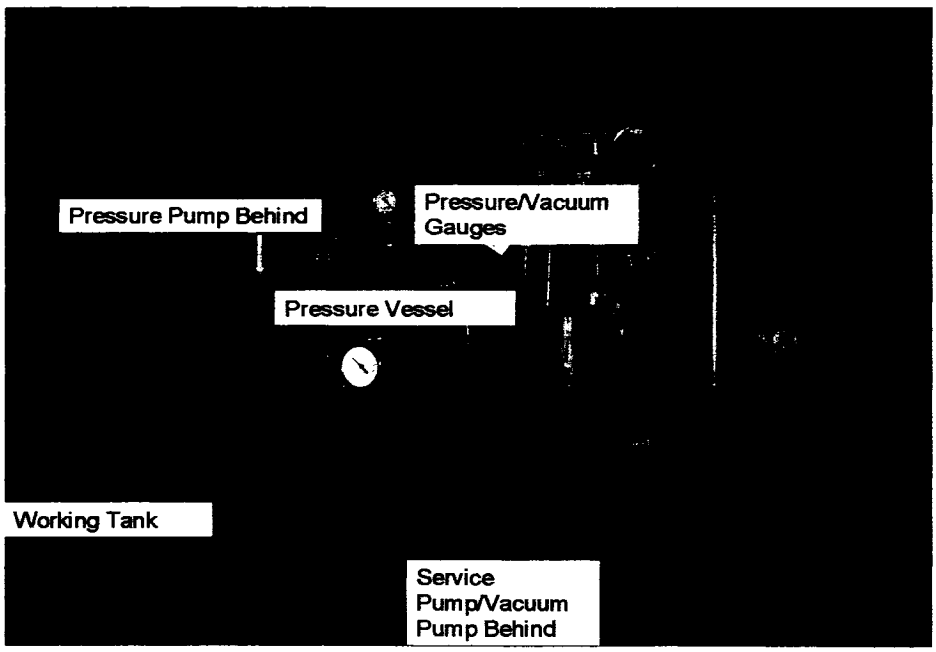

Figure 3.14. Intermediate pilot plant with a 23 L treatment chamber also designed by the author and used to extract slats (see notes below).

Notes for both plants:

Design Pressure – 350 Psi = 2411 kPa

Operating Pressure – 150 psi = 1033 kPa

Relief Valve – 160 psi = 1102 kPa

Vacuum required – 27 in Hg = 91 kPa

Service Pump = 20 L/h small – 50 L/h large

All schedule 40 piping, cylinder also constructed of seamless pipe for a maximum pressure of 2500 psi = 17,225 kPa

Viton Gasket, 2.5 cm flange secured with schedule 80 bolts on pressure chamber

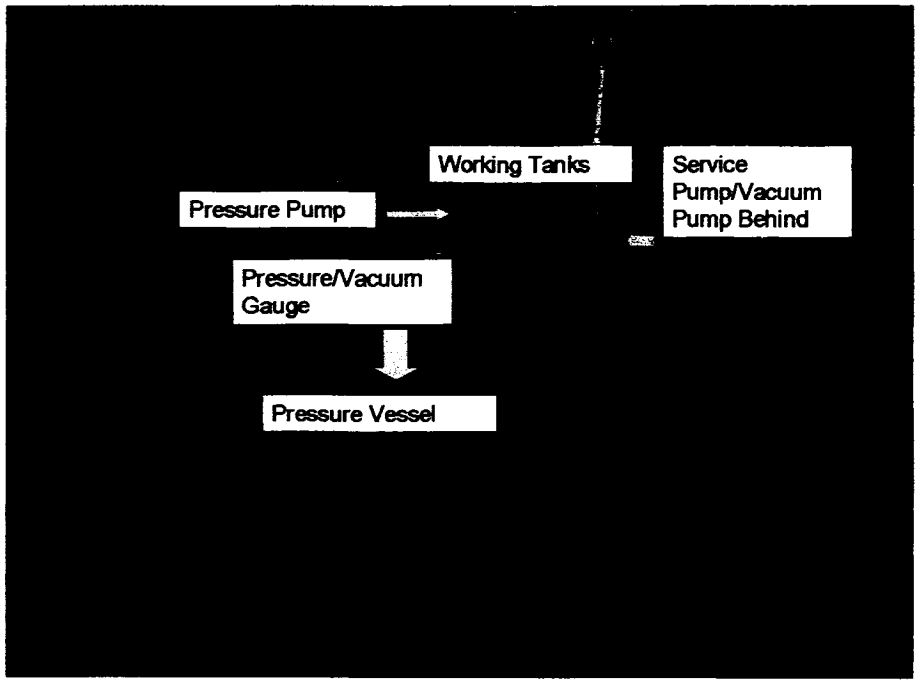

Figure 3.15. Largest pilot plant with a 1500 L treatment chamber built by Domtar Inc. and used to extract full pole sections.

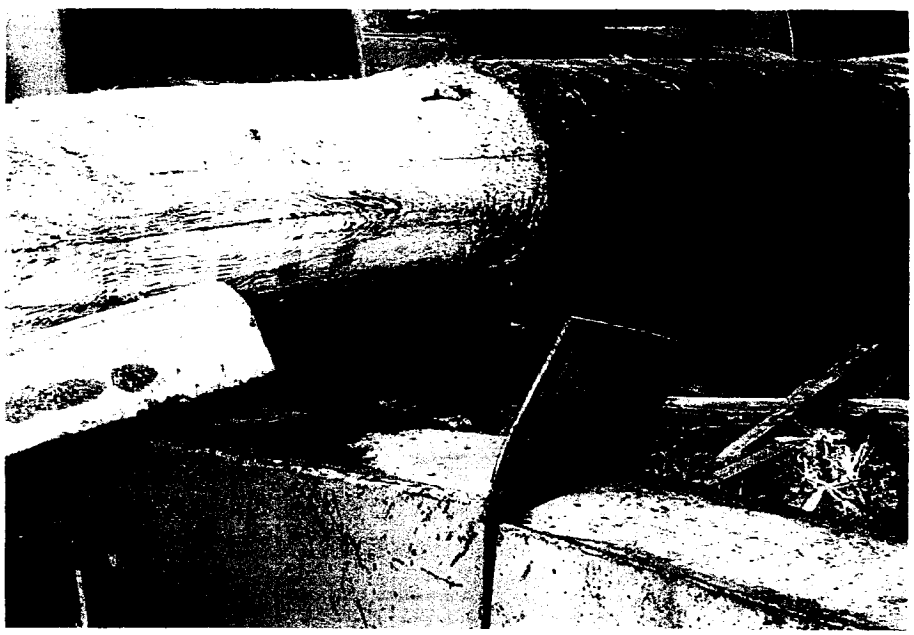

Figure 3.16. Pole peeler removing first section of 0 to 10 mm

Figure 3.17. View of resulting peeler sample.

This machine also has the ability to peel the treated portion from a pole, leaving behind the inner "peeler cores" which consist of untreated heartwood. The resulting peeled treated wood represented the first material to be subjected to NaOH treatment within the pilot plants using Rueping cycles (Figure 2.7). The treatment solvent was 1N NaOH. This concentration was chosen by initial experimentation. It is also easy to prepare and 1N NaOH and 1N HCl are both commonly used to adjust the pH of laboratory solutions. Other concentrations, beyond the 0.5N and 0.75N NaOH tested initially, were not tested with the larger wood samples since the purpose of this research was to develop a patentable PCP extraction process.

To ensure homogeneity of the sample each bag of peeler strips was shaken immediately after collection, then prior to a brief storage, and again prior to extraction to determine both the initial concentration of PCP (chlorinated products) and the concentration after the solvent-Rueping extraction process in the 2 L pilot plant (Figure 3.13). The extraction was carried out with a standard Rueping cycle using 1 N NaOH in the working tank and filled under 344 kPa initial air pressure to a ultimate fluid pressure of 1034 kPa, which was then held for 2 h for penetration of the thicker samples and to ensure the probability of solvent contact with the target preservative. A final vacuum of 91 kPa for 2 h was used to enhance preservative expulsion from the wood. All samples were analyzed for chloride ion using an Oxford X-ray fluorescence instrument. The chloride ion level was used to determine the percentage reduction of PCP in the extracted wood.

c) Wooden slats were then manufactured using the plant resaw. The sizes employed were selected as the minimum that could be processed by the existing equipment. A reclaimed pentachlorophenol-treated pole was cut to obtain a random sample one meter in length (Figures 3.18 and 3.19). This 1m sample was further divided into four quarter wedges. One of these 1 m pie-shaped wedges was randomly selected as the subsample for analysis. The heartwood was removed from the wedge and the remaining sapwood was cut into lengthwise slats of various thicknesses (3, 6, 9, 18, and 25 mm). Each of the replicated wedges was assigned a letter code and all the slats from that wedge had the same letter code. Each slat was divided into alternating 10 cm and 20 cm sections. Each section was assigned a number code in addition to the letter code for the slats. The

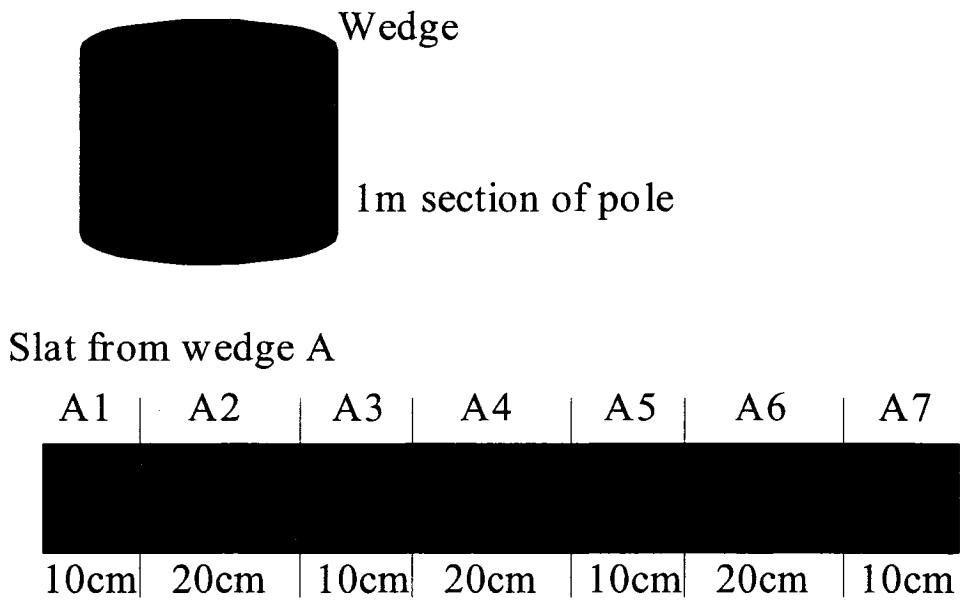

Figure 3.18. Schematic of the division of pole and numbering of slats.

numbers continued sequentially until all sections of a wedge were numbered (eg, A1, ..., A77). Therefore the whole wedge could be pieced back together in order.

The 10 cm sections from each slat were combined and used as a control to determine initial concentration in the slat. To determine the initial level of PCP (chlorinated products) the controls were ground, the sawdust sieved through a 2 mm mesh and analysed by X-ray fluorescence. The 20 cm sections were subjected to a detreating (extraction) process using a 1N NaOH solution and a Rueping process in the 23 L pilot plant (Figure 3.14). The extraction was carried out with a standard Rueping cycle with 1

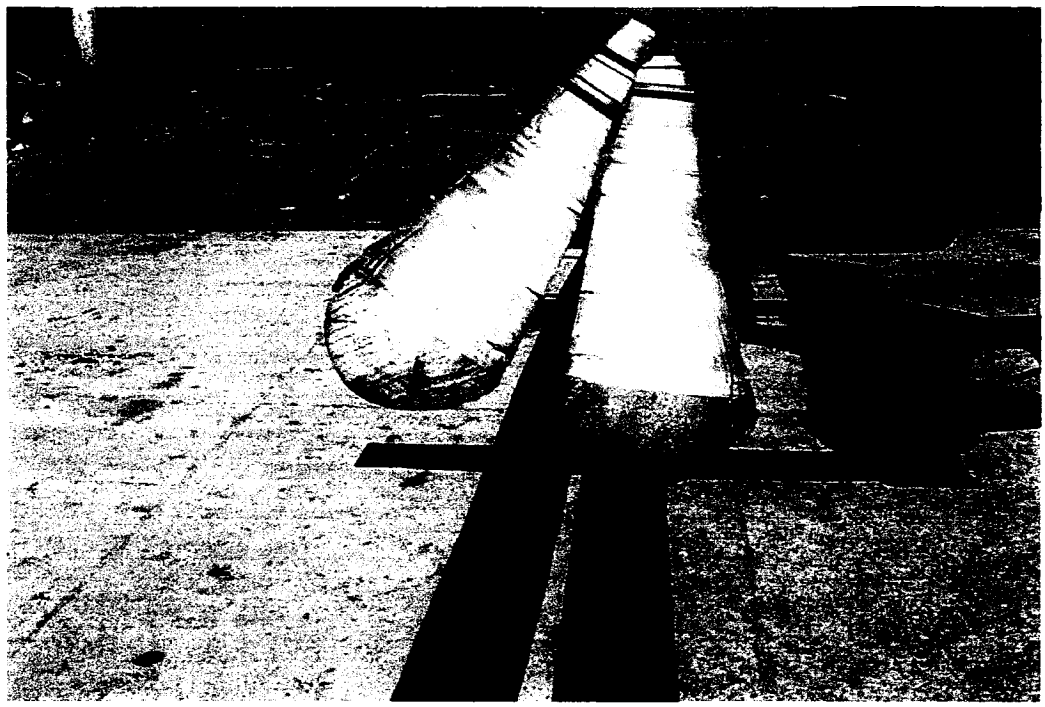

Figure 3.19. Illustration of resaw initial bisection of the pole for slats.

N NaOH in the working tank and filled under 344 kPa initial air pressure to an ultimate fluid pressure of 1034 kPa, which was held for 2 h for penetration of the thicker samples and to ensure the probability of solvent contact with the target preservative. A final vacuum of 91 kPa was used for 2 h to enhance preservative expulsion from the treated wood. After the detreating process, the 20 cm sections were subjected to the same process as the 10 cm controls, where they were ground and analysed for PCP (chlorinated product) content. The PCP content of the controls was then compared to that of the sections subjected to the detreating process to determine the percent reduction of PCP from the wood.

d) Five intact pole sections, 2 m in length, were taken from 35/4 poles which are 10.7m in length and of a diameter capable of withstanding a 14,000 kPa horizontal breaking force treated in 1973. They were used in the final scale up to full pole sections to ensure that poles could be extracted. Initial sampling of the pole for PCP was done using 10 borings taken randomly per 2 m length and plugged as per CSA standards to ensure that the borings had minimal influence on penetration of the NaOH (Figures 3.20 and 3.21). The pole sections were then exposed to 1N NaOH using a Rueping process to ensure maximum kickback, or expulsion of extracted preservative. The extraction was carried out with a standard Rueping cycle with 1 N NaOH in the working tank and filled

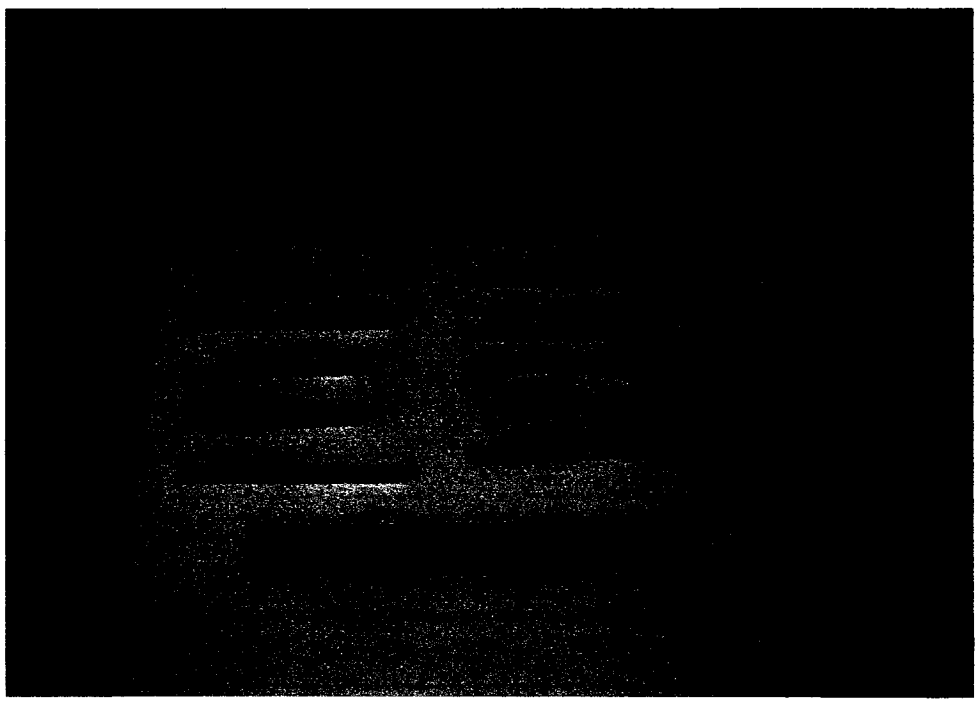

Figure 3.20. Examples of core samples taken from full pole sections.

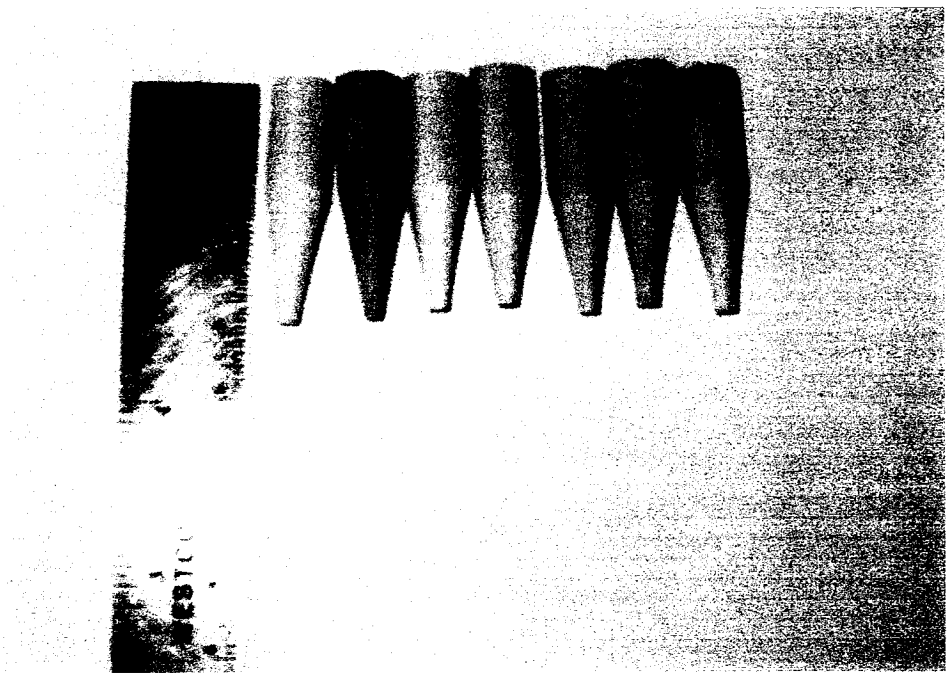

Figure 3.21. Examples of plugs used before extraction was performed on the full pole sections.

under 344 kPa initial air pressure to an ultimate fluid pressure of 1034 kPa, which was held for 2 h for penetration of thicker samples and to ensure the probability of solvent contact with the target preservative. A final vacuum of 91 kPa, was used for 2 h to enhance preservative expulsion from the treated wood. This was performed in the 1500 L pilot plant (Figure 3.15). The detreated poles were then bored 20 times randomly around the circumference of the detreated pole and the cores also analyzed by X-ray fluorescence. The results of the chloride ion present (PCP) after detreatment were compared to starting conditions. Given the required sample volume for analysis, 20 borings were used for each X-ray florescence test to ensure that only penetrated sapwood was analysed.

3.3.1 Pilot Plant Cycles

The same pilot plant cycles were used in all cylinders in order to mimic the typical PCP treatment process for a pole. Contents of the charging tank containing the Na-PCP were then isolated for conversion back to PCP through acid addition using 1N HCl. The 2 L pilot plant system was employed for the peeler strips, the 23 L system for the wood slats, and the 1500 L system for the pole sections. It is important to note that success at any scale used would be a positive result. This process would also be further enhanced at the full production level through the SJI statistical quality improvement process.

3.4 Commercialization of the Extraction Process

Upon completion of the experiments outlined in Sections 3.1 and 3.2, a method to successfully commercialize this process was deemed feasible. In order to reduce costs existing plant equipment was employed. A flowchart and value chain analysis was prepared to assess costs, handling, storage and what upgrades would be required to existing plant equipment. The author has extensive experience in costing out these processes on behalf of SJI.

The use of a value chain analysis system is a costing tool used by businesses where each step in the production process is analyzed to determine its relative cost and addition or subtraction to the profit generated. An example of this can be found in the author's

M.B.A thesis (Murray, 2001). This method can best be described as a combination of industrial engineering and accounting. Any manufacturing process can be subjected to this analysis. The degree to which each step is analyzed is the driver behind the resulting accuracy. Any point in the value chain that has a negative impact is subjected to engineering analysis to determine what improvements could be made to enhance the system into the positive value added position. An example of the process for one of the SJI plants is shown in Table 3.1.

Another tool used to determine whether or not a company should enter into a new business line is termed the competitive forces model (Murray, 2001). This looks at the threat of new entrants into the market place, the bargaining power of buyers for the service or product, the intensity of rivalry in the industry, the bargaining power of suppliers, and the threat of product substitutes. Each potential competitor is then subjected to a strength, weakness, opportunity and threat analysis (SWOT) before undertaking a new line of business (Murray, 2001). The answers stemming from these processes allow a company to determine the viability of a new business venture and then to proceed with the design of a facility.

Table 3.1. Example of a value chain analysis - overall plant operations

(Murray, 2001)

Inbound Logistics	***Rating: Fair*** Narrow supplier base and relations, cross Canada presence, high freight costs due to distances involved on poles and ties.
Operations	***Rating: Needs Improvement*** More integration and communication required between the strategic business units.
Outbound Logistics	***Rating: Good*** Export shipping in Nova Scotia lower costs to shipping companies. All plants are located near rail-lines. Scales to maximize loads.
Marketing and Sales	***Rating: Improving*** Sales force being trained and or hired with more technical abilities. National presence is a tremendous advantage if exploited.
Service	***Rating: Good-Excellent*** Ability to customize and treat wood products with all leading preservative treatments is a key advantage for Stella-Jones, Inc. Excellent relationships with long-term customers locally.
Technology Development	***Rating: Good*** Research and development has increased. Hiring several graduate students in conjunction with the Nova Scotia Agricultural College and Dalhousie University.
Human Resource Management	***Rating: Improving*** Addition of full time resource manager at head office to help with formulating policies.
Firm Infrastructure	***Rating: Good*** Recent acquisition of Guelph Utility Pole helps solidify national presence.

4.0 Results and Discussion

The results obtained from this research and the ensuing discussion are presented in the order outlined in the Materials and Methods (Section 3).

4.1 Pole Mapping Experiment

The pole mapping experiment was performed to establish the distribution of PCP within a treated pole with respect to pole length and preservative penetration depth. A summary of the characteristics of the test poles used in this study is shown in Table 4.1. Measurements were taken using the ring sampling method as outlined in Section 3.1 to ensure a representative sample around the circumference of the pole.

4.1.1 Sample Analysis

The initial focus of the research was to determine the repeatability of the measurements for both the GC-MS and the Oxford X-ray fluorescence instruments to prove that both the sample homogenization method and the analytical procedures used were valid. For this experiment all samples, taken from the randomly selected pole C, were analyzed by both methods to test the validity of the sample preparation and analytical procedures. Figure 3.6 previously gave a representative picture of the degree of sample homogenization obtained prior to analysis. Method B (Section 3.1.4.2) was chosen for grinding the wood

Table 4.1. Qualitative and quantitative description of used PCP-treated poles employed in the pole mapping study.

Pole ID	Year treated	Length* (feet/class)	Actual length (m)	Tip diameter (m)	Butt diameter (m)	Pole visual appearance
B	1970	35/4	10.69	0.222	0.315	Oil 66 cm from butt, clean remainder of pole to tip, and weathering leading to porosity increases.
C	1970	35/4	10.75	0.205	0.270	Oil 66 cm from butt, clean remainder of pole to tip, and weathering leading to porosity increases.
D	1976	35/4	10.70	0.174	0.312	Oil 66 cm from butt, clean remainder of pole to tip, and weathering leading to porosity increases.
E	1974	35/4	10.71	0.215	0.314	Oil 66 cm from butt, clean remainder of pole to tip, and weathering leading to porosity increases.
G	1977	35/4	10.70	0.228	0.266	Oil 66 cm from butt, clean remainder of pole to tip, and weathering leading to porosity increases.
U	2004	35/4	10.70	0.224	0.275	Light gray weathered pole air seasoned to moisture content for treating.
T	2004	35/4	10.72	0.23	0.322	Uniform dark brown, dry to the touch, freshly treated pole.

* The industry standard is to use pole length in feet rather than metres, and the class designation is related to this standard.

samples as it was much more efficient and produced an equivalent degree of homogeneity.

4.1.2 GC-MS Analysis

The triplicate samples from pole C were prepared for GC-MS analysis using a modified USEPA Method 3540C soxhlet extraction procedure for acid chlorophenolics, as outlined in Section 3.1.7.1. This has been shown to give much higher percentage recoveries for chlorphenolics and PAHs in previous studies, when compared to the sonification method used in most commercial labs (Miller, 2002). The results of the GC-MS analysis are summarized in Table 4.2 along with the corresponding X-ray fluorescence data. The full data sets are shown in Appendix A, Tables A.1 and A.2. Statistical results for this experiment are presented in Section 4.1.3.

4.1.3 Oxford Lab-X 3500 Data versus RPC's GC-MS Data

The data obtained for chlorinated products ($\mu g \cdot g^{-1}$ wood) from Stella-Jones' Oxford Lab-X 3500 were compared to the data from RPC for chlorophenols, but using only the tetra- and pentachlorophenolics (Appendix A, Tables A.1 and A.2), as detected by GC - MS ($\mu g \cdot g^{-1}$ wood). Only the tetra- and pentachlorophenolics were considered, since preliminary analyses found that all other chlorophenolics were below detection limits.

Table 4.2. Comparison of results from Oxford X-Ray fluorescence and GC-MS on pole C samples.

Sample ID*	Oxford chlorinated products, 5 Reps ($\mu g \cdot g^{-1}$ wood)		GC-MS penta + tetra, 3 Reps ($\mu g \cdot g^{-1}$ wood)	
	Mean	Standard deviation	Mean	Standard deviation
C2 0-1.5	2315.92	184.35	2301.33	365.01
C2 1.5-3	1662.61	162.99	1260.83	388.31
C2 3-4.5	709.68	204.87	1082.37	412.58
C4 0-1.5	2324.89	427.94	2642.33	1201.22
C4 1.5-3	2041.40	307.24	1202.23	403.86
C4 3-4.5	1489.94	149.15	900.83	469.71
C6 0-1.5	2690.59	410.85	2289.13	1554.62
C6 1.5-3	1869.01	102.78	1501.33	84.81
C6 3-4.5	743.44	145.17	2411.73	1131.34
C8 0-1.5	2479.69	209.25	2144.67	102.48
C8 1.5-3	2245.45	257.40	7552.43	5222.48
C8 3-4.5	1189.40	162.51	833.53	221.40
C10 0-1.5	2620.98	635.15	2563.00	1361.00
C10 1.5-3	1925.44	165.32	1668.47	460.54
C10 3-4.5	724.49	95.08	916.07	552.02
C12 0-1.5	1944.48	85.20	2003.53	1160.48
C12 1.5-3	1973.80	267.36	6077.00	5599.90
C12 3-4.5	1197.62	197.94	890.47	57.53
C14 0-1.5	2342.38	325.22	8492.80	5179.42
C14 1.5-3	1801.67	346.54	4908.67	4446.24
C14 3-4.5	670.93	121.76	2054.07	1946.24
C16 0-1.5	2338.26	219.61	2233.67	355.22
C16 1.5-3	1666.94	115.05	896.30	328.26
C16 3-4.5	508.76	114.54	398.93	54.91
C18 0-1.5	1780.12	217.36	1895.17	309.99
C18 1.5-3	2217.45	120.47	1674.60	126.01
C18 3-4.5	1227.10	90.76	1650.67	417.41
C20 0-1.5	3928.98	340.87	4255.53	236.67
C20 1.5-3	3117.18	575.61	4464.33	1419.88
C20 3-4.5	632.99	33.01	650.63	141.31
C22 0-1.5	3476.67	376.58	2635.30	162.75
C22 1.5-3	4054.88	213.79	3753.33	462.64
C22 3-4.5	587.26	83.62	778.03	124.03

* Analysis for each instrument done on individual samples not split samples, complete data sets in Appendix A, Tables A.1 and A.2.

The initial statistical analysis, used to obtain the summary and descriptive statistics for each data set, was performed using the Univariate Procedure in SAS. This procedure can verify whether the assumptions of an analysis of variance are met, such as whether data are normally distributed.

The Normality test provides a D test statistic for testing whether a data set variable is normally distributed. If the value is greater than 0.1 then the population is normally distributed. The Oxford X-ray fluorescence vs GC-MS data were not normally distributed so a transformation (lconc =$(conc-850)^{0.5}$) was performed. The transformed data were normal as indicated by the D-statistic p-value ($p = 0.1500$; Appendix A, Figure A.1) and the various univariate procedure plots. Transformed data were used for statistic tests but the untransformed data are reported in the summary tables and figures for convenience. Several outliers had to be removed as identified by the SAS Univariate procedure.

The plots provided by the Univariate procedure are the Normal Probability plot, Stem Leaf plot and the Box plot. These plots, along with the test for normality, should be used when making conclusions on normality. The Normal Probability plot is an X-Y plot of values. Each '*' indicates a sample value and the '+' signs form a straight line. For a perfect normal distribution the + symbols would all be covered by the *s. If a large number of + signs are visible, then the distribution is not normal. With the Stem Leaf plot the symmetry of the plot and the presence of skewing and/or kurtosis is noted. The details of the diagram of the Boxplot should be examined. The vertical line hashes are the

'whiskers' and each indicates 1.5 interquartile ranges from the box. Outlier points are indicated by a 'O' or a '*' depending on its interquartile range from the box. The normality plot for the Oxford x-ray fluorescence vs GS-MS data was straight and the majority of the + symbols were covered by *s. The Stem Leaf and Box plots were also acceptable (see output handout in Appendix A, Figure A.1).

The Univariate procedure also provides a plot of residuals vs predicted values which assesses if the variances are the same for each level (Homogeneity of Variance). Constant variance can be assumed if the majority of points (letters) can be contained within two horizontal bands (an upper and a lower) on the plot. Letters falling outside these bands are considered outliers, with the letter determining the number of observations (A = 1 observation, B = 2 observations, etc.). If constant variance is not detected due to a distinct pattern (curvature) of the plot, the transformation of the data would be used to get the data to meet this assumption. The majority of the letter points on the plot of residuals vs predicted values for the Oxford x-ray fluorescence vs GC-MS data could be contained within two horizontal bands and therefore constant variance could be concluded.

For the lab comparison, repeated measures statistics were not required because the data are independent from one another (Montgomery, 1997), in that the result obtained on one instrument does not affect the result obtained on the other instrument. To test the Oxford X-ray fluorescence versus the GC-MS data the GLM analysis of variance procedure in SAS was used. This procedure uses the method of least squares to fit linear models. The

fact that the p-value from the F-test was 0.3136 (Appendix A, Figure A.1), which is greater than the alpha 0.05 (5% level of significance), indicates there is no significant difference between the two analytical procedures. It was concluded that the much more time and cost efficient Oxford X-ray fluorescence analysis could be used to collect the rest of the experimental data.

For the balance of this thesis X-ray fluorescence data are used as a measure of PCP levels. X-ray fluorescence data are actually given as total chlorinated products, but can also be reported as %PCP (chlorinated products).

An additional analysis was performed once all pole samples had been chemically analyzed to determine if Pole C could be considered representative of the 5 poles employed in the study. The Univariate procedure (to test the normality and constant variance assumptions), GLM procedure (to test the significance of the model) and an LSD test was performed for means comparisons on the pole data from the study. The pole comparison data were not normally distributed so a transformation (lconc = (conc+4250)**$^{0.5}$) was performed. The transformed data were normal, as indicated by the p-value (p = 0.1121; Appendix A, Figure A.2) and the various univariate procedure plots. Transformed data were then back-transformed to report the means. The Proc GLM produced an F-test p-value of <0.0001, which means there is a significant difference among some of the test poles and a means comparison was necessary. Least significant difference (LSD) testing was a suitable selection for means comparison, due

to the fact that the poles were weathered in a field setting, as opposed to a lab setting, indicating that more variability is likely to be present (Littell *et al.*, 1998). The results of this LSD test confirmed that the data were not statistically the same because there was a relationship between two separate pairs of poles, namely B and G and C and D. It was considered that pole C was an acceptable choice as a representative sample for the Oxford X-ray fluorescence vs GC-MS analysis. Again, complete SAS outputs are found in Appendix A, Figure A.2.

4.1.4 Determination of Analytical Methodology Summarized

The experiment comparing the GC-MS versus the X-ray fluorescence analysis on PCP treated wood was the first to be performed. Results showed no significant variation between the two methodologies and made the research much more economical by allowing use of X-ray fluorescence, which then allowed for a more thorough look at the scaling up process (Section 4.1.3). It is not surprising that the data led to this conclusion, given that X-ray fluorescence uses the interaction of Cl ion with radiation to determine concentrations with only sample homogenization required to ensure that each particle of wood is penetrated and thermalizes the radiation incident upon it in the same manner (KanngieBer, 2003). The extensive extraction method required for the GC-MS allows for laboratory error in any one of its numerous steps (Fortune-Phillips, 2003). While the GC-MS is more sensitive, the spread in the data received versus X-ray fluorescence proves that experimental error can play a significant role. This result is no doubt the reason why

all of the major chemical suppliers rely on X-ray fluorescence machines for quality control analysis versus atomic absorption or GC-MS (Ziabro, 2005; Hildebrant, 2005; Mitchell, 2006).

The method of using rings cut at various lengths or blocks, as shown in Figures 3.1 to 3.3, seemed to yield more homogeneous samples as the variation between sapwood and heartwood around the circumference of a tree is a documented fact (Fortune-Phillips, 2003). This was also noticed by the author through extensive wood sampling of SJI products for quality control purposes. The lack of interaction between the two laboratory methods made the statistics straightforward, as shown in Appendix A. No published literature is available using this type of sampling protocol for comparison purposes.

4.1.5 X-ray Fluorescence

One purpose of this experiment was to determine whether the method of sample preparation was appropriate for the accurate quantification of PCP using the Oxford Lab-X 3500 X-ray fluorescence instrument. This was done to ensure that the method of sample preparation did not contribute any errors to the analysis. To accomplish this, three different tests were performed using the randomly selected C10 0-1.5 cm ground wood sample. This was done while awaiting the results for the samples sent for GC-MS analysis at the RPC laboratories which were to be used in analytical comparisons.

All pole samples were analyzed for PCP (chlorinated products) content using the Oxford Lab-X 3500. Each PCP pole sample was analyzed five times using a different sub sample for each analysis. The sample container was shaken prior to analysis in order to thoroughly mix the contents. The Oxford sample cup was disassembled and a new mylar window film was installed as directed in the operating instructions, also using a new polyethylene inner sample cell and lid.

Given the matrix interference and the need to homogenize samples, as documented in the literature, several small experiments were performed to determine the effect of variations in the preparation of samples for X-ray florescence, as follows:

1) Undisturbed readings involved placing a sample of the test material in the instrument and taking 10 individual readings without removing the sample from the instrument. These readings gave a measure of instrument precision and repeatability of analysis. The results showed a range of 0.611% PCP (chlorinated products) to 0.612% PCP (chlorinated products) with an average reading of 0.6115 $\pm$ 0.001% PCP (chlorinated products).

2) Reintroduced reading required that the sample be removed from the instrument holder in between readings so that the same sample was read each time, but the orientation of the cell within the instrument varied. These readings gave a measure of any error caused by sample introduction or by the orientation of the sample within the

instrument. The five reintroduced readings ranged from 0.606% PCP (chlorinated products) to 0.615% PCP (chlorinated products) with an average reading of 0.6114 ± 0.0039% PCP (chlorinated products).

3) Sub sampling required repeated measurements being taken using different sub samples of the same ground ring section for each reading. These readings measured any error caused by sample preparation. Ten sub samples were analyzed with the readings ranging from 0.607% PCP (chlorinated products) to 0.616% PCP (chlorinated products) with an average reading of 0.6112 ± 0.0029% PC P (chlorinated products). These readings appeared to vary depending on the mass (and thus the density) of sample loaded into the sample holder.

The results from this experiment were statistically compared using a simple one way analysis of variance (see SAS output Appendix A, Figure A.3). The large number of identical values within the data set meant that the data were not normally distributed and transforming the data was unsuccessful at inducing normality (best p-value was 0.0024 with a square root transformation). However, given the closeness of the means, no significant difference can be assumed. As well, an ANOVA was still run on the data followed by a Tukey's means test (Appendix A, Figure A.3). The Tukey's test showed no significant difference between the data sets even though there was a significant F-test ($p=0.0276$). This verifies the accuracy and reproducibility of the X-ray fluorescence method.

4.1.6 Oxford Lab-X 3500 Detection Limit Determination for Percent Chloride

Since X-ray fluorescence was used in all further analysis, it was important to determine its practical detection limit for chloride. The detection limit for chloride ion is reported by the manufacturer of the Oxford Lab-X 3500 to be 10-50 ppm. To verify this, 3 random samples were analyzed from pole U (untreated) with the understanding that Red Pine may contain up to 0.005% Cl (%wt) (ECN, 2005). These results are shown in Table 4.3. Additional experiments were performed to provide a dilution series based on a known concentration of Cl within treated wood, gradually being reduced through the additions of pure whitewood.

Table 4.3. Detection limit study on untreated pole.

Pole Section	Depth (cm)	%Cl	Total chlorinated products ($\mu g \cdot g^{-1}$)
U6	0 -1.5	0.031	0.0973
U4	1.5 – 3	0.031	0.0973
U10	3-4.5	0.031	0.0973

Note : The analysis was performed 6 times for each sample and all replications gave the same result of 0.031% Cl or 0.0973 ($\mu g \cdot g^{-1}$). So it could be concluded that the detection limit for this study is 0.0973 ($\mu g \cdot g^{-1}$), which is above the background level of Cl in whitewood.

Table 4.4. RPC analysis of untreated wood samples.

ID	Cl concentration ($\mu g \cdot g^{-1}$)
SJ1	<10
SJ1 Duplicate	< 10
SJ2	<10
SJ3	<10
SJ4	30*
SJ5	<10
SJ6	<10

* This value while falling within the lowest detection limits reported for the Oxford X-ray fluorescence instrument is most likely a laboratory error.

To determine if the Cl results obtained from the Oxford X-ray fluorescence were accurate, 6 samples of pole U were sent to the RPC laboratory for analysis of Cl ion to verify that the samples really were 0 ppm or below the machine's actual detection limit. All results were below the detection limit of 10 ($\mu g \cdot g^{-1}$), with the exception of one sample which contained 30 ($\mu g \cdot g^{-1}$) (Table 4.4). Laboratory error is the only explanation for this 30 ($\mu g \cdot g^{-1}$) result.

A dilution series experiment was carried out by starting with 3 g of weathered sawdust from pole G. For sawdust sample A, five sample analyses were carried out with the wood sample being removed from the sampling cup, a fresh cup prepared, agitation of the sample, and placement in the fresh cup for each analysis from the ground pole sample. Sawdust sample B was handled the same way, but used 1.5 g of sample A mixed with

1.5 g of pole U (untreated). Sawdust sample C was handled in the same way, but 2.25 g of sample B was mixed with 0.75 g of sample U. Sawdust sample D was handled in the same way, only 2.50 g of sample C was mixed with 0.50 g of sample U. Finally, sawdust sample E was again handled the same way, with 2.8 g of sawdust D being mixed with 0.2 g of sample U. Sample E was so close to the pure untreated readings from pole U that no further dilutions were prepared. Results are shown in Table 4.5, and show that the 0.031% Cl consistently obtained from analyses of white wood samples is indeed the detection limit of the Lab-X 3500 when analyzing ground wood for percent chloride.

4.2 Pole Mapping Variations based on Oxford Lab-X 3500 Measurements

The next analysis was done to compare variations within the pole with respect to length (also shown as Block in some statistics tables) and depth (as shown as Ring in some statistics tables). X-ray fluorescence data were used in this experiment. Since the results

Table 4.5. Detection limit study using a dilution series.

Sample ID	Mean %Cl
Sawdust A	0.822
Sawdust B	0.262
Sawdust C	0.098
Sawdust D	0.045
Sawdust E	0.036*

* Untreated pole U gives the lowest value of 0.031% Cl consistently (Table 4.3)

from both of the blocks (pole length sections), and rings (penetration depth), are dependent on the concentration of PCP preservative in either the blocks above and below or the inner and outer rings, repeated measures statistics had to be used to analyze these data (Littell *et al.*, 1998).

Trends in preservative distribution are to be expected, due to the migration of preservative down the pole after treating and variations in permeability of wood at the time of treatment. Poles become less permeable with depth as sapwood is converted to heartwood, and higher concentrations are generally found in the lower sections of a pole where the sapwood is deeper (FPS, 1999). Repeated measures design is one in which measurements of the same response are made on each experimental unit over time (temporal) or distance (spatial). The Mixed procedure in SAS was designed to analyze repeated measures data by modeling the variance and correlation structure of the repeated measures. The covariance structure is then used to generate least squares means (LSMeans) which are estimates of the true measured means based on pooling the data. Table values shown below for each pole are mean estimates computed from repeated measures analysis of Oxford X-ray fluorescence data (μg chlorinated products · g^{-1} wood). In the tables LSMeans followed by the same letter do not differ significantly at $\alpha = 0.05$.

For all poles, the Proc Univariate procedure was performed first to check for normality and to assess constant variance of the data sets. In order to obtain normality it was

necessary to transform only the data for poles E and G using a natural log transformation. Once normality and constant variance were assured, the Mixed procedure was performed, LSMeans were generated, and significance was determined at the 5% level.

4.2.1 Pole C Data

Pole C data were analyzed using repeated measures to account for the spatial dependence of one concentration value versus another. The Univariate procedure produced a D: Normal test statistic p-value of >0.1500 and there was constant variance (see Appendix A, Figure A.4). Since the model assumptions were satisfied the Mixed procedure could be performed. This showed that all the effects (both main and interaction) were significant, each with a P-value of <0.0001. The results in Tables 4.6 and 4.7 indicate that the pentachlorophenol concentration in pole C (as determined using chloride levels or chlorinated products), was inversely proportional to depth, but not uniformly correlated to length. Since there were significant preservative trends for Pole C, linear regression using the CORR procedure in SAS was performed to quantify trends for the pole at each depth (Figure A.4). Statistical linear regression analyses equations for pole C, with respect to length at the various depths, are shown in Table 4.8. Depth 1 showed a weak positive relationship with 18% of the variability explained by the model. This equation indicates that from the top to the bottom of the pole preservative concentration increases linearly. The explanation for this is the higher percentage of sapwood in the butt end of

Table 4.6 Estimated least squares means (LSMeans) of the concentration of PCP (chlorinated products) ($\mu g \cdot g^{-1}$) over the length of Pole C*.

Length (m) = Block #	LSMeans of chlorinated product concentration ($\mu g \cdot g^{-1}$)	LSMeans letter grouping
1 Top	1562.74	FG
2	1890.97	CD
3	1767.68	DE
4	1971.51	C
5	1679.72	EFG
6	1705.30	EF
7	1604.99	EFG
8	1504.65	G
9	1741.56	DE
10	2485.02	B
11 Bottom	2706.27	A

* Table values are mean estimates computed from repeated measures analysis of Oxford chlorinated products data ($\mu g \cdot g^{-1}$ wood). LSMeans followed by the same letter do not differ significantly at $\alpha = 0.05$. SAS printouts are shown in Appendix A, Figure A.4.

the pole and the downward migration of preservative over the pole's service life. Depth 2 showed the same trend but with 38% of the variability explained by the model and the same pole sapwood and preservative migration factors at work. Depth 3 showed the opposite trend with 11% of the trend explained by the model. This is more difficult to explain as the sapwood argument does not apply. It must, therefore, be the result of binding with the heartwood chemicals or simply the lack of water influence at the greater depth. A plot of the concentration of PCP (chlorinated products) in Pole C is shown in Figure 4.1.

Table 4.7. Estimated least squares means (LSMeans) of the concentration of PCP (chlorinated products) ($\mu g \cdot g^{-1}$) at various depths of Pole C*.

Depth (cm) (Ring)	LSMeans of chlorinated products concentration ($\mu g \cdot g^{-1}$)	LSMeans letter grouping
0-1.5 (1)	2529.81	A
1.5-3 (2)	2213.80	B
3-4.5 (3)	880.15	C

* Table values are mean estimates computed from repeated measures analysis of Oxford chlorinated products data ($\mu g \cdot g^{-1}$ wood). LSMeans followed by the same letter do not differ significantly at $\alpha = 0.05$. SAS printouts are shown in Appendix A, Figure A.4.

Table 4.8. Summary of results of statistical regression analysis on Pole C*.

Pole	Depth (cm) (Ring)	r (correlation coefficient)	p-value	R^2	Relationship equation
C	0-1.5 (1)	0.4248	0.0015	0.1804	Y = 89.6x + 1994.2
	1.5-3 (2)	0.6144	< 0.0001	0.3775	Y = 136.5x + 1392
	3-4.5 (3)	-0.3411	0.0108	0.1163	Y = -36.4x + 1098.5

* SAS printouts are shown in Appendix A, Figure A.4.

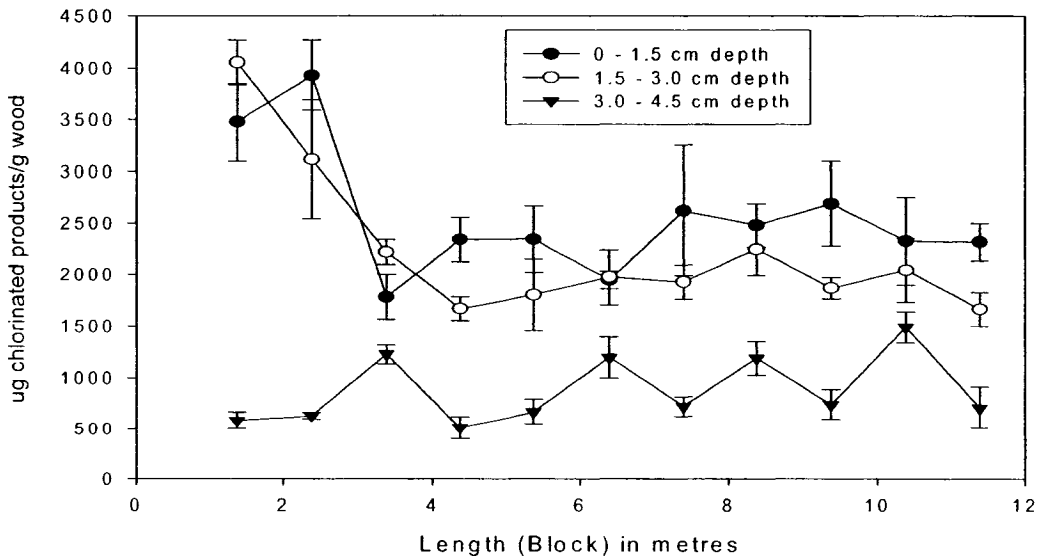

Figure 4.1. Mapping of chlorinated products through pole C.

4.2.2 Pole B Data

Pole B data were analyzed by repeated measures. The Univariate procedure produced a D: Normal test statistic p-value of >0.1500 and there was constant variance (see Appendix A, Figure A.5). Since the model assumptions were satisfied the Mixed procedure could be performed. This showed that all the effects (both main and interaction) were significant, each with a P-value of <0.0001. The results in Tables 4.9 and 4.10 indicate that the concentration of preservative is much more uniform in this pole with respect to length, with the bottom and top sections having the same LSMeans grouping. Again the PCP (as chlorinated products) concentration is inversely proportional to depth. Since there were significant preservative trends for Pole B, linear regression using the CORR procedure in SAS was performed to quantify trends for the pole at each depth (Figure A.5). Overall, the regression of length versus depth showed only a weak negative relationship (see Table 4.11) with 14% of the variation explained by the model on the shallow sapwood layer. This could only be explained by thicker than normal sapwood or less mechanical weathering at the top of this pole. No other relationships were present. A plot of the concentration of PCP (chlorinated products) with respect to length and depth for pole B is shown in Figure 4.2.

Table 4.9. Estimated least squares means (LSMeans) of the concentration of PCP (chlorinated products) ($\mu g \cdot g^{-1}$) over the length of Pole B*.

Length (m) = Block #	LSMeans of chlorinated product concentration ($\mu g \cdot g^{-1}$)	LSMeans letter grouping
1 Top	3792.03	A
2	3349.82	C
3	3676.62	AB
4	3529.91	B
5	3337.49	C
6	2848.13	D
7	2785.61	D
8	2873.25	D
9	2795.99	D
10	3669.38	AB
11 Bottom	3799.64	A

* Table values are mean estimates computed from repeated measures analysis of Oxford chlorinated products data ($\mu g \cdot g^{-1}$ wood). LSMeans followed by the same letter do not differ significantly at $\alpha = 0.05$. SAS printouts are shown in Appendix A, Figure A.5.

Table 4.10. Estimated least squares means (LSMeans) of the concentration of PCP (chlorinated products) ($\mu g \cdot g^{-1}$) at various depths of Pole B*.

Depth (cm) (Ring)	LSMeans of the PCP concentration ($\mu g \cdot g^{-1}$)	LSMeans letter grouping
0-1.5 (1)	3807.40	A
1.5-3 (2)	3163.31	B
3-4.5 (3)	2972.34	C

* Table values are mean estimates computed from repeated measures analysis of Oxford chlorinated products data ($\mu g \cdot g^{-1}$wood). LSMeans followed by the same letter do not differ significantly at $\alpha = 0.05$. SAS printouts are shown in Appendix A, Figure A.5.

Table 4.11. Summary of results of statistical regression analysis on Pole B*.

Pole	Depth (cm) (Ring)	r (correlation coefficient)	p-value	R^2	Relationship equation
B	0-1.5 (1)	-0.3761	0.0047	0.1414	Y = -64.0x + 4191.6
	1.5-3 (2)	-0.2289	0.0928	-	No significant relationship
	3-4.5 (3)	0.1528	0.2653	-	No significant relationship

* SAS printouts are shown in Appendix A, Figure A.5.

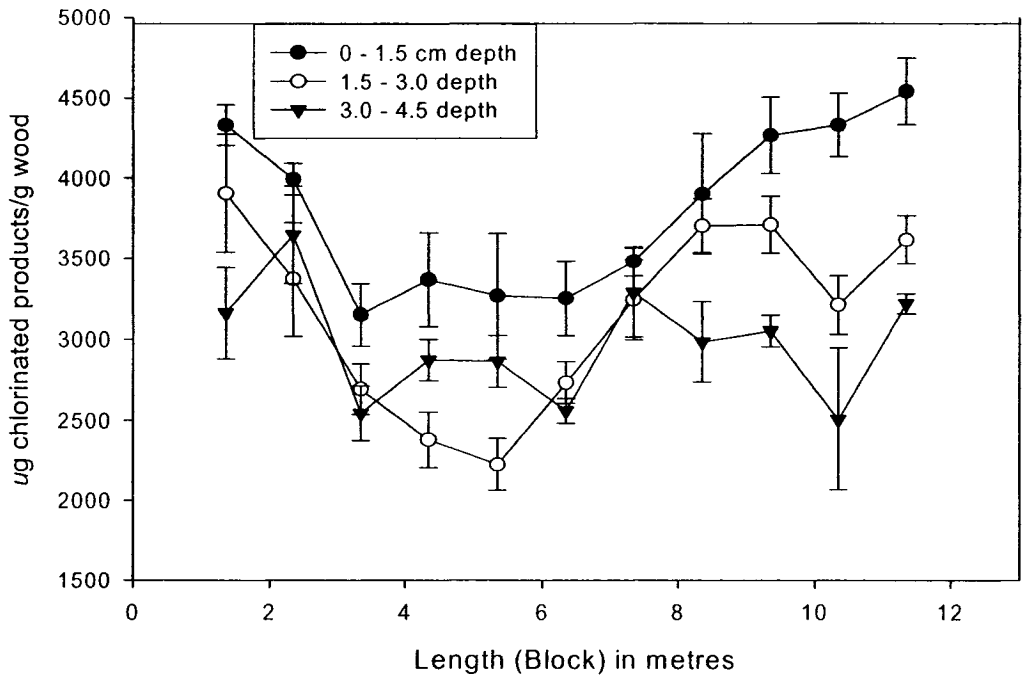

Figure 4.2. Mapping of chlorinated products through pole B.

4.2.3 Pole D Data

Pole D data were analyzed by repeated measures. The Univariate procedure produced a D: Normal test statistic p-value of >0.1500 and there was constant variance (see Appendix A, Figure A.6). Since the model assumptions were satisfied the Mixed procedure could be performed. This showed that all the effects (both main and interaction) were significant, each with a P-value of 0.0001 or less. The results in Tables 4.12 and 4.13 indicate more variation with respect to height than in pole B and the same inverse concentration level with respect to depth. The regression analysis (summarized in Table 4.14) also shows the second highest and most uniform regression equations with respect to length and depth. The first depth showed a positive correlation with 32% of the variation being explained by the model. This indicates that concentration increases with length in the outer layer as would be expected by gravitational migration and general weathering. The middle depth shows a negative relationship with 32% of the variation being explained by the model. This indicates that the concentration decreases towards the top length of the pole. The most likely explanation for this is a variation in sapwood depth and a lack of weathering not allowing for as much vertical migration by precipitation. The same explanation is true for the inner most depth where the model explains 25% of the negative variation. The graph of the PCP (chlorinated products) concentration in Pole D is shown in Figure 4.3.

Table 4.12. Estimated least squares means (LSMeans) of the concentration of PCP (chlorinated products) ($\mu g \cdot g^{-1}$) over the length of Pole D*.

Length (m) = Block #	LSMeans of chlorinated product concentration ($\mu g \cdot g^{-1}$)	LSMeans letter grouping
1 Top	2695.10	A
2	1894.50	CD
3	1766.06	D
4	1378.63	F
5	1219.44	G
6	1381.10	F
7	1493.43	E
8	1585.16	E
9	1625.62	E
10	2332.06	B
11 Bottom	1995.67	C

* Table values are mean estimates computed from repeated measures analysis of Oxford chlorinated products data ($\mu g \cdot g^{-1}$ wood). LSMeans followed by the same letter do not differ significantly at $\alpha = 0.05$. SAS printouts are shown in Appendix A, Figure A.6.

Table 4.13. Estimated least squares means (LSMeans) of the concentration of PCP (chlorinated products) ($\mu g \cdot g^{-1}$) at various depths of Pole D*.

Depth (cm) (Ring)	LSMeans of the PCP concentration ($\mu g \cdot g^{-1}$)	LSMeans letter grouping
0-1.5 (1)	2335.15	A
1.5-3 (2)	1930.43	B
3-4.5 (3)	1016.26	C

* Table values are mean estimates computed from repeated measures analysis of Oxford chlorinated products data ($\mu g \cdot g^{-1}$ wood). LSMeans followed by the same letter do not differ significantly at $\alpha = 0.05$. SAS printouts are shown in Appendix A, Figure A.6.

Table 4.14. Summary of results of statistical regression analysis on pole D*.

Pole	Depth (cm) (Ring)	r (correlation coefficient)	p-value	R^2	Relationship equation
D	0-1.5 (1)	0.5640	< 0.0001	0.3181	Y = 149.0x + 1441.1
	1.5-3 (2)	-0.5694	< 0.0001	0.3243	Y = -86.5x + 2449.3
	3-4.5 (3)	-0.5002	0.0001	0.2502	Y = -102.9x + 1633.9

* SAS printouts are shown in Appendix A, Figure A.6.

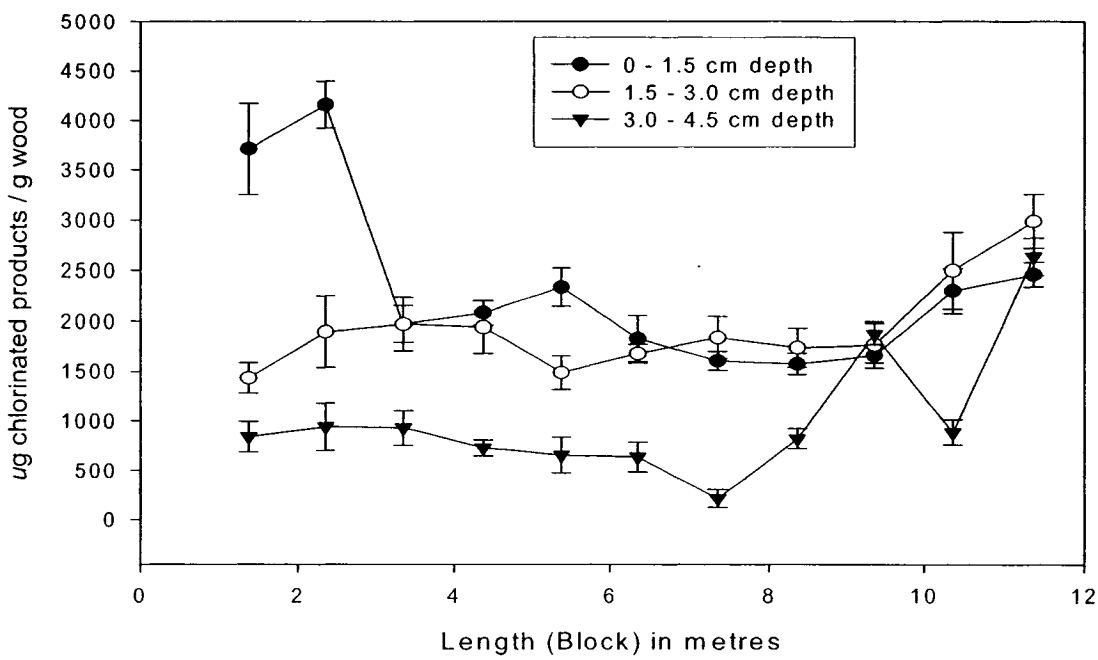

Figure 4.3. Mapping of chlorinated products through Pole D.

4.2.4 Pole E Data

Pole E data were analyzed by repeated measures. The data set was not normal so a natural log transformation was performed to induce normality. The Univariate procedure on the transformed data produced a W: Normal test statistic p-value of 0.3511 and there was constant variance (see Appendix A, Figure A.7). Since the model assumptions were satisfied the Mixed procedure could be performed. This showed that all the effects (both main and interaction) were significant, each with a p-value of <0.0001. The results in Tables 4.15 and 4.16 indicate more variation with respect to height than in pole D, with higher concentrations in the middle, and the same inverse concentration level with respect to depth. Since there were significant preservative trends for Pole E, linear regression using the CORR procedure in SAS was performed to quantify trends for the pole at each depth. The regression analysis showed the strongest relationships with respect to the first and second depths but none for the third. In the first length to depth interaction a strong positive relationship exists with 80% of the variation being explained by the model. The second depth shows the second highest positive relationship with 65% of the variation explained by the model. This is an indication of deeper sapwood and gravitational migration both acting together to increase concentration from top to bottom. The rate of migration, however, seems to have been lower in Pole E than in other poles based on PCP (chlorinated products) concentrations being present at peak levels mid-way down the pole and then being at higher levels again at the lower sections. A plot of the

concentration of PCP (chlorinated products) with respect to length and depth for pole E is shown in Figure 4.4.

Table 4.15. Estimated least squares means (LSMeans) of the concentration of PCP (chlorinated products) ($\mu g \cdot g^{-1}$) over the length of Pole E*.

Length (m) = Block #	LSMeans chlorinated product concentration ($\mu g \cdot g^{-1}$)	LSMeans letter grouping
1 Top	1371.69	H
2	1430.10	H
3	1534.41	G
4	1785.23	F
5	2049.81	C
6	2296.63	A
7	1835.18	D
8	2048.99	C
9	2146.94	B
10	2330.18	D
11 Bottom	1604.07	D

* Table values are mean estimates computed from repeated measures analysis of Oxford chlorinated products data ($\mu g \cdot g^{-1}$ wood). LSMeans followed by the same letter do not differ significantly at $\alpha = 0.05$. SAS printouts are shown in Appendix A, figure A.7.

Table 4.16. Estimated least squares means (LSMeans) of the concentration of PCP (chlorinated products) ($\mu g \cdot g^{-1}$) at various depths of Pole E*.

Depth (cm) (Ring)	LSMeans of chlorinated product concentration ($\mu g \cdot g^{-1}$)	LSMeans letter grouping
0-1.5 (1)	2343.97	A
1.5-3 (2)	1836.65	B
3-4.5 (3)	1419.70	C

* Table values are mean estimates computed from repeated measures analysis of Oxford chlorinated products data ($\mu g \cdot g^{-1}$ wood). LSMeans followed by the same letter do not differ significantly at $\alpha = 0.05$. SAS printouts are shown in Appendix A, figure A.7.

Table 4.17. Summary of results of statistical regression analysis on Pole E*.

Pole	Depth (cm) (Ring)	r (correlation coefficient)	p-value	R^2	Relationship equation
E	0-1.5 (1)	0.8936	< 0.0001	0.7985	Y = 123.8x + 1643.5
	1.5-3 (2)	0.8052	< 0.0001	0.6484	Y = 141.2x + 1066.7
	3-4.5 (3)	-0.1349	0.3261	-	No significant relationship

* SAS printouts are shown in Appendix A, figure A.7.

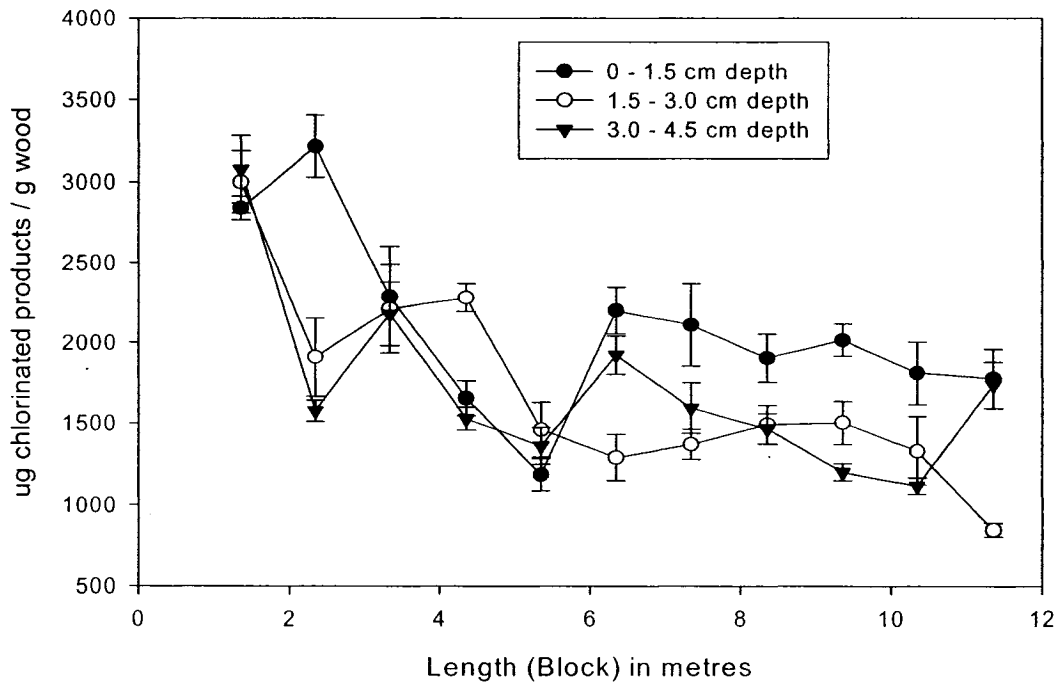

Figure 4.4. Mapping of chlorinated products through Pole E.

4.2.5 Pole G Data

Pole G was the final pole to be analyzed by repeated measures. The data set was not normal so a natural log transformation was performed to induce normality. The Univariate procedure on the transformed data produced a D: Normal test statistic p-value of >0.1500 and there was constant variance (see Appendix A, Figure A.8). Since the model assumptions were satisfied the Mixed procedure could be performed. This showed that all the effects (both main and interaction) were significant, with a p-values of 0.0001 or less. The results in Tables 4.18 and 4.19 indicate less variation with respect to height than in pole E, with the highest concentration at the groundline, and the same inverse concentration level with respect to depth. Since there were significant preservative trends for Pole G, linear regression using the CORR procedure in SAS was performed to quantify trends for the pole at each depth. The regression analysis shows weak positive relationships with respect to the first and second depths, but none for the third. In the first length to depth interaction a very weak positive relationship exists with 7% of the variation being explained by the model. The second depth shows a greater positive relationship with 22% of the variation explained by the model. This is an indication of deeper sapwood and gravitational migration both acting together to increase preservative concentration from top to bottom. The rate of migration, however, seems to have been lowest in pole G based on the highest level of PCP (chlorinated products) uniformity throughout the pole. This was most likely due to a more uniform sapwood depth. The one anomaly is the extreme spike at the ground line indicating that this pole may have

had significant surface bleeding at the time of installation. A plot of the concentration of PCP (chlorinated products) with respect to length and depth for pole G is shown in Figure 4.5.

Table 4.18. Estimated least squares means (LSMeans) of the concentration of PCP (chlorinated products) ($\mu g \cdot g^{-1}$) over the length of Pole G*.

Length (m) = Block #	LSMeans of chlorinated product concentration ($\mu g \cdot g^{-1}$)	LSMeans letter grouping
1 Top	2935.11	B
2	2603.47	E
3	2451.86	F
4	2442.07	F
5	2829.34	D
6	2585.31	E
7	2397.30	F
8	2437.43	F
9	2903.87	D
10	5079.15	A
11 Bottom	2929.25	C

* Table values are mean estimates computed from repeated measures analysis of Oxford chlorinated product data ($\mu g \cdot g^{-1}$ wood). LSMeans followed by the same letter do not differ significantly at $\alpha = 0.05$. SAS printouts are shown in Appendix A, Figure A.8.

Table 4.19. Estimated least squares means (LSMeans) of the concentration of PCP (chlorinated product) ($\mu g \cdot g^{-1}$) at various depths of Pole G*.

Depth (cm) (Ring)	LSMeans of chlorinated product concentration ($\mu g \cdot g^{-1}$)	LSMeans letter grouping
0-1.5 (1)	2664.58	A
1.5-3 (2)	2747.09	B
3-4.5 (3)	3014.23	C

* Table values are mean estimates computed from repeated measures analysis of Oxford chlorinated products data ($\mu g \cdot g^{-1}$ wood). LSMeans followed by the same letter do not differ significantly at $\alpha = 0.05$. SAS printouts are shown in Appendix A, Figure A.8.

Table 4.20. Summary of results of statistical regression analysis on Pole G*.

Pole	Depth (cm) (Ring)	r (correlation coefficient)	p-value	R^2	Relationship equation
G	0-1.5 (1)	0.2726	0.0441	0.0743	Y = 83.8x + 2307.1
	1.5-3 (2)	0.4685	0.0003	0.2195	Y = 225.0x + 1650.8
	3-4.5 (3)	0.1944	0.1589	-	No significant relationship

* SAS printouts are shown in Appendix A, Figure A.8.

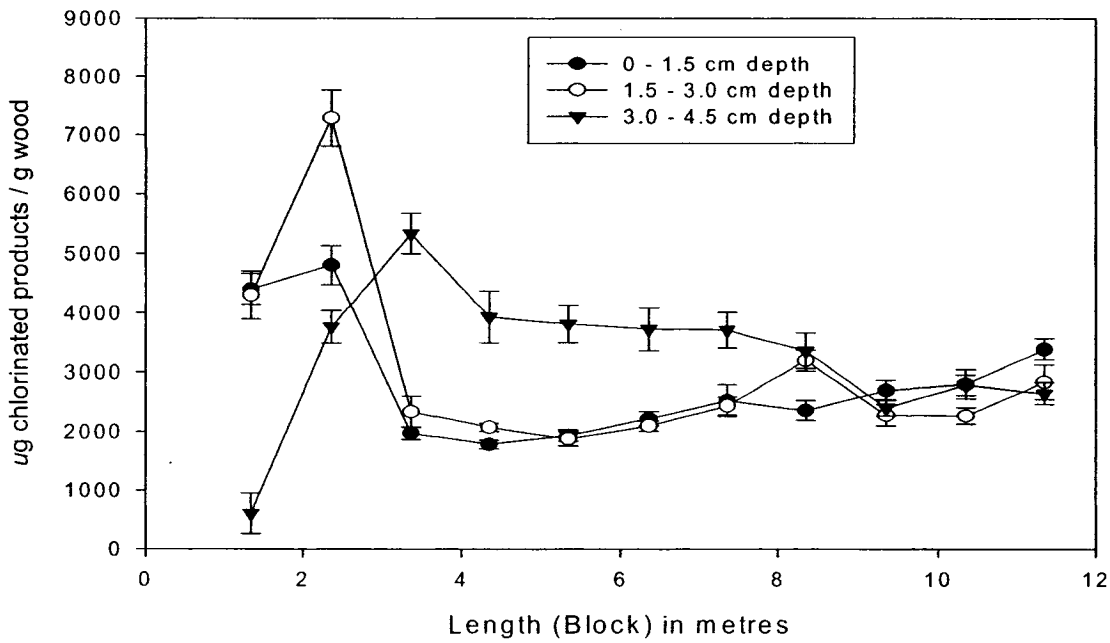

Figure 4.5. Mapping of chlorinated products through Pole G.

Overall, in all of the poles the trend was towards downward migration of PCP being the dominant relationship, as is expected during a pole's service life. The differences noted are a function of not knowing what the initial preservative concentrations were, or the exact environment in which the poles were installed. This will determine the amount of weathering and whether or not bleeding dominated over leaching. For comparison, a graph of the preservative levels in the newly treated pole T is shown in Figure 4.6. Fluctuations occur even in newly treated material based on the variability of heartwood to sapwood ratios and the amount of pit aspiration that occurred during drying (FPS, 1999).

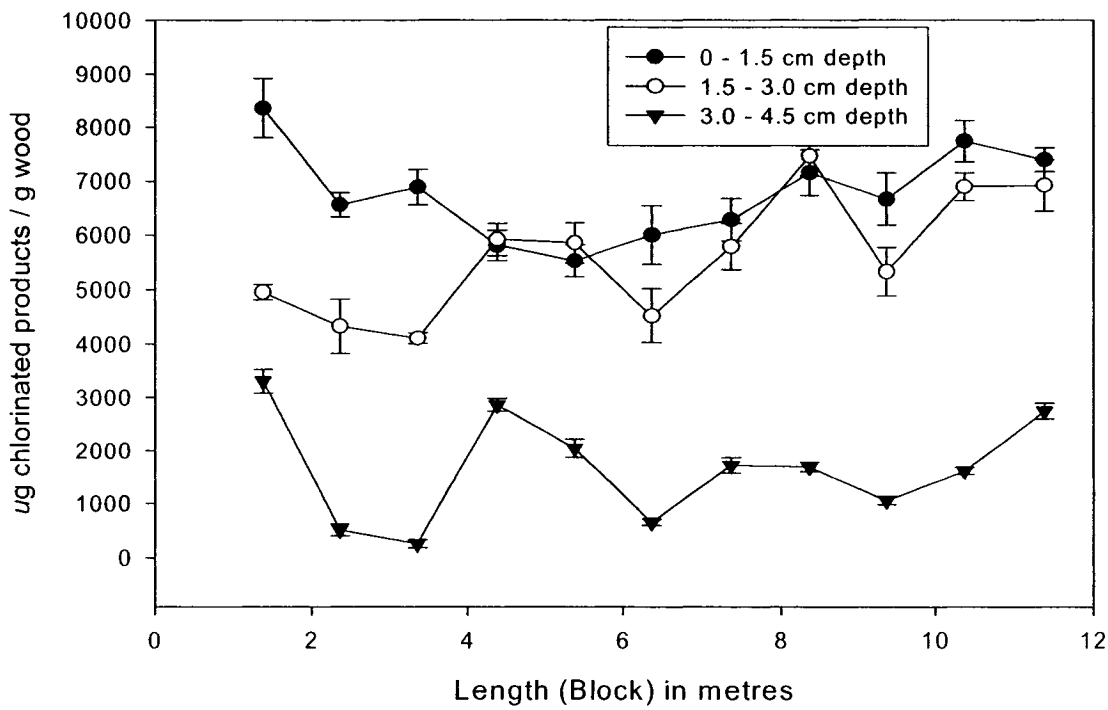

Figure 4.6. Mapping of chlorinated products through Pole T.

4.2.6 Pole Mapping Overview and Discussion

The distribution of PCP within a long service life pole had never been determined before and was a crucial step in determining the levels of preservative requiring conversion prior to extraction. As expected, the general trend was for a higher concentration of preservative in the lower sections of the pole, followed by the expected trend towards a lower concentration with depth of penetration, as sapwood is converted to heartwood (FPS, 1999). The lack of universally excessive migration of preservative in a pole is in keeping with the most recent preservative reviews done by the USEPA (USEPA, 2004e). Anomalies in preservative distribution within poles are almost certainly the result of improper treatment, thereby causing the bleeding phenomenon as antecedent moisture is too high at the time of treatment. The equalization of the moisture within the pole forces preservative out, enhancing both gravitational migration and leaching from the surface (Murray, 2005a). This was illustrated by the highest preservative concentration at the groundline in pole G in the outer ring.

It is also important to reinforce weathering as a strong influence on the migration of preservative (Cooper *et al.*, 1996). Weather plays a role relative to the freeze thaw action in the development of wood checks (cracks) which expose inner layers to water and, depending on the time of year that the wood was treated, may lead to bursts of moisture equalization from the center of the pole (Murray, 2005a). This helps to explain the lesser degree of preservative migration in the inner portions of the pole where outer layers

provide protection from direct weathering influences. These results are in keeping with the literature on the migration of PCP in soil around the base of poles and its rapid decline within 30 cm of the base (Miller, 2002; USEPA, 2004f). Large environmental impacts are historically linked to actual preservative spills, old thermal or temperature variation treatment technologies, or the widespread use of PCP and Na-PCP as a pesticide and fungicide in agricultural and forestry applications (Crosby, 1981; Sieler, 1991).

Repeated measures statistics were required to determine what interactions existed between penetration depth and pole length, since concentration variations adjacent to the samples would influence each resulting concentration (Littell *et al.*, 1998). Although some equations were developed to describe preservative trends within the poles, with R^2 values as high as 79% for the outer ring of pole E, we have no knowledge of the initial preservative concentrations, other than the fact that CSA specifications were met at the time of treatment. Therefore, it is unlikely that these relationships are applicable to preservative migration in general.

The overall opinion is that these values do not represent anything other than variations in wood growth patterns, moisture content at the time of treatment and the degree of weathering to which the poles were subjected. This is based on years of direct observation of the products in use, as well as the mass balance studies conducted by SJI (Nauss, 2001; Fortune-Phillips, 2003). A pole or other treated product can be bored in 20 places and yield 20 different results because of the variability of wood (Murray, 2005a).

The CSA standards account for this variation by allowing statistically representative sampling and the pooling of results in order to decide if a lot of treated wood is considered to pass or fail. This is normally 20 borings per lot with a pass rate of 80% (CSA, 2004).

4.3 Solvent Selection

Early in the project it was hypothesized, after numerous discussions and a thorough review of the literature, that conversion of PCP to Na-PCP would be the most desirable method of removing the PCP preservative from out-of-service poles. In order to establish if this hypothesis had merit, a standard PCP treating solution was subjected to NaOH additions to determine if this would release PCP from the oil. The images shown in Figures 4.7 and 4.8 document the dissolving of the PCP from the oil as the pH changed, along with the precipitation of Na-PCP and some solution debris. This precipitate was later subjected to treatment with HCl and was converted back to PCP, which was once again oil soluble. The same quantity of 1N HCl as 1N NaOH was used. After drying, the resulting precipitate is shown in Figure 4.9. Top oil analysis is shown in Figure 4.10 and gave a result of 0.031% Cl which is the Oxford Lab-X 3500's detection limit for percent chloride (see Section 4.1.5). The important point to note is that a PCP concentration of 8% is very close to the upper limit of saturation. A concentration of 8.5% PCP is the highest used at the SJI Truro facility, since at higher levels PCP comes out of solution.

The theoretical reaction for the conversion from PCP to Na-PCP is as follows:

$$C_6Cl_5OH + NaOH \text{ ---> } C_6Cl_5NaO + H_2O$$

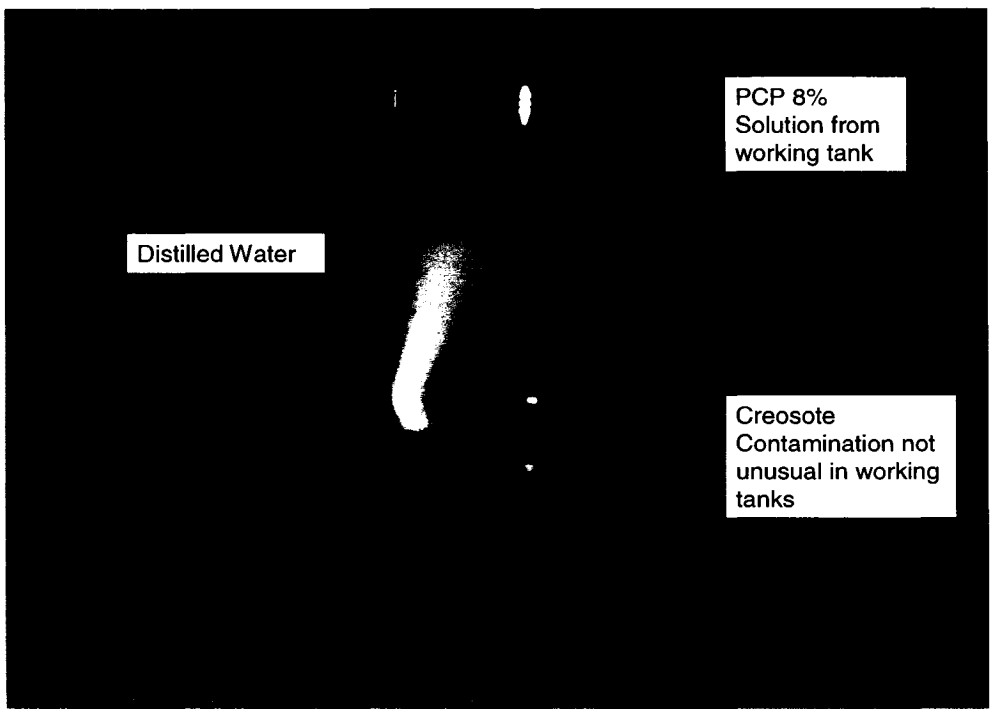

Figure 4.7. Working tank solution over distilled water.

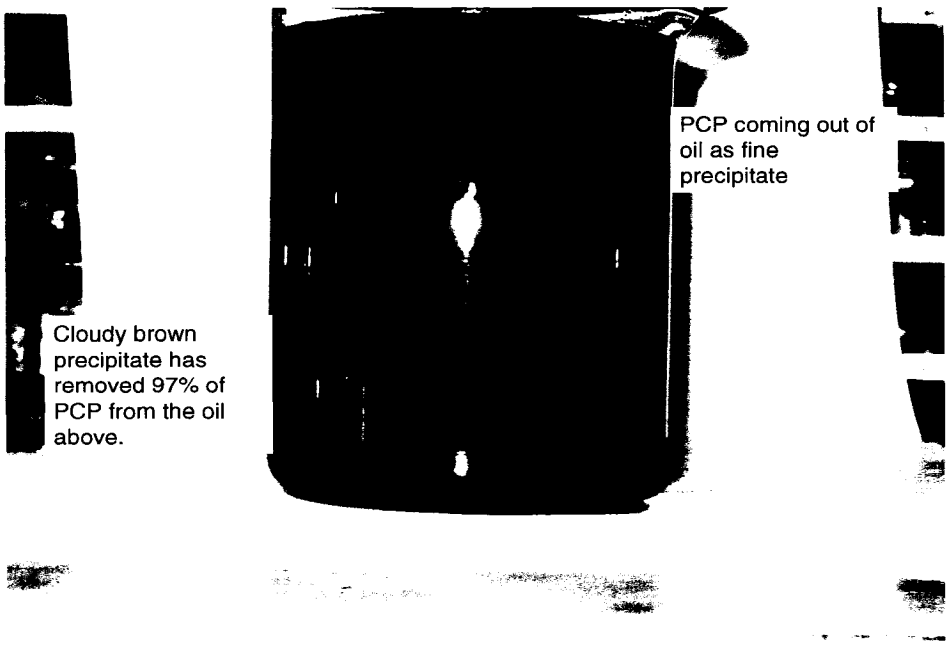

Figure 4.8. Same solution as Figure 4.7 with the addition of 1N NaOH forming Na-PCP.

Figure 4.9. Na-PCP prior to re-conversion to PCP with HCl.

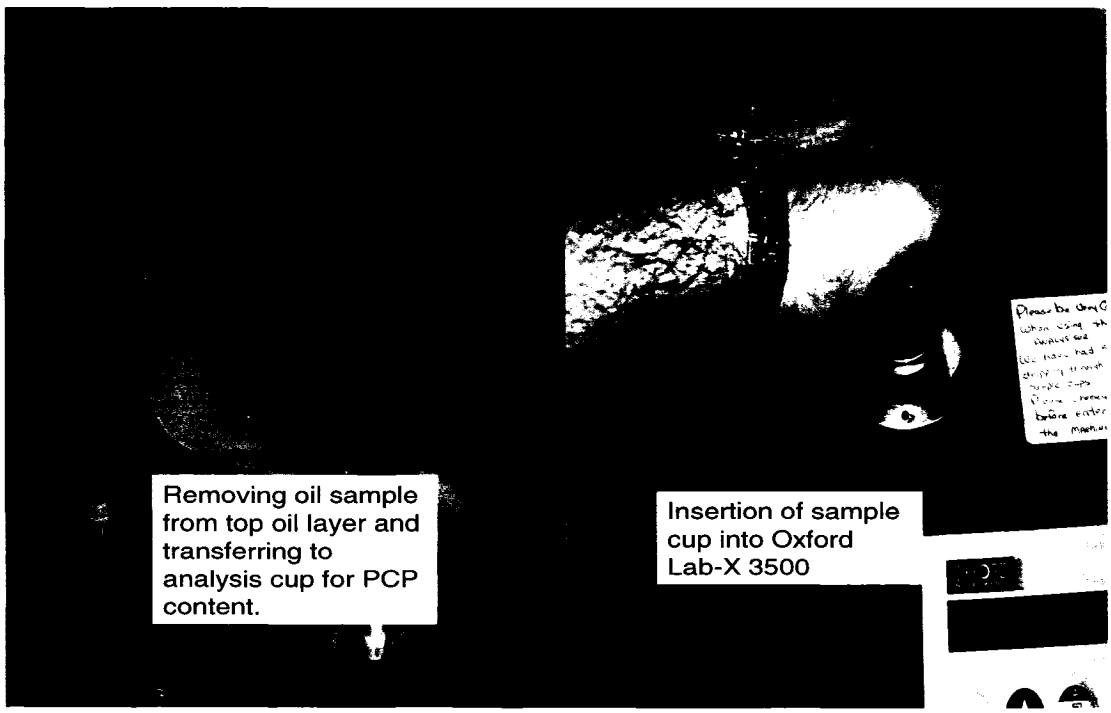

Figure 4.10. Removal and analysis of top oil layer for PCP content.

4.3.1 Solvent Optimization

Sawdust samples prepared from treated wood were subjected to 0.5N, 0.75N and 1N NaOH solutions and the results are shown in Table 4.21. The 1N solution was selected for its efficacy, ease of preparation, and rapid ability to assess the amount of acid required for re-conversion.

Table 4.21. NaOH concentration optimization trial results.

Penta-treated sawdust in % Cl	De-treated sawdust 0.50 N NaOH in % Cl	De-treated sawdust 0.75 N NaOH in % Cl	Detreated sawdust 1 N NaOH in % Cl
0.222	0.168	0.102	ND
0.309	0.241	0.704*	ND
0.311	0.201	0.112	0.008
0.285	0.191	0.139	ND
0.306	0.190	0.108	ND
0.317	0.209	0.138	ND
0.302	0.205	0.121	ND
0.280	0.211	0.143	ND
0.319	0.196	0.140	ND
Ave = 0.295	Ave = 0.201	Ave = 0.125	ND
% Reduction	31.9	57.6	>99

*Outlier not used in calculations; ND – below machine detection limit

4.3.2 Solvent Selection Summary and Discussion

The selection of solvent was based on the use of NaOH within SJI's waste water system as the second stage in the flocculation process. In order to produce a precipitate prior to carbon filtration the waste water treatment operator adds Al_2SO_4 followed by NaOH to begin the process of flocculant formation, finishing with an anionic polymer designed to increase the weight of the flocculant to allow for more rapid precipitation. For carbon absorption the ideal pH upon the completed reaction is 5.5, but occasionally the pH reaches above 7, which causes a spike in PCP levels in the supernatant of over 100 times the normal value of approximately 20 ppm PCP (Murray, 2005a).

Taking this a step further during the present research the experiments were completed on oil over water and elicited the rapid formation of a brownish precipitate and a 99% drop in the concentration of PCP in the surface oil, from 8.5% to non-detectable concentration as shown in Figures 4.7 to 4.11. Once the solvent concentration of 1N NaOH versus 0.5N and 0.75N NaOH was selected, the scale up process began (Table 4.21).

4.4 Surface Area to Volume Optimization for Extraction

In each scaling up of the samples being extracted it was important to use wood sizes that were able to be manufactured by existing plant equipment. The scaling, therefore, was based on sawdust from chipping operations, pole peeler strips, band saw derived slats and finally full pole sections.

4.4.1 Sawdust

Sawdust data showing the percentage reduction of preservative in each sample from each individual pole studied is presented in Table 4.22. In all cases the average reduction was > 99% since the detreated samples had PCP (chlorinated product) levels below the instruments detection limit. As a general statement, all samples from all depths and all poles showed an average reduction of >99% of the original PCP (chlorinated product) concentration.

Table 4.22. Results of NaOH detreatment process on sawdust from PCP poles removed from service.

sample ID		sample mass in cell (g)	% PCP (chlorinated products) before detreatment	Oxford chlorinated products ($\mu g \cdot g^{-1}$ wood)	% PCP (chlorinated products) after detreatment	% Reduction of PCP (chlorinated products)
B2	0-1.5	5.066	0.699	4765.65	ND	>99
B2	1.5-3	4.694	0.554	3500.01	ND	>99
B2	3-4.5	5.094	0.463	3173.85	0.013	97.1
B4	0-1.5	4.499	0.763	4619.26	ND	>99
B4	1.5-3	4.529	0.546	3327.64	ND	>99
B4	3-4.5	3.663	0.471	2321.87	ND	>99
B6	0-1.5	4.979	0.635	4255.22	ND	>99
B6	1.5-3	4.975	0.548	3669.27	ND	>99
B6	3-4.5	4.470	0.493	2965.88	ND	>99
B8	0-1.5	5.304	0.613	4375.58	ND	>99
B8	1.5-3	5.253	0.551	3894.99	0.01	98.1
B8	3-4.5	4.244	0.48	2741.55	ND	>99
B10	0-1.5	4.743	0.553	3529.72	ND	>99
B10	1.5-3	4.871	0.495	3244.91	ND	>99
B10	3-4.5	5.073	0.49	3345.61	ND	>99
B12	0-1.5	4.490	0.499	3015.14	ND	>99
B12	1.5-3	4.642	0.462	2886.33	0.007	98.4
B12	3-4.5	4.815	0.408	2644.01	ND	>99
B14	0-1.5	4.990	0.545	3660.04	ND	>99
B14	1.5-3	3.862	0.39	2027.12	ND	>99
B14	3-4.5	5.091	0.421	2884.41	ND	>99
B16	0-1.5	5.372	0.398	2877.34	ND	>99
B16	1.5-3	4.196	0.461	2602.94	ND	>99
B16	3-4.5	4.093	0.486	2676.99	0.011	97.8
B18	0-1.5	5.525	0.4	2974.43	ND	>99
B18	1.5-3	4.652	0.46	2879.90	ND	>99
						Continued...

sample ID		sample mass in cell (g)	% PCP (chlorinated products) before detreatment	Oxford chlorinated products ($\mu g \cdot g^{-1}$ wood)	% PCP (chlorinated products) after detreatment	% Reduction of PCP (chlorinated products)
B18	3-4.5	4.081	0.47	2581.59	ND	>99
B20	0-1.5	4.459	0.669	4014.16	ND	>99
B20	1.5-3	4.187	0.6	3381.24	ND	>99
B20	3-4.5	5.083	0.482	3297.41	ND	>99
B22	0-1.5	4.102	0.767	4233.89	ND	>99
B22	1.5-3	4.364	0.74	4345.97	ND	>99
B22	3-4.5	4.653	0.576	3606.83	ND	>99
C2	0-1.5	3.8521	0.473	2452.10	ND	>99
C2	1.5-3	4.434	0.513	3061.21	ND	>99
C2	3-4.5	4.1786	0.453	2547.47	ND	>99
C4	0-1.5	3.9433	0.434	2303.19	ND	>99
C4	1.5-3	4.5624	0.494	3033.19	ND	>99
C4	3-4.5	3.2791	0.236	1041.47	ND	>99
C6	0-1.5	3.7392	0.352	1771.34	ND	>99
C6	1.5-3	3.6688	0.335	1654.05	ND	>99
C6	3-4.5	4.8645	0.312	2042.55	0.006	98
C8	0-1.5	3.3623	0.341	1543.02	ND	>99
C8	1.5-3	3.994	0.385	2069.42	ND	>99
C8	3-4.5	3.7209	0.143	716.08	ND	>99
C10	0-1.5	3.6787	0.34	1683.27	ND	>99
C10	1.5-3	3.78	0.328	1668.57	ND	>99
C10	3-4.5	3.8096	0.045	230.71	ND	>99
C12	0-1.5	4.4514	0.359	2150.66	0.008	97.8
C12	1.5-3	4.3536	0.298	1746.00	ND	>99
C12	3-4.5	4.8371	0.134	872.31	ND	>99
C14	0-1.5	4.9387	0.386	2565.55	ND	>99
C14	1.5-3	4.5119	0.278	1688.05	ND	>99
C14	3-4.5	4.2964	0.101	583.99	ND	>99
						Continued...

sample ID		sample mass in cell (g)	% PCP (chlorinated products) before detreatment	Oxford chlorinated products ($\mu g \cdot g^{-1}$ wood)	% PCP (chlorinated products) after detreatment	% Reduction of PCP (chlorinated products)
C16	0-1.5	4.4879	0.348	2101.85	ND	>99
C16	1.5-3	4.7278	0.277	1762.46	ND	>99
C16	3-4.5	2.9887	0.151	607.35	ND	>99
C18	0-1.5	4.4023	0.332	1966.97	ND	>99
C18	1.5-3	4.7409	0.333	2124.64	ND	>99
C18	3-4.5	3.5063	0.244	1151.38	ND	>99
C20	0-1.5	4.0752	0.697	3822.62	ND	>99
C20	1.5-3	4.3438	0.22	1286.09	ND	>99
C20	3-4.5	2.9038	0.233	910.55	ND	>99
C22	0-1.5	5.0451	0.667	4528.72	ND	>99
C22	1.5-3	4.066	0.29	1586.88	ND	>99
C22	3-4.5	3.0591	0.217	893.37	ND	>99
E2	0-1.5	3.8271	0.406	2091.10	ND	>99
E2	1.5-3	3.029	0.212	864.20	ND	>99
E2	3-4.5	2.9383	0.413	1633.15	ND	>99
E4	0-1.5	3.5296	0.414	1966.55	ND	>99
E4	1.5-3	2.68	0.281	1013.49	0.006	98
E4	3-4.5	2.5372	0.304	1038.03	ND	>99
E6	0-1.5	3.5341	0.408	1940.52	ND	>99
E6	1.5-3	3.4499	0.368	1708.58	ND	>99
E6	3-4.5	2.9677	0.295	1178.21	ND	>99
E8	0-1.5	3.6696	0.374	1847.01	ND	>99
E8	1.5-3	3.4388	0.345	1596.64	ND	>99
E8	3-4.5	3.0241	0.387	1575.02	ND	>99
E10	0-1.5	3.279	0.584	2577.12	ND	>99
E10	1.5-3	3.441	0.489	2264.51	ND	>99
E10	3-4.5	3.279	0.417	1840.17	0.01	97.7
E12	0-1.5	2.999	0.584	2357.05	ND	>99
						Continued...

sample ID		sample mass in cell (g)	% PCP (chlorinated products) before detreatment	Oxford chlorinated products ($\mu g \cdot g^{-1}$ wood)	% PCP (chlorinated products) after detreatment	% Reduction of PCP (chlorinated products)
E12	1.5-3	4.08	0.505	2772.88	ND	>99
E12	3-4.5	3.4312	0.42	1939.44	ND	>99
E14	0-1.5	3.339	0.549	2467.00	ND	>99
E14	1.5-3	3.447	0.444	2059.70	ND	>99
E14	3-4.5	3.221	0.294	1274.44	0.006	97.9
E16	0-1.5	3.333	0.589	2641.99	ND	>99
E16	1.5-3	3.229	0.445	1933.78	ND	>99
E16	3-4.5	3.0042	0.35	1415.07	ND	>99
E18	0-1.5	3.578	0.614	2956.57	ND	>99
E18	1.5-3	3.566	0.481	2308.38	0.008	98.3
E18	3-4.5	3.498	0.301	1416.99	ND	>99
E20	0-1.5	3.505	0.612	2886.82	ND	>99
E20	1.5-3	3.892	0.567	2969.86	ND	>99
E20	3-4.5	3.6113	0.343	1667.01	0.008	97.7
E22	0-1.5	3.444	0.598	2771.69	ND	>99
E22	1.5-3	3.662	0.455	2242.38	ND	>99
E22	3-4.5	3.456	0.212	986.03	0.005	97.6
G2	0-1.5	3.5966	0.737	3567.30	ND	>99
G2	1.5-3	4.0430	0.505	2747.74	ND	>99
G2	3-4.5	4.0625	0.509	2782.86	ND	>99
G4	0-1.5	3.4761	0.641	2998.68	ND	>99
G4	1.5-3	3.7468	0.443	2233.80	ND	>99
G4	3-4.5	3.5007	0.580	2732.52	ND	>99
G6	0-1.5	3.3433	0.613	2758.14	ND	>99
G6	1.5-3	3.5940	0.497	2403.89	ND	>99
G6	3-4.5	2.9578	0.599	2384.38	ND	>99
G8	0-1.5	3.0976	0.545	2271.97	ND	>99
G8	1.5-3	3.9062	0.591	3106.86	ND	>99
						Continued...

sample ID		sample mass in cell (g)	% PCP (chlorinated products) before detreatment	Oxford chlorinated products ($\mu g \cdot g^{-1}$ wood)	% PCP (chlorinated products) after detreatment	% Reduction of PCP (chlorinated products)
G8	3-4.5	3.8463	0.710	3675.20	ND	>99
G10	0-1.5	3.4941	0.600	2821.41	ND	>99
G10	1.5-3	3.6572	0.529	2603.66	0.015	97.1
G10	3-4.5	4.2449	0.695	3970.38	ND	>99
G12	0-1.5	2.9742	0.556	2225.49	ND	>99
G12	1.5-3	3.6093	0.455	2210.11	ND	>99
G12	3-4.5	4.5227	0.703	4278.91	ND	>99
G14	0-1.5	2.6180	0.544	1916.68	ND	>99
G14	1.5-3	3.5657	0.410	1967.47	ND	>99
G14	3-4.5	4.2790	0.690	3973.48	ND	>99
G16	0-1.5	2.5299	0.532	1811.32	ND	>99
G16	1.5-3	3.7432	0.418	2105.71	ND	>99
G16	3-4.5	4.1715	0.839	4710.14	ND	>99
G18	0-1.5	2.7013	0.517	1879.50	ND	>99
G18	1.5-3	4.1054	0.470	2596.77	ND	>99
G18	3-4.5	4.3118	0.963	5588.11	ND	>99
G20	0-1.5	3.3185	1.069	4774.19	ND	>99
G20	1.5-3	4.3300	1.276	7435.64	ND	>99
G20	3-4.5	3.7144	0.741	3704.14	ND	>99
G22	0-1.5	3.8016	0.944	4829.68	ND	>99
G22	1.5-3	3.0264	1.208	4920.09	ND	>99
G22	3-4.5	4.2401	0.132	753.23	ND	>99

* >99% means removal was below the detection limit of the Oxford.
ND means below the detection limit of the instrument (0.097 $\mu g \cdot g^{-1}$)

4.4.2 Peeler Strips

The peeler strips represented the first time a pressure process was used to ensure good contact between NaOH and PCP, given the higher surface area to volume ratio of these samples. As with the sawdust, the results summarized in Table 4.23 on peeler strips show that the PCP levels were reduced to below the detection limit (greater than 99% reduction).

4.4.3 Slats

As with the peeler strips, the slats (data shown in Table 4.24) were subject to a pressure process to improve the probability of contact of the solvent (NaOH) and the existing PCP preservative. The reductions in PCP were again, almost exclusively greater than 99%. Slat thickness did not have any impact on the efficacy of PCP (chlorinated products) removal, nor did the initial PCP (chlorinated products) concentration. Statistical testing was not necessary because nearly all the data were identical (>99% reduction).

Table 4.23. Results of NaOH detreatment process on PCP treated pole strips removed from service and subject to pole peeling (strips).

Sample ID		Sample mass in cell (g)	% PCP (chlorinated products) before detreatment	% PCP (chlorinated products) after detreatment	% reduction of PCP (chlorinated products)
1A	0-10mm	3.2142	0.627	ND	>99
1A	11-20mm	3.2733	0.51	ND	>99
1A	21-30mm	3.3012	0.331	0.007	97.9
1A	31-40mm	3.1081	0.264	ND	>99
1A	41-50mm	4.0444	0.198	0.009	95.4
1B	0-10mm	3.9066	0.603	ND	>99
1B	11-20mm	3.8042	0.557	ND	>99
1B	21-30mm	3.6717	0.404	ND	>99
1B	31-40mm	3.6355	0.199	ND	>99
1B	41-50mm	3.2967	0.099	0.008	92
1C	0-10mm	3.7833	0.598	ND	>99
1C	11-20mm	3.5695	0.501	ND	>99
1C	21-30mm	3.2412	0.396	ND	>99
1C	31-40mm	3.4984	0.287	0.009	97.9
1C	41-50mm	3.2189	0.111	ND	>99
1D	0-10mm	3.3011	0.562	ND	>99
1D	11-20mm	3.0055	0.489	ND	>99
1D	21-30mm	3.3597	0.40	ND	>99
1D	31-40mm	3.4011	0.208	ND	>99
1D	41-50mm	3.4621	0.089	ND	>99
1E	1-10mm	4.0994	0.587	ND	>99
1E	11-20mm	3.2134	0.507	ND	>99
1E	21-30mm	3.1484	0.371	ND	>99
1E	31-40mm	3.2366	0.255	ND	>99
1E	41-50mm	2.9188	0.103	ND	>99
2A	0-10mm	3.5191	0.534	ND	>99
2A	21-30mm	3.2676	0.389	ND	>99
2A	31-40mm	3.3009	0.197	ND	>99
2A	41-50mm	3.3512	0.088	ND	>99
2B	0-10mm	3.0334	0.498	ND	>99
2B	11-20mm	4.0108	0.422	ND	>99
2B	21-30mm	2.8981	0.357	ND	>99
2B	31-40mm	3.2222	0.301	ND	>99
2B	41-50mm	2.9529	0.108	ND	>99
					Continued...

Sample ID		Sample mass in cell (g)	% PCP (chlorinated products) before detreatment	% PCP (chlorinated products) after detreatment	% reduction of PCP (chlorinated products)
2C	0-10mm	3.4647	0.488	0.008	98.4
2C	11-20mm	3.1006	0.411	ND	>99
2C	21-30mm	3.0993	0.442	ND	>99
2C	31-40mm	3.4311	0.299	ND	>99
2C	41-50mm	2.9189	0.108	ND	>99
2D	0-10mm	3.9333	0.608	ND	>99
2D	11-20mm	3.7391	0.574	ND	>99
2D	21-30mm	3.8442	0.578	ND	>99
2D	31-40mm	3.5522	0.461	ND	>99
2D	41-50mm	3.8021	0.236	ND	>99
2E	0-10mm	4.2192	0.590	ND	>99
2E	11-20mm	3.054	0.639	ND	>99
2E	21-30mm	3.4466	0.686	ND	>99
2E	31-40mm	3.0062	0.653	ND	>99
2E	41-50mm	2.9224	0.618	ND	>99

- ND means below the detection limit of the instrument.

4.4.4 Full Pole Sections

The pole sections required the use of the largest pilot plant in order to get representative samples of full pole sections to be detreated. This was the most crucial experiment, since it would determine if pre-processing of the material would be required. As with the other results, core samples from the poles before and after the detreatment process showed similar PCP reductions to levels below the machine's detection limit. These post treatment levels were the same as those given for untreated wood. The results are presented in Table 4.25. Statistical analyses were again not applicable, since the % reduction values were the same.

Table 4.24. Results of NaOH detreatment process on PCP treated poles removed from service and cut into slats.

sample ID	Slat Thickness (mm)	Weight (g)	% PCP (chlorinated products) before detreatment	% PCP (chlorinated products) after detreatment	% reduction of PCP (chlorinated products)
A1-7	25	3.819	0.522	0.010	98.1
A8-14	12	3.627	0.506	ND	>99
A15-21	9	3.861	0.202	0.007	96.4
A22-28	6	3.321	0.286	ND	>99
A29-35	3	4.505	0.576	ND	>99
A36-42	3	3.696	0.693	ND	>99
A45-49	6	3.905	0.536	ND	>99
A50-56	9	3.997	0.718	ND	>99
A57-61	3	3.635	0.197	ND	>99
B1-7	12	3.422	0.393	ND	>99
B8-14	6	3.877	0.666	ND	>99
B15-21	9	3.696	0.719	ND	>99
B22-27	18	3.431	0.751	ND	>99
B28-34	18	3.894	0.567	0.009	98.4
B35-41	25	3.734	0.647	ND	>99
B42-48	6	3.030	0.612	ND	>99
B49-55	3	3.736	0.65	ND	>99
C1-7	25	3.579	0.595	ND	>99
C8-14	18	3.623	0.551	ND	>99
C15-20	9	3.795	0.727	ND	>99
C21-27	6	4.115	0.517	ND	>99
C28-34	3	3.680	0.632	ND	>99
C35-41	18	3.484	0.631	ND	>99
C42-48	25	3.635	0.539	0.009	98.3
D1-7	18	3.456	0.238	ND	>99
D8-14	3	3.352	0.734	ND	>99
D15-21	6	3.310	0.742	ND	>99
D22-28	9	3.686	0.627	ND	>99
D29-35	6	3.591	0.470	0.008	98.3
D36-42	24	3.323	0.388	ND	>99
D43-49	12	3.677	0.267	ND	>99
D50-56	12	4.068	0.412	ND	>99
					Continued...

sample ID	Slat Thickness (mm)	Weight (g)	% PCP (chlorinated products) before detreatment	% PCP (chlorinated products) after detreatment	% reduction of PCP (chlorinated products)
D57-63	3	4.127	0.347	ND	>99
D64-70	6	3.032	0.399	ND	>99
D71-77	18	3.353	0.369	ND	>99
D79-83	25	3.746	0.388	0.008	97.9
D84-90	9	3.164	0.781	ND	>99
D91-97	9	3.120	0.818	ND	>99
E1-7	24	3.401	0.389	ND	>99
E8-14	12	3.331	0.585	ND	>99
E15-21	6	3.279	0.618	ND	>99
E22-28	12	3.379	0.674	ND	>99
E29-35	3	3.184	0.567	ND	>99
E36-42	24	3.555	0.661	ND	>99
E43-49	9	3.402	0.736	ND	>99
E50-56	6	3.361	0.690	ND	>99
E57-63	18	3.054	0.639	ND	>99
E64-70	6	3.447	0.686	ND	>99
E71-77	3	3.006	0.653	ND	>99
E78-84	6	2.922	0.618	0.011	98.2
E85-91	3	3.148	0.650	ND	>99
E92-98	9	3.039	0.659	ND	>99
E99-105	3	3.422	0.697	ND	>99
F1-7	12	3.345	0.425	ND	>99
F8-14	3	3.638	0.628	0.009	98.6
F15-21	3	3.761	0.581	ND	>99
F22-28	3	2.928	0.546	ND	>99
F29-35	24	3.229	0.577	ND	>99
F36-42	6	3.648	0.259	ND	>99
F43-50	9	3.809	0.299	ND	>99
F51-56	24	3.444	0.567	ND	>99
G1-7	9	3.7	0.500	0.009	98
G8-14	24	3.718	0.556	ND	>99
G15-21	3	3.419	0.761	ND	>99
G22-28	6	3.802	0.838	ND	>99
G29-35	3	3.34	0.612	ND	>99
G36-42	24	4.011	0.491	ND	>99
G43-47	3	3.841	0.591	ND	>99
					Continued...

sample ID	Slat Thickness (mm)	Weight (g)	% PCP (chlorinated products) before detreatment	% PCP (chlorinated products) after detreatment	% reduction of PCP (chlorinated products)
G49-51	3	3.691	0.612	ND	>99
G53-59	3	3.238	0.552	ND	>99
G60-66	3	3.649	0.536	ND	>99
G67-73	6	3.550	0.611	ND	>99
G74-78	6	3.471	0.605	ND	>99
G80-86	9	3.145	0.550	ND	>99

ND – Below the detection limit of the instrument.

4.4.5 Cross Check of the Extracted Material by RPC for Leachable Chlorophenolics

Given that our target was to have the PCP (chlorinated product) level substantially below any existing hazardous waste criteria, as summarized by the main licensed hazardous waste disposal facilities, Clean Harbours and Stablex, each system was evaluated based on its total PCP (chlorinated product) reduction. Similar reductions as those found with sawdust would have been acceptable if the criteria were met and the amount of pre-processing was significantly lower. The untreated poles must also pass the leachate analysis test for recyclable materials as published by the Government of Canada and the USEPA (Canadian Government, 2006).

Table 4.25. Results of NaOH detreatment process on a 2 m long PCP treated pole removed from service.

		Before detreatment		After detreatment		
ID – Date Treated	Mid point diameter (m)	Weight (g)	% PCP (chlorinated products)	Weight (g)	% PCP (chlorinated products)	% reduction of PCP (chlorinated products)
1-1973	0.259	3.212	0.577	3.081	ND	>99
2-1973	0.268	3.714	0.481	2.892	ND	>99
3-1973	0.278	3.602	0.508	3.644	0.011	97.9
4-1973	0.302	2.994	0.521	3.989	ND	>99
5- 1973	0.310	4.5049	0.576	3.208	ND	>99

* % PCP (chlorinated products) based on average of 20 cores taken before and after treatment

** Cores taken before detreatment were plugged as per the CSA specifications.

Representative samples were taken from the extracted material (peeler strips, slats and poles) and subjected to the leachate test given by the Canadian and United States Governments to ensure that the detreating process was in fact rendering the material harmless and within the guidelines of non-toxic recyclable material. These guidelines and testing protocol are found in the Export and Import of Hazardous Waste and Recyclable Material Regulations (Schedule 5) as published by the Canadian Government in 2004 (Canadian Government, 2006). Results are shown in Table 4.26 (GC-MS data). The guidelines state that the leachate must be below 6 ppm ($mg \cdot L^{-1}$) of PCP. The level of PCP and all chlorphenolics were below the detection limit of 1 ppb ($\mu g \cdot L^{-1}$). This verifies the efficacy of the detreatment process.

Table 4.26. Results ($\mu g \cdot L^{-1}$) of the "Standard Leachate Test for Landfill and Recyclable Materials" on ten samples of extracted ground detreated wood removed from service.

	Sample									
Analytes	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
2,3,4,5-Tetrachlorophenol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
2,3,4,6-Tetrachlorophenol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
2,3,5,6-Tetrachlorophenol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
2,3,4-Trichlorophenol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
2,3,5-Trichlorophenol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
2,4,5-Trichlorophenol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
2,4,6-Trichlorophenol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
2,4-Dimethylphenol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
2,4-Dinitrophenol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
2,4-Dichlorophenol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
2,6-Dichlorophenol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
4,6-Dinitro-o-cresol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
2-Chlorophenol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
4-Chloro-3-methylphenol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
4-Nitrophenol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
m-Cresol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
o-Cresol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
p-Cresol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Pentachlorophenol	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Phenol	2.1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1

Reporting limit: 1 $\mu g \cdot L^{-1}$ (ppb)
Samples 1, 2 and 3 were detreated slats, 4 and 5 were detreated peeler strips, 6,7 and 8 were detreated slats and 9 and 10 were detreated pole cores.

4.4.6 Patenting the Process

The process developed by this research is in the final stages of patenting by Stella-Jones Inc. through the legal firm Faskin, Martineau and Poulin. Unfortunately, scientific publication of these results are not allowed until this patent process is complete. Some of the patenting information is summarized in Appendix B.

4.4.7 Scaling Up to Full Production Summary

The only possible guideline at this stage in the research was to use existing treating plant wood processing equipment whenever possible. Experimentation began with sawdust, as the Europeans remove CCA from poles by first grinding the poles into sawdust, then extracting them with H_2SO_4 and using the residual CCA sawdust in composite poles (Stella SPA, 2004). Given the actual binding of Cr with the wood fibers, this is much less successful than the results the present research was able to obtain. The change of C^{+6} to Cr^{+3} is the process of fixation in CCA treatment, as mention in Section 2.6. A logical progression for Canadian and US operations was to start with sawdust, then move to pole peeler strips, then to slats from the resaw sawmill and finally to full pole sections. These steps represent lower and lower preprocessing costs prior to the recycling detreatment process. The use of pressure vessels on wood sample sizes other than sawdust was done to ensure that the NaOH was able to reach all PCP within the pole. Pressure was not required with sawdust relative to surface area to volume ratios, nor was it practical in terms of fouling all of the pumps in a system. The only other method found in the literature was steam explosion on CCA treated wood on several types of products (Shiau *et. al.*, 2000). These experiments gave maximum reductions of each component in CCA that varied to the point that the author's concluded that "steam explosion does not increase the extractability of chemical components" (Shiau *et.al.*, 2000).

The significant percentage removal of PCP at all wood sizes can be attributed to the lower viscosity of the NaOH solution versus the PCP and carrier oil, and most importantly the weathering of the pole which significantly increases permeability (Cooper *et al.*, 1996). This increased the probability of contact between the extractant and the preservative, coupled with the gravitational migration of carrier oil made the wood less hydrophobic (Penta Council, 2003). It is the author's opinion that poles must be in the field for at least 20 years for this process to be successful without significant pre-processing to increase surface area to volume ratios to ensure chemical conversion. It should be stressed that even with sawdust alone the removal of preservative to below detectable levels would have been considered a success by the sponsor, as their CCA recycling process obtains only a 50% reduction.

Statistical comparisons of the various size fractions were not possible, as the data were virtually identical in terms of percentage reduction to the point that a p value could not be generated (Montgomery, 1997). Unfortunately, no other papers are available on PCP removal systems, only overviews of alternate uses (Morrell, 2004; Townsend *et al.*, 2004). The one question that remained was whether the analytical instrument detection limit was low enough to conclude that the recycled material was indeed below any hazardous waste criteria for the import or export of recycled material (Canadian Government, 2006). This is a leachate level of 6 ppm of pentachlorophenol when extracted with acetic acid (Canadian Government, 2006). The samples from the present study that were selected at random and tested showed all chlorophenolics to be below 0.1

ppb or, more than 60,000 times below the required limit (Table 4.26). An extensive literature review found no data to compare these results with for discussion purposes.

4.5 Wood Extraction Summary and Discussion

The project met all of its objectives. Most importantly, it resulted in the development of a commercially viable recycling technology for the sponsor and by achieving this, broke new ground in several directions. Several papers will be published upon completion of the patent work for which this thesis is the final document required by our legal counsel. The papers will discuss the distribution of pentachlorophenol in out-of service utility poles, a comparison of the GC-MS versus the X-ray fluorescence methods of analyzing chlorinated compounds, a better method of chipping wood for analysis, some unique and inexpensive methodologies for designing pilot plants, a new type of sludge reduction unit and the full scale up to a pole recycling system using existing treating plant equipment.

The most unique point of the whole recycling concept is that it began with the simple observation that when the pH was increased in a plant's waste water effluent system the levels of PCP present in the water, after re-acidification for analysis, increased by a factor of several hundred. Given the normally low solubility of PCP in water further investigation indicated that the pH was increasing the concentration by conversion to Na-PCP (Hildebrant, 2002).

It is important to note, that with the exception of information on wood structure, data on both treatment methodologies, general analytical methodologies and reuse as a recycling technology are difficult to find in peer reviewed scientific literature. An extensive review of the archives of the International Research Group on Wood Protection (IRG) from 1959 to 2006 has shown no comparable research, and only tangential mention of the need for the recycling of treated wood. This emphasizes the originality of the present project and the fact that hands on experience within an industry can be a useful guide to research.

5.0 Commercialization of the Process

This project was undertaken specifically to provide a long term revenue stream for the wood preserving industry in a declining market place, and to use existing plant infrastructure for other purposes (Murray, 2001). Though demand for treated poles has rebounded slightly, this has mostly been the result of market share gained through storm events, acquisitions and retirement of the resulting surplus capacity. Although plant conversion diagrams may look costly, it can be assured that as long as large pressure vessel cylinders are available, the worst case dollar conversion value for a PCP recycling system would be $300,000. The one unknown cost is whether or not there can be the continued reuse of PCP in the future. Current disposal costs being paid by SJI at the plant door is $500/metric ton for PCP sludge, plus transportation. All one can do is read the positive USEPA and PMRA reviews of PCP and the announcement by the PCP producer that they will eliminate co-contaminants, such as dioxins and furans, by 2007 (USEPA, 2004a; Hildebrant, 2005; PMRA, 2005). This should result in a resurgence of PCP at the expense of other treatments and substitutes (Mitchell, 2006). This change will be accomplished by the formation of PCP in the presence of an organic hydrogen donor and the elimination of forcing conditions (Crosby, 1981).

The research sponsor firmly believes that the launching of this PCP-treated pole recycling program will eliminate claims made by SJI's competitors about their substitute products being more environmentally friendly. Also, PCP manufacturers have expressed interest in the patent expansion into use with poles manufactured from other species and, most

importantly, their desire to pay royalties.

5.1 Scale up from Pilot Plant to Full Production

The first step in scaling up the detreatment process to full production is to perform a competitive forces model with respect to the need for the technology or product and the impact of potential competitors, as this could be a difficult patent to enforce given the nature of the wood preserving industry. This model looks at the threat of new entrants into the market place, the bargaining power of buyers of the service or product, the intensity of rivalry in the industry, the bargaining power of suppliers, and the threat of substitute products. Each potential competitor is then subjected to a strength, weakness, opportunity and threat analysis before undertaking a new line of business (Murray, 2001). The answers stemming from these processes allow the company to determine the viability of a new business venture and then proceed with the design of a facility.

The bargaining power of the suppliers remains high as long as the landfill ban on treated wood products remains in effect, but all indications from the treated wood lobbies and the tenders from the utility companies show that they recognize the importance of the impending ban. The tenders always ask where suppliers stand on re-cycling (Stella-Jones Inc. Sales force, 2006). Intensity of rivalry is declining, as the leadership strategy SJI has used in acquiring our competitors and putting SJI in control of raw materials has been initiated. Bargaining power of suppliers is moderate, as the preservatives and quality of

wood required for poles is in limited supply, but SJI is quickly becoming their only customer. The threat of substitutes remains low, except on high capacity transmission lines where steel is often used. In any type of northern climate, nothing can compete with the modulus of elasticity or low cost of installation (as a function of weight and simple burial) for wood. SJI's biggest steel competitor went bankrupt in 2004. Concrete has both weight, cost and fracture issues and SJI has not competed against this product directly in over 10 years.

In this case, the threat of new entrants into the market is low. The last competitor within logistical range of SJI customers is being acquired as of mid-May. They are the last PCP treater in Canada and their customer base reached as far as 800 km into the northern United States.

Based on these results: the absence of competition, a very promising value chain analysis (Table 5.1) and continually expanding market share in all product groups, particularly poles, SJI can proceed to the hypothetical design of a pole detreating and recycling system based on modifying existing plant equipment.

Table 5.1. Value chain analysis overall re-cycling process.

Inbound Logistics	Rating:Good Cross Canada presence reduces freight costs as each plant could be modified. Strong ties with utilities and pole trucking firms would allow for almost every out going load to return with poles in need of re-cycling
Operations	Rating Good Integration and communication required between the strategic business units has been the author's responsibility and the equipment and technical ability would be easy to communicate plant to plant.
Outbound Logistics	Rating: Excellent All plants are located near rail-lines for stockpiled out of service poles. Scales exist to maximize loads on outgoing trucks. Backhauls will reduce freight costs by 50%.
Marketing and Sales	Rating: Very Good Sales force being trained and or hired with more technical abilities. National and international presence is a tremendous advantage when exploited.
Service	Rating: Good-Excellent Ability to customize and treat wood products with all leading preservative treatments is a key advantage for Stella-Jones, Inc. Excellent relationships with long-term customers from coast to coast.
Technology Development	Rating: Good Research and development has increased. Hiring several graduate students in conjunction with the Nova Scotia Agricultural College and Dalhousie University.
Human Resource Management	Rating: Improving Addition of full time resource manager at head office to help with formulating policies.
Firm Infrastructure	Rating: Excellent All plants have the capability to be modified for this process at a cost of $200,000 assuming all new equipment.

5.2 Alteration of Plants to Allow for Re-cycling Process

The key alterations required will be to the quantity of tanks, and to service and pressure pumps. Modifications to water treatment systems and expansion of existing containment areas to allow for both vertical pole storage and the additional tankage will be needed. A schematic of each is shown in Figure 5.1 and 5.2. An explanation of each modification will be provided and it will be differentiated from the typical plant equipment. It is very important to note that while presented as two separate plants, much of the equipment can be re-used by simply running the plant on PCP treating for a period of time and then starting a run on PCP re-cycling after some minor flushing of the lines.

A flow chart for material handling for recycling would be as shown in Figure 5.3. The key would be to maximize inbound out-of-service pole freight with outgoing new pole deliveries, and to store the material upright on a hydrologically secure containment pad. Yard area would be the key variable in deciding tank layout and to what degree equipment would be shared, based on existing capacity and expected demand for the new process.

Minimal additional equipment would include a NaOH mix system, a HCl acid feed tank, NaOH charging equipment, storage and raw effluent tanks, vertical pole storage racks on a proper containment pad and appropriate air actuated valves. The waste generated would be largely recycled and the returned oil will be of similar quality to new carrier oil.

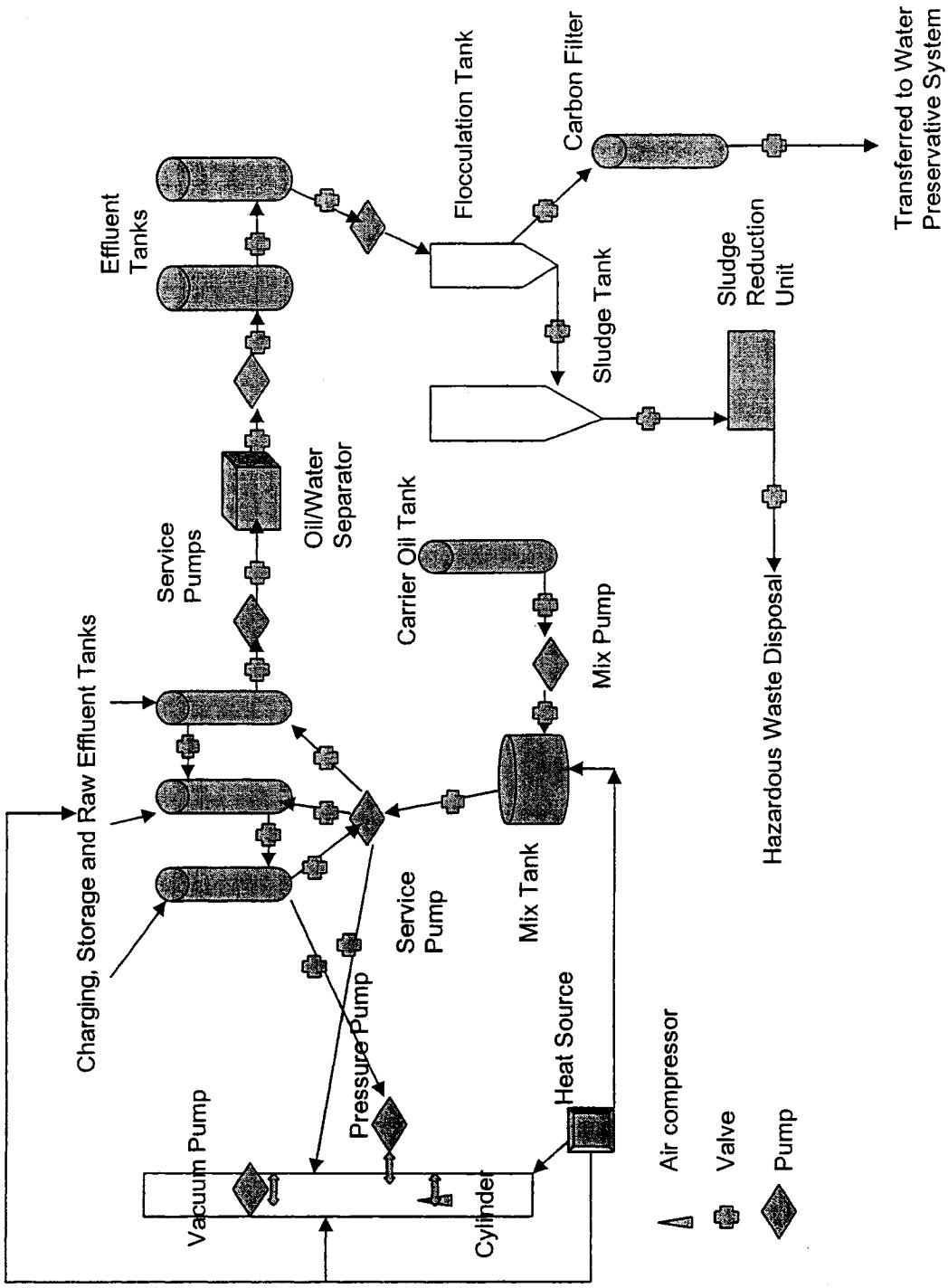

Figure 5.1: Typical PCP treating plant layout

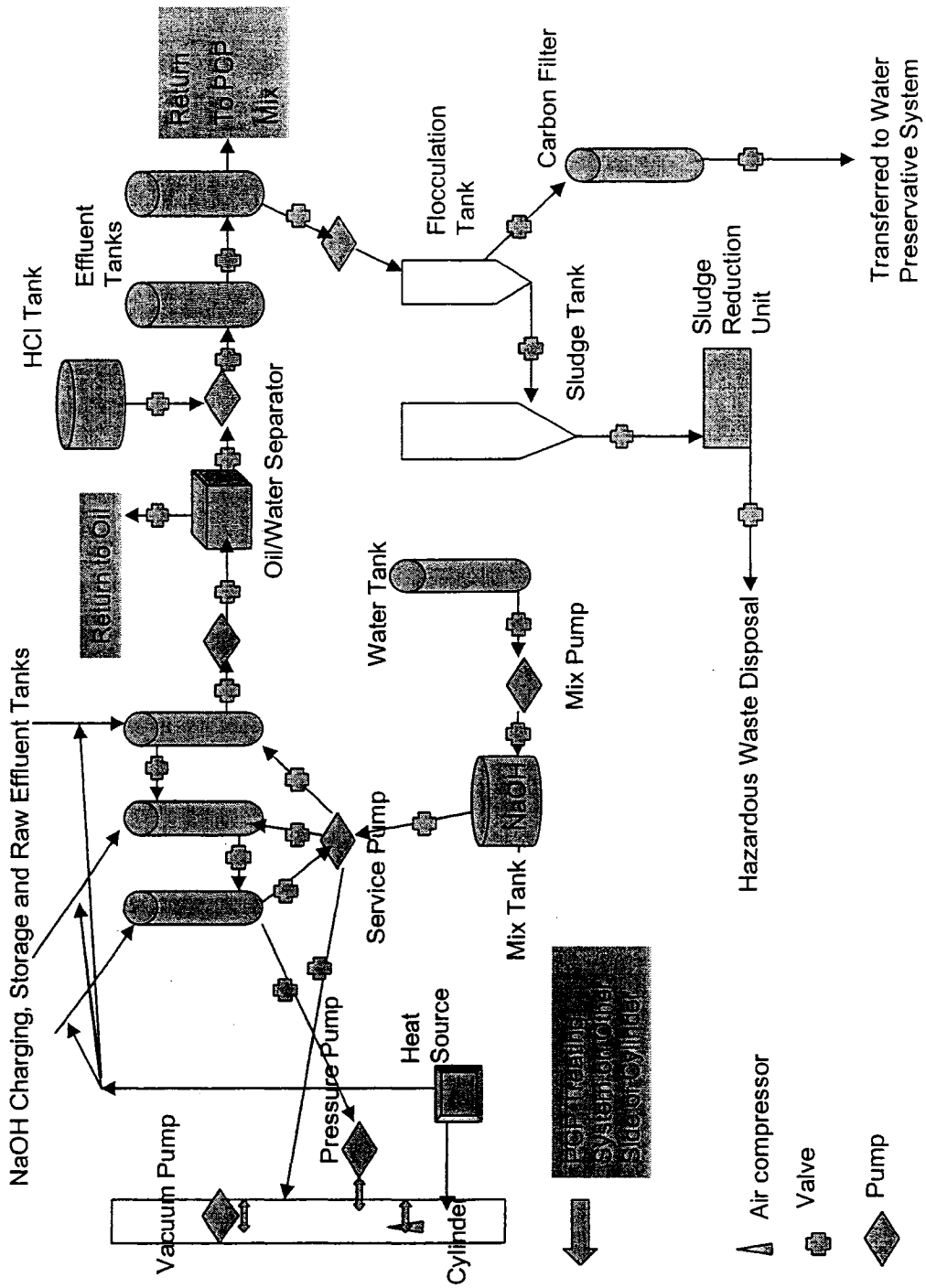

Figure 5.2: Changes to PCP plant to accommodate recycling with NaOH

Some PCP will be lost in the re-conversion process but this can be handled by existing waste water treatment systems which are designed for PCP and carrier oil. A key to the systems function will be the addition of the author's original sludge reduction unit design, which uses the new Miratech GT 500 dewatering system liner. This is shown in Figure 5.4. It is the most efficient way to dewater sludge without a filter press and can be constructed of fiber glassed plywood, thereby keeping costs to a minimum. Dry sludge is scraped off into an auger barreling system.

Poles which have been subjected to the recycling process may be used as fuel and if suitable enough may used in treated or untreated form as timbers, poles, piling, consumer lumber or softwood ties (Cooper *et al.*, 1996). The methods for determining the strength of wood are illustrated in the American Standard for Testing Materials and the University of British Columbia has approached us for old treated products and fresh whitewood to quantify more rapid testing methodologies for strength.

The information presented here clarifies the feasibility of the patent pending process designed through this research.

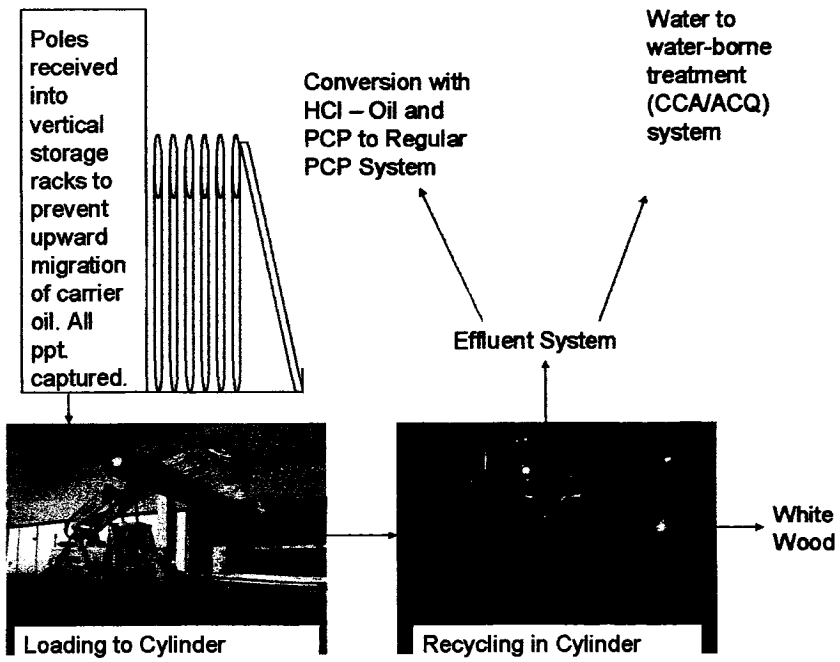

Figure 5.3 Flowchart for material, effluent and separation of PCP from Na-PCP

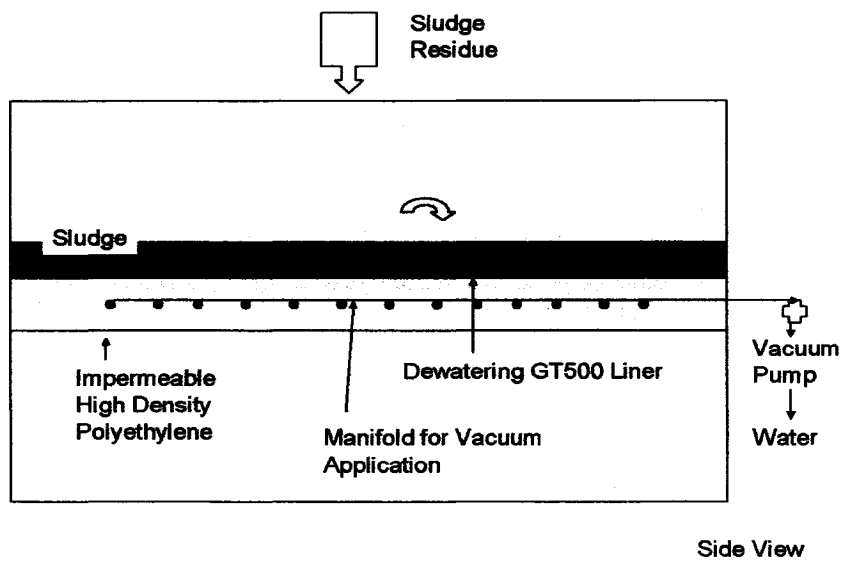

Figure 5.4 Schematic of sludge de-watering unit.

5.3 Environmental Impact

The advantage of being able to continually recycle your product after a cost effective service life and being able to reuse the extracted residual PCP and the recycled wood back into the process represents an enormous step forward in the North American utility pole market.

Both the positive impacts on landfill volumes, which would be felt immediately, and the potential for eliminating the misuse of out-of-service utility poles would be the greatest benefits to the general public (Maleki, 1998; Morrell, 2004). If properly presented from a marketing point of view, the detreatment of out-of -service utility poles and the recycling of the raw materials could be used to improve the image of the wood preserving industry. On the landfill side alone over 200,000 poles are removed every year in Canada (Stephens *et al.*, 2001). This represents and average volume of 147,248 m^3 which is substantial volume both in terms of landfill and the potential for fuel or structural uses.

6.0 Conclusion

The author's career in the wood preserving industry has coincided with an uphill battle for acceptance, rather than tolerance, of SJI's and the other treating industry's product lines, ranging from poles to consumer lumber. This is in spite of the fact that wood preserving has reduced the harvesting of trees by increasing the lifespan of wood in structures. The author believes that having presented this research in the form of a doctoral thesis will have sufficient acceptance as a thoroughly researched process, and therefore it will be accepted by the utility companies. The desire is to make SJI the providers of information rather than the victim of it.

Each of the objectives of the research were achieved and the success in removing PCP from wood of all sample sizes can be attributed to the increased permeability of the poles after 30 years of service and the simplistic nature of the conversion of PCP to Na-PCP by pH change alone. Cylinder pressure was kept uniform in terms of time and level to ensure the probability of contact of NaOH with residual PCP. A summary of the results obtained in order of experimental progression are as follows:

1) Mapping of PCP within the pole was completed with respect to pole length and penetration depth. Although modeling of the distribution was attempted, the variability of wood kept these results minimally useful.

2) The comparison between the non-extraction X-ray florescence procedure and the extraction dependent gas chromatography mass spectrum analysis of wood fiber showed no significant differences, thereby allowing for the use of less expensive and quicker non-extraction methods using X-ray florescence.

3) The correct solvent to provide a reversible chemical reaction, NaOH, and its concentration (1 normal) were determined in liquid and solid samples.

4) Scaling up of PCP extraction from sawdust, to peeler strips, to wood slats, to full pole sections was successful in terms of results and the lack of variability in these results.

5) During the scale up process necessary pilot plant modifications were performed, which allowed for the theoretical scale up to full plant-level production.

The results of this research reached beyond the original expectations; with the qualifier that wood must have been in service for a minimum of 30 years for the process to work without expensive pre-processing of the poles, as demonstrated by the experimental work. Further research is required to investigate the complete chemical reaction sequence of the conversion process from PCP to Na-PCP and back to PCP, the optimization of "detreatment" cycles, and additional experiments on a non-destructive scanning method to separate poles that are structurally sound (and can be re-used) from

those that cannot be used in structural applications. Work on other utility pole wood species will be started immediately, but based on their shallower sapwood when compared to Red Pine, it is not expected that any problems will occur in the removal of preservative. Overall, the ability to recycle PCP treated wood is a large step forward in the environmental acceptability of the preservative and the revenue stream it represents.

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8.0 Appendix A

Statistical Printouts

Table A.1: Full data set from Oxford X-ray fluorescence analysis on pole C samples for comparison of analytical methods.

sample ID*	rep	sample mass in cell (g)	red pine density (kg m^{-3})	Oxford %penta	Oxford chlorinated products (µg g^{-1} wood)
C2 0-1.5	1	2.8221	389.237	0.547	2077.49
	2	2.8089	389.237	0.580	2192.52
	3	3.0897	389.237	0.588	2444.97
	4	3.0241	389.237	0.573	2332.01
	5	3.2059	389.237	0.587	2532.61
				mean	**2315.92**
				std dev	**184.35**
C2 1.5-3	1	3.0391	389.237	0.377	1541.94
	2	2.9035	389.237	0.374	1461.41
	3	3.3356	389.237	0.417	1871.93
	4	3.2558	389.237	0.387	1695.70
	5	3.1805	389.237	0.407	1742.09
				mean	**1662.61**
				std dev	**162.99**
C2 3-4.5	1	3.6004	389.237	0.149	721.97
	2	3.2941	389.237	0.156	689.80
	3	3.0873	389.237	0.147	610.76
	4	2.9929	389.237	0.121	487.37
	5	3.9573	389.237	0.195	1038.52
				mean	**709.68**
				std dev	**204.87**
C4 0-1.5	1	3.1864	389.237	0.535	2294.21
	2	3.1455	389.237	0.531	2247.83
	3	2.8888	389.237	0.508	1974.97
	4	2.9585	389.237	0.516	2054.48
	5	3.5951	389.237	0.631	3052.95
				mean	**2324.89**
				std dev	**427.94**

sample ID*	rep	sample mass in cell (g)	red pine density (kg m^{-3})	Oxford %penta	Oxford chlorinated products (µg g^{-1} wood)
C4 1.5-3	1	4.1317	389.237	0.446	2479.95
	2	3.3912	389.237	0.435	1985.28
	3	3.2022	389.237	0.429	1848.78
	4	2.9626	389.237	0.425	1694.50
	5	3.7043	389.237	0.441	2198.49
				mean	**2041.40**
				std dev	**307.24**
C4 3-4.5	1	3.4116	389.237	0.281	1290.16
	2	3.9499	389.237	0.273	1451.20
	3	4.0073	389.237	0.296	1596.33
	4	4.1035	389.237	0.303	1673.31
	5	3.7119	389.237	0.288	1438.69
				mean	**1489.94**
				std dev	**149.15**
C6 0-1.5	1	3.5471	389.237	0.599	2859.43
	2	3.5539	389.237	0.657	3142.32
	3	3.5041	389.237	0.615	2900.22
	4	3.0317	389.237	0.598	2439.87
	5	2.5758	389.237	0.609	2111.10
				mean	**2690.59**
				std dev	**410.85**
C6 1.5-3	1	3.2636	389.237	0.395	1734.90
	2	3.3562	389.237	0.397	1793.16
	3	3.5001	389.237	0.404	1903.01
	4	3.5083	389.237	0.408	1926.36
	5	3.3952	389.237	0.435	1987.63
				mean	**1869.01**
				std dev	**102.78**

sample ID*	rep	sample mass in cell (g)	red pine density (kg m^{-3})	Oxford %penta	Oxford chlorinated products (µg g^{-1} wood)
C6 3-4.5	1	4.1532	389.237	0.154	860.76
	2	4.1539	389.237	0.152	849.73
	3	4.0129	389.237	0.155	837.09
	4	3.8313	389.237	0.115	592.96
	5	3.5707	389.237	0.120	576.65
				mean	**743.44**
				std dev	**145.17**
C8 0-1.5	1	2.8980	389.237	0.620	2418.08
	2	3.2216	389.237	0.623	2701.09
	3	2.7381	389.237	0.588	2166.74
	4	2.9635	389.237	0.621	2476.72
	5	3.1287	389.237	0.626	2635.83
				mean	**2479.69**
				std dev	**209.25**
C8 1.5-3	1	3.7172	389.237	0.451	2256.17
	2	3.9576	389.237	0.434	2311.54
	3	4.2750	389.237	0.458	2635.01
	4	3.4864	389.237	0.428	2008.17
	5	3.5588	389.237	0.421	2016.35
				mean	**2245.45**
				std dev	**257.40**
C8 3-4.5	1	4.1932	389.237	0.231	1303.58
	2	4.0887	389.237	0.223	1227.07
	3	4.5323	389.237	0.220	1341.90
	4	4.0572	389.237	0.209	1141.18
	5	3.6887	389.237	0.188	933.28
				mean	**1189.40**
				std dev	**162.51**

sample ID*	rep	sample mass in cell (g)	red pine density (kg m^{-3})	Oxford %penta	Oxford chlorinated products (µg g^{-1} wood)
C10 0-1.5	1	2.2740	389.237	0.616	1885.17
	2	2.7326	389.237	0.613	2254.32
	3	3.1386	389.237	0.597	2521.68
	4	3.4994	389.237	0.616	2901.04
	5	4.1917	389.237	0.628	3542.66
				mean	**2620.98**
				std dev	**635.15**
C10 1.5-3	1	3.3449	389.237	0.387	1742.10
	2	3.5268	389.237	0.410	1946.01
	3	3.4077	389.237	0.425	1949.08
	4	3.3710	389.237	0.400	1814.67
	5	3.6000	389.237	0.449	2175.35
				mean	**1925.44**
				std dev	**165.32**
C10 3-4.5	1	3.9940	389.237	0.147	790.14
	2	3.8235	389.237	0.113	581.46
	3	3.7406	389.237	0.147	740.01
	4	4.1621	389.237	0.147	823.40
	5	4.0221	389.237	0.127	687.44
				mean	**724.49**
				std dev	**95.08**
C12 0-1.5	1	2.9087	389.237	0.499	1953.35
	2	3.0764	389.237	0.496	2053.55
	3	2.8475	389.237	0.485	1858.60
	4	3.0837	389.237	0.481	1996.17
	5	2.8986	389.237	0.477	1860.74
				mean	**1944.48**
				std dev	**85.20**

sample ID*	rep	sample mass in cell (g)	red pine density (kg m^{-3})	Oxford %penta	Oxford chlorinated products (µg g^{-1} wood)
C12 1.5-3	1	3.7262	389.237	0.472	2366.94
	2	2.7729	389.237	0.467	1742.73
	3	3.0870	389.237	0.430	1786.43
	4	3.0528	389.237	0.448	1840.59
	5	3.4369	389.237	0.461	2132.30
				mean	**1973.80**
				std dev	**267.36**
C12 3-4.5	1	3.8820	389.237	0.261	1363.57
	2	3.6549	389.237	0.237	1165.75
	3	3.7443	389.237	0.257	1295.04
	4	3.8527	389.237	0.250	1296.24
	5	3.1912	389.237	0.202	867.53
				mean	**1197.62**
				std dev	**197.94**
C14 0-1.5	1	2.9024	389.237	0.546	2132.70
	2	3.3238	389.237	0.555	2482.61
	3	2.6987	389.237	0.558	2026.60
	4	2.8723	389.237	0.577	2230.41
	5	3.5641	389.237	0.592	2839.56
				mean	**2342.38**
				std dev	**325.22**
C14 1.5-3	1	3.3675	389.237	0.347	1572.60
	2	3.3349	389.237	0.354	1588.79
	3	3.7942	389.237	0.358	1828.03
	4	4.4029	389.237	0.404	2393.87
	5	3.5411	389.237	0.341	1625.07
				mean	**1801.67**
				std dev	**346.54**

sample ID*	rep	sample mass in cell (g)	red pine density (kg m^{-3})	Oxford %penta	Oxford chlorinated products (µg g^{-1} wood)
C14 3-4.5	1	4.1073	389.237	0.160	884.42
	2	3.7216	389.237	0.131	656.12
	3	3.7570	389.237	0.121	611.80
	4	3.5027	389.237	0.130	612.81
	5	3.4491	389.237	0.127	589.51
				mean	**670.93**
				std dev	**121.76**
C16 0-1.5	1	2.9303	389.237	0.573	2259.68
	2	3.0801	389.237	0.639	2648.78
	3	2.8073	389.237	0.594	2244.17
	4	2.6506	389.237	0.583	2079.66
	5	3.0504	389.237	0.599	2459.03
				mean	**2338.26**
				std dev	**219.61**
C16 1.5-3	1	3.3617	389.237	0.394	1782.52
	2	3.1601	389.237	0.378	1607.58
	3	2.9554	389.237	0.376	1495.49
	4	3.2850	389.237	0.391	1728.59
	5	3.1723	389.237	0.403	1720.52
				mean	**1666.94**
				std dev	**115.05**
C16 3-4.5	1	3.8817	389.237	0.105	548.52
	2	3.3807	389.237	0.085	386.73
	3	3.8270	389.237	0.122	628.35
	4	4.1152	389.237	0.107	592.59
	5	3.4700	389.237	0.083	387.60
				mean	**508.76**
				std dev	**114.54**

sample ID*	rep	sample mass in cell (g)	red pine density (kg m^{-3})	Oxford %penta	Oxford chlorinated products (µg g^{-1} wood)
C18 0-1.5	1	2.6460	389.237	0.482	1716.39
	2	2.9448	389.237	0.474	1878.51
	3	2.9905	389.237	0.493	1984.13
	4	2.9629	389.237	0.474	1890.06
	5	2.3585	389.237	0.451	1431.50
				mean	**1780.12**
				std dev	**217.36**
C18 1.5-3	1	3.7016	389.237	0.451	2246.70
	2	3.1569	389.237	0.479	2035.06
	3	3.5114	389.237	0.477	2254.13
	4	3.3434	389.237	0.486	2186.78
	5	3.5495	389.237	0.495	2364.57
				mean	**2217.45**
				std dev	**120.47**
C18 3-4.5	1	2.4379	389.237	0.366	1200.82
	2	2.5786	389.237	0.378	1311.76
	3	2.5274	389.237	0.373	1268.71
	4	2.2761	389.237	0.353	1081.30
	5	2.5843	389.237	0.366	1272.93
				mean	**1227.10**
				std dev	**90.76**
C20 0-1.5	1	3.0851	389.237	0.940	3902.81
	2	3.2972	389.237	0.926	4109.00
	3	3.4070	389.237	0.939	4305.44
	4	3.2148	389.237	0.910	3937.09
	5	2.9432	389.237	0.856	3390.58
				mean	**3928.98**
				std dev	**340.87**

sample ID*	rep	sample mass in cell (g)	red pine density (kg m^{-3})	Oxford %penta	Oxford chlorinated products (µg g^{-1} wood)
C20 1.5-3	1	2.6914	389.237	0.701	2539.08
	2	2.8104	389.237	0.716	2708.08
	3	3.8261	389.237	0.781	4021.49
	4	3.1228	389.237	0.760	3194.02
	5	3.0943	389.237	0.750	3123.23
				mean	**3117.18**
				std dev	**575.61**
C20 3-4.5	1	2.5838	389.237	0.175	608.52
	2	2.5941	389.237	0.170	593.49
	3	2.5762	389.237	0.182	631.00
	4	2.5900	389.237	0.192	669.24
	5	2.5513	389.237	0.193	662.67
				mean	**632.99**
				std dev	**33.01**
C22 0-1.5	1	3.3585	389.237	0.747	3376.34
	2	3.6114	389.237	0.813	3951.36
	3	2.9953	389.237	0.731	2946.71
	4	3.2284	389.237	0.786	3414.99
	5	3.3803	389.237	0.812	3693.95
				mean	**3476.67**
				std dev	**376.58**
C22 1.5-3	1	3.3462	389.237	0.890	4007.95
	2	3.2247	389.237	0.900	3905.82
	3	3.5146	389.237	0.934	4417.77
	4	3.3264	389.237	0.905	4051.38
	5	3.0827	389.237	0.938	3891.47
				mean	**4054.88**
				std dev	**213.79**

sample ID*	rep	sample mass in cell (g)	red pine density (kg m^{-3})	Oxford %penta	Oxford chlorinated products (µg g^{-1} wood)
C22 3-4.5	1	2.6464	389.237	0.151	537.79
	2	2.8672	389.237	0.180	694.56
	3	2.5024	389.237	0.148	498.42
	4	2.8666	389.237	0.170	655.84
	5	2.4906	389.237	0.164	549.70
				mean	**587.26**
				std dev	**83.62**

* All sample blocks have even numbers. Refer to labeling schematic, Figure 3.3.

Table A.2: Full data set from GC-MS analysis on pole C samples for comparison of analytical methods.

sample ID*	rep	GC-MS penta+tetra ($\mu g \cdot g^{-1}$ wood)	GC-MS penta ($\mu g\ g^{-1}$ wood)	GC-MS tetra ($\mu g\ g^{-1}$ wood)
C2 0-1.5	1	2279.00	2160	119
	2	2677.00	2520	157
	3	1948.00	1830	118
	mean	**2301.33**		
	std dev	**365.01**		
C2 1.5-3	1	1491.00	1370	121
	2	812.50	757	56
	3	1479.00	1370	109
	mean	**1260.83**		
	std dev	**388.31**		
C2 3-4.5	1	796.20	744	52
	2	895.60	837	59
	3	1555.30	1470	85
	mean	**1082.37**		
	std dev	**412.58**		
C4 0-1.5	1	4022.00	3870	152
	2	1828.70	1760	69
	3	2076.30	1990	86
	mean	**2642.33**		
	std dev	**1201.22**		
C4 1.5-3	1	1668.20	1580	88
	2	985.30	933	52
	3	953.20	878	75
	mean	**1202.23**		
	std dev	**403.86**		
C4 3-4.5	1	367.40	330	37
	2	1252.50	1180	73
	3	1082.60	1020	63
	mean	**900.83**		
	std dev	**469.71**		

sample ID*	rep	GC-MS penta+tetra ($\mu g \cdot g^{-1}$ wood)	GC-MS penta ($\mu g\ g^{-1}$ wood)	GC-MS tetra ($\mu g\ g^{-1}$ wood)
C6 0-1.5	1	1748.00	1650	98
	2	1077.40	1040	37
	3	4042.00	3850	192
	mean	**2289.13**		
	std dev	**1554.62**		
C6 1.5-3	1	1421.00	1320	101
	2	1590.00	1470	120
	3	1493.00	1400	93
	mean	**1501.33**		
	std dev	**84.81**		
C6 3-4.5	1	1140.20	1080	60
	2	2788.00	2760	28
	3	3307.00	3280	27
	mean	**2411.73**		
	std dev	**1131.34**		
C8 0-1.5	1	2173.00	2050	123
	2	2230.00	2120	110
	3	2031.00	1930	101
	mean	**2144.67**		
	std dev	**102.48**		
C8 1.5-3	1	12935.00	12800	135
	2	7216.00	7120	96
	3	2506.30	2430	76
	mean	**7552.43**		
	std dev	**5222.48**		
C8 3-4.5	1	583.00	555	28
	2	914.70	872	43
	3	1002.90	947	56
	mean	**833.53**		
	std dev	**221.40**		

sample ID*	rep	GC-MS penta+tetra ($\mu g \cdot g^{-1}$ wood)	GC-MS penta ($\mu g\ g^{-1}$ wood)	GC-MS tetra ($\mu g\ g^{-1}$ wood)
C10 0-1.5	1	1573.00	1470	103
	2	4115.00	3940	175
	3	2001.00	1890	111
	mean	**2563.00**		
	std dev	**1361.00**		
C10 1.5-3	1	1388.40	1290	98
	2	1417.00	1290	127
	3	2200.00	2090	110
	mean	**1668.47**		
	std dev	**460.54**		
C10 3-4.5	1	361.10	329	32
	2	922.00	870	52
	3	1465.10	1390	75
	mean	**916.07**		
	std dev	**552.02**		
C12 0-1.5	1	2259.00	2140	119
	2	3015.00	2860	155
	3	736.60	689	48
	mean	**2003.53**		
	std dev	**1160.48**		
C12 1.5-3	1	2433.00	2360	73
	2	3273.00	3030	243
	3	12525.00	12400	125
	mean	**6077.00**		
	std dev	**5599.90**		
C12 3-4.5	1	912.40	852	60
	2	933.80	890	44
	3	825.20	772	53
	mean	**890.47**		
	std dev	**57.53**		

sample ID*	rep	GC-MS penta+tetra ($\mu g \cdot g^{-1}$ wood)	GC-MS penta ($\mu g\ g^{-1}$ wood)	GC-MS tetra ($\mu g\ g^{-1}$ wood)
C14 0-1.5	1	10855.00	10800	55
	2	2553.40	2460	93
	3	12070.00	12000	70
	mean	**8492.80**		
	std dev	**5179.42**		
C14 1.5-3	1	9980.00	9910	70
	2	1680.00	1680	
	3	3066.00	2960	106
	mean	**4908.67**		
	std dev	**4446.24**		
C14 3-4.5	1	1054.20	994	60
	2	811.00	767	44
	3	4297.00	4270	27
	mean	**2054.07**		
	std dev	**1946.24**		
C16 0-1.5	1	2489.00	2380	109
	2	2384.00	2230	154
	3	1828.00	1710	118
	mean	**2233.67**		
	std dev	**355.22**		
C16 1.5-3	1	716.00	716	
	2	1275.20	1180	95
	3	697.70	647	51
	mean	**896.30**		
	std dev	**328.26**		
C16 3-4.5	1	348.00	331	17
	2	391.70	376	16
	3	457.10	416	41
	mean	**398.93**		
	std dev	**54.91**		

sample ID*	rep	GC-MS penta+tetra ($\mu g \cdot g^{-1}$ wood)	GC-MS penta ($\mu g\ g^{-1}$ wood)	GC-MS tetra ($\mu g\ g^{-1}$ wood)
C18 0-1.5	1	2182.00	2070	112
	2	1937.20	1850	87
	3	1566.30	1500	66
	mean	**1895.17**		
	std dev	**309.99**		
C18 1.5-3	1	1562.70	1470	93
	2	1811.10	1730	81
	3	1650.00	1650	
	mean	**1674.60**		
	std dev	**126.01**		
C18 3-4.5	1	2120.00	2120	
	2	1321.00	1310	11
	3	1511.00	1500	11
	mean	**1650.67**		
	std dev	**417.41**		
C20 0-1.5	1	4179.00	4020	159
	2	4066.60	4000	67
	3	4521.00	4360	161
	mean	**4255.53**		
	std dev	**236.67**		
C20 1.5-3	1	4040.00	3750	290
	2	6048.00	5940	108
	3	3305.00	3060	245
	mean	**4464.33**		
	std dev	**1419.88**		
C20 3-4.5	1	755.80	715	41
	2	490.00	490	
	3	706.10	665	41
	mean	**650.63**		
	std dev	**141.31**		

sample ID*	rep	GC-MS penta+tetra ($\mu g \cdot g^{-1}$ wood)	GC-MS penta ($\mu g\ g^{-1}$ wood)	GC-MS tetra ($\mu g\ g^{-1}$ wood)
C22 0-1.5	1	2500.00	2500	
	2	2815.90	2720	96
	3	2590.00	2590	
	mean	**2635.30**		
	std dev	**162.75**		
C22 1.5-3	1	3850.00	3850	
	2	4160.00	4160	
	3	3250.00	3250	
	mean	**3753.33**		
	std dev	**462.64**		
C22 3-4.5	1	827.00	827	
	2	637.00	637	
	3	870.10	822	48
	mean	**778.03**		
	std dev	**124.03**		

* All sample blocks have even numbers. Refer to labeling schematic, Figure 3.3.

Figure A.1: Statistical analysis output of the comparison of results from Oxford X-ray fluorescence and GC-MS on pole C samples.

The **UNIVARIATE** Procedure
Variable: resids

Tests for Normality

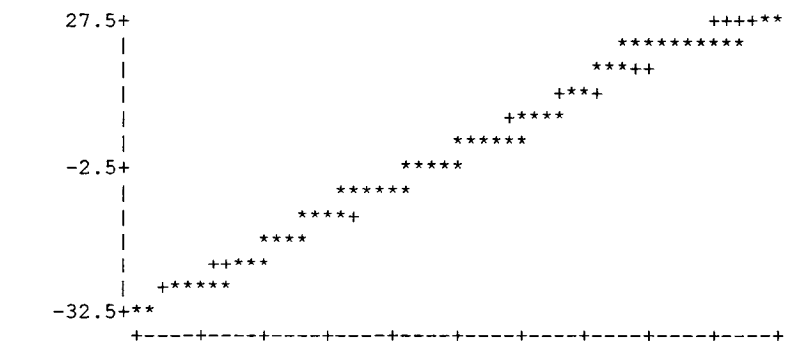
Test	--Statistic---		-----p Value------	
Shapiro-Wilk	W	0.985287	Pr < W	0.0300
Kolmogorov-Smirnov	D	0.048073	Pr > D	**>0.1500**
Cramer-von Mises	W-Sq	0.109953	Pr > W-Sq	0.0859
Anderson-Darling	A-Sq	0.78261	Pr > A-Sq	0.0431

Used the transformation: (lconc=(conc-850)$^{0.5}$)

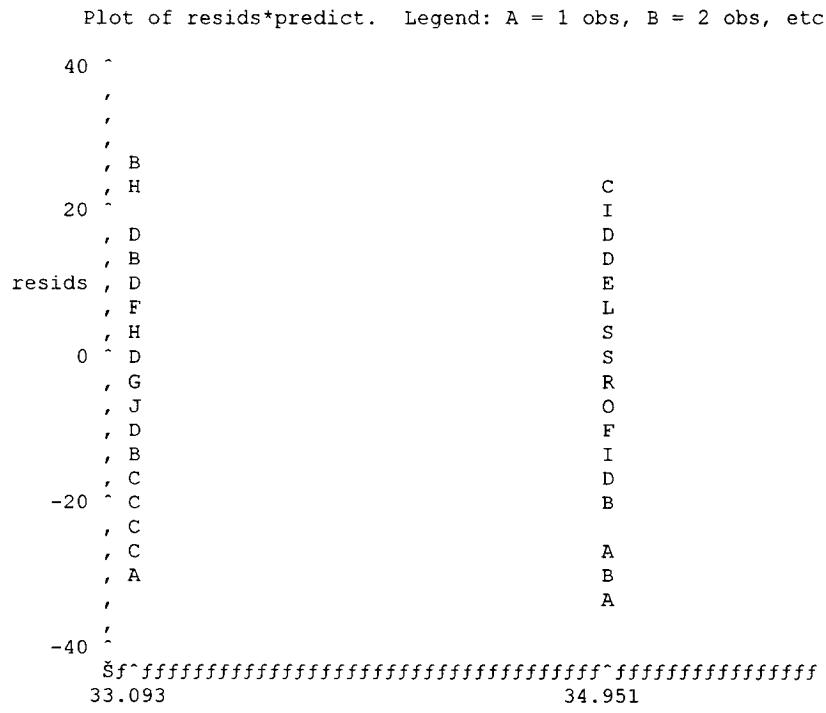
Stem	Leaf	#	Boxplot
2	5567	4	|
2	00011112223334444	17	|
1	556666678	9	|
1	00000111233334	14	|
0	55555555666677777888889	23	+-----+
0	000111111122222222333333334444444	34	| + |
-0	444444433333333332222222111111111000	36	*-----*
-0	99988888887777666666665555555	29	+-----+
-1	444444333221110000	18	|
-1	98887666	8	|
-2	431110	6	|
-2	9966555	7	|
-3	21	2	0

Multiply Stem.Leaf by 10**+1

Normal Probability Plot



The SAS System



NOTE: 57 obs had missing values.

The GLM Procedure

LAB COMPARISON

Class Level Information

Class	Levels	Values
Block	11	1 2 3 4 5 6 7 8 9 10 11
Ring	3	1 2 3
rep	5	1 2 3 4 5
lab	2	O R

Number of observations 264

NOTE: Due to missing values, only 207 observations can be used in this analysis.

Dependent Variable: lconc

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	163.97670	163.97670	1.02	**0.3136**
Error	205	32941.23663	160.68896		
Corrected Total	206	33105.21333			

R-Square	Coeff Var	Root MSE	lconc Mean
0.004953	36.97154	12.67631	34.28668

Source	DF	Type III SS	Mean Square	F Value	Pr > F
lab	1	163.9767015	163.9767015	1.02	**0.3136**

The SAS System
The GLM Procedure

t Tests (**LSD**) for lconc

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha	**0.05**
Error Degrees of Freedom	205
Error Mean Square	160.689
Critical Value of t	1.97160
Least Significant Difference	3.6246
Harmonic Mean of Cell Sizes	95.09179

NOTE: Cell sizes are not equal.

Means with the same letter are not significantly different.

t Grouping	transformed mean	N	lab	**untransformed mean**
A	34.951	133	O	**2071.57**
A	33.093	74	R	**1945.15**

Figure A.2: Statistical analysis output of the comparison of the poles used in the study

The SAS System

The **UNIVARIATE** Procedure
Variable: resids

Tests for Normality

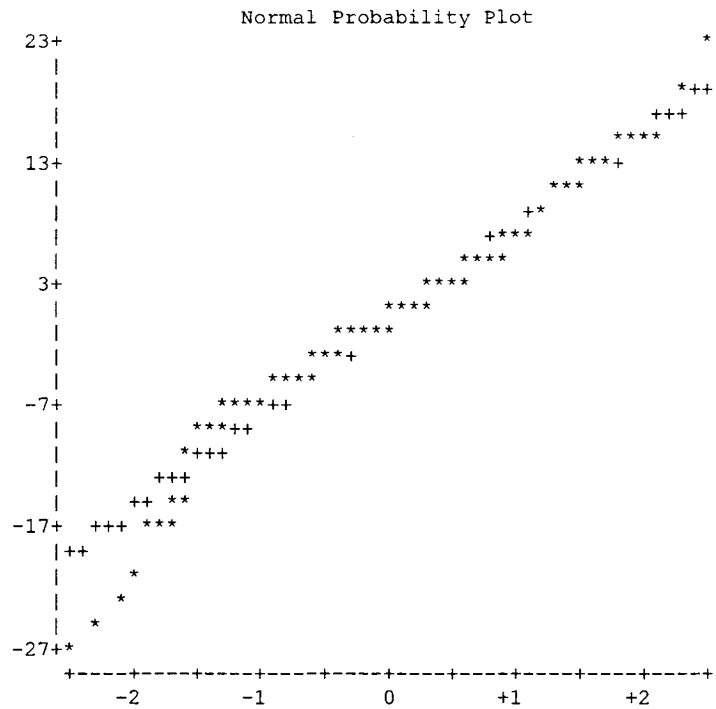
Test	--Statistic---		-----p Value------	
Shapiro-Wilk	W	0.968885	Pr < W	0.0010
Kolmogorov-Smirnov	D	0.062844	Pr > D	**0.1121**
Cramer-von Mises	W-Sq	0.20506	Pr > W-Sq	<0.0050
Anderson-Darling	A-Sq	1.364676	Pr > A-Sq	<0.0050

Transformation used: (lconc=(conc+4250)**0.5)

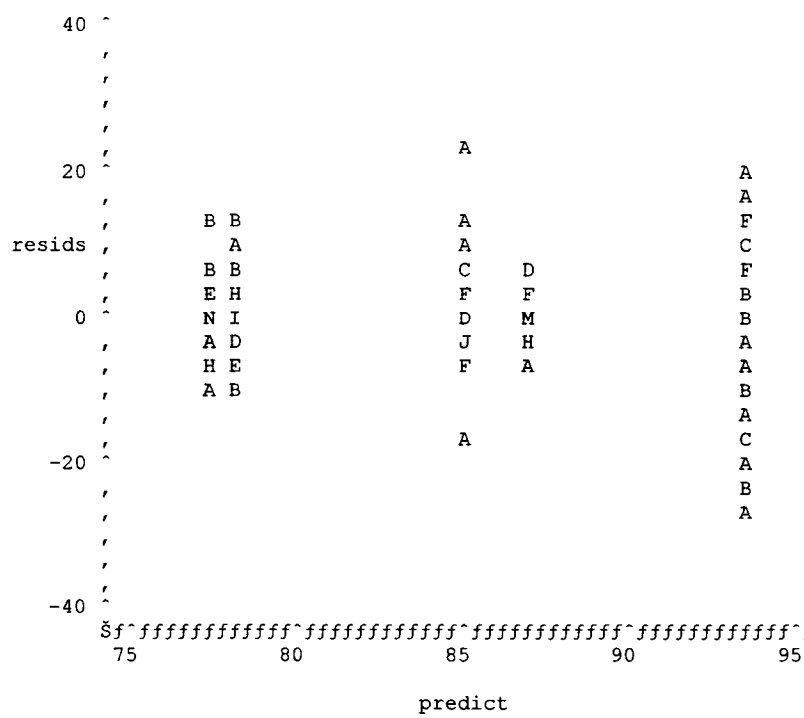
The UNIVARIATE Procedure
Variable: resids

Stem	Leaf	#	Boxplot
22	4	1	0
20			
18	6	1	0
16			
14	3469	4	|
12	13902	5	|
10	138999	6	|
8	007	3	|
6	677924677	9	|
4	222567881234557	15	+-----+
2	112233449900226789	18	| |
0	001222456778902235568	21	*--+--*
-0	977632111000887755554433	24	| |
-2	9885528774210	13	| |
-4	775433976644322	15	+-----+
-6	7654438874110	13	|
-8	32630	5	|
-10	50	2	|
-12			|
-14	33	2	|
-16	164	3	|
-18			
-20	8	1	0
-22	7	1	0
-24	7	1	0
-26	5	1	0

----+----+----+----+----



Plot of resids*predict. Legend: A = 1 obs, B = 2 obs, etc.



NOTE: 1 obs had missing values.

The SAS System
The GLM Procedure
POLE COMPARISON
Class Level Information

Class	Levels	Values
length	11	2 4 6 8 10 12 14 16 18 20 22
depth	3	1.5 3 4.5
pole	5	B C D E G

Number of observations 165

NOTE: Due to missing values, only 164 observations can be used in this analysis.

Dependent Variable: lconc

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	4	5982.32772	1495.58193	24.23	**<.0001**
Error	159	9814.75737	61.72803		
Corrected Total	163	15797.08509			

R-Square	Coeff Var	Root MSE	lconc Mean
0.378698	9.326608	7.856719	84.23984

Source	DF	Type III SS	Mean Square	F Value	Pr > F
pole	4	5982.327721	1495.581930	24.23	**<.0001**

The SAS System
The GLM Procedure

t Tests (**LSD**) for lconc

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha	**0.05**
Error Degrees of Freedom	159
Error Mean Square	61.72803
Critical Value of t	1.97500
Least Significant Difference	3.8319
Harmonic Mean of Cell Sizes	32.79503

NOTE: Cell sizes are not equal.

Means with the same letter are not significantly different.

t Grouping	TransMean	N	pole	BacktransMean
A	93.630	33	E	**4516.58 A**
B	87.109	32	B	**3337.98 B**
B	85.040	33	G	**2981.80 B**
C	78.167	33	C	**1860.08 C**
C	77.340	33	D	**1731.48 C**

Figure A.3: Statistical analysis output for the Oxford reproducibility tests

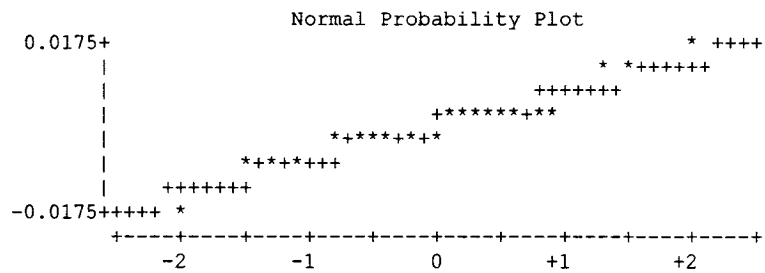
The UNIVARIATE Procedure
Variable: resides

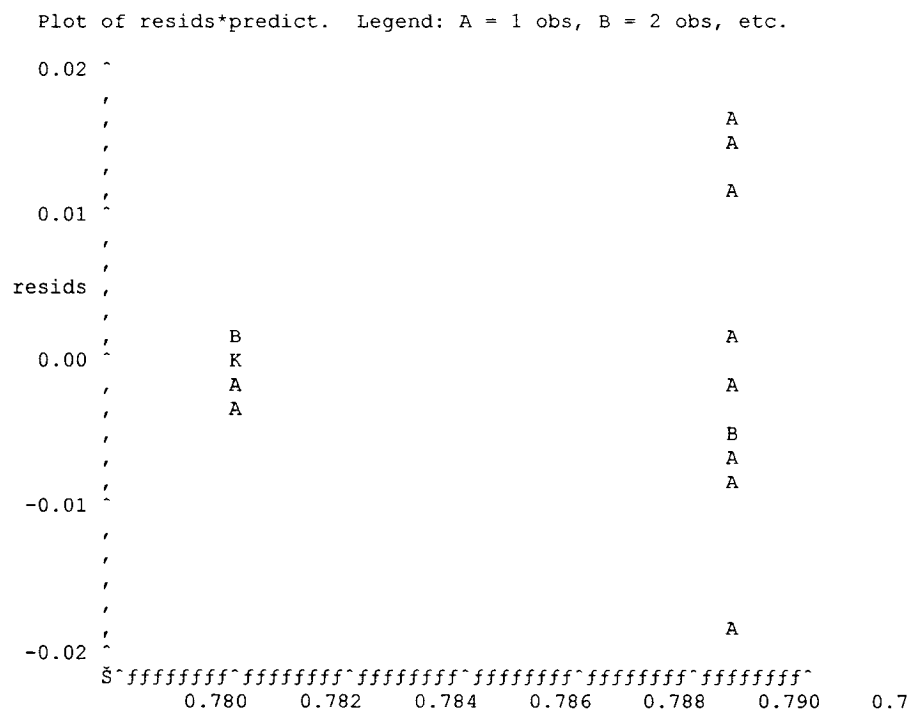
Tests for Normality

Test	--Statistic---		-----p Value------	
Shapiro-Wilk	W	0.856653	Pr < W	**0.0024**
Kolmogorov-Smirnov	D	0.250625	Pr > D	<0.0100
Cramer-von Mises	W-Sq	0.334595	Pr > W-Sq	<0.0050
Anderson-Darling	A-Sq	1.7308	Pr > A-Sq	<0.0050

Stem	Leaf	#	Boxplot
1	56	2	*
1	2	1	*
0			
0	000000222	9	+--+--+
-0	32200000	8	*-----*
-0	8666	4	0
-1			
-1	8	1	*

Multiply Stem.Leaf by 10**-2





The GLM Procedure

Class Level Information

Class	Levels	Values
test	3	R S U
rep	10	1 2 3 4 5 6 7 8 9 10

Number of observations 25

The GLM Procedure

Dependent Variable: lconc

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	0.00045015	0.00022508	4.25	**0.0276**
Error	22	0.00116631	0.00005301		
Corrected Total	24	0.00161646			

R-Square	Coeff Var	Root MSE	lconc Mean
0.278479	0.927023	0.007281	0.785427

Source	DF	Type III SS	Mean Square	F Value	Pr > F
test	2	0.00045015	0.00022508	4.25	**0.0276**

The GLM Procedure

Tukey's Studentized Range (HSD) Test for lconc

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	22
Error Mean Square	0.000053
Critical Value of Studentized Range	3.55259
Minimum Significant Difference	0.0094
Harmonic Mean of Cell Sizes	7.5

NOTE: Cell sizes are not equal.

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	test
A	**0.790624**	**10**	**S**
A	**0.781985**	**10**	**U**
A	**0.781918**	**5**	**R**

Figure A.4: Statistical analysis output for pole C.

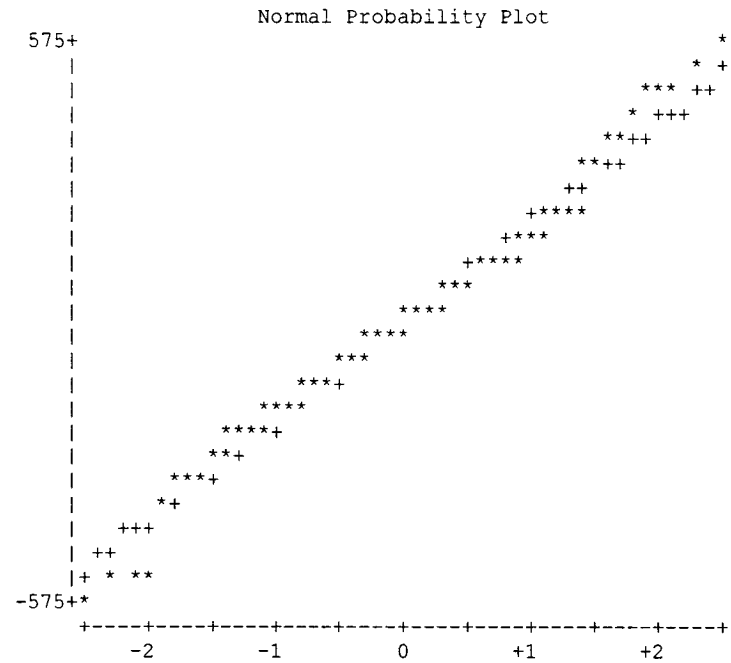
The UNIVARIATE Procedure
Variable: Resid

Tests for **Normality**

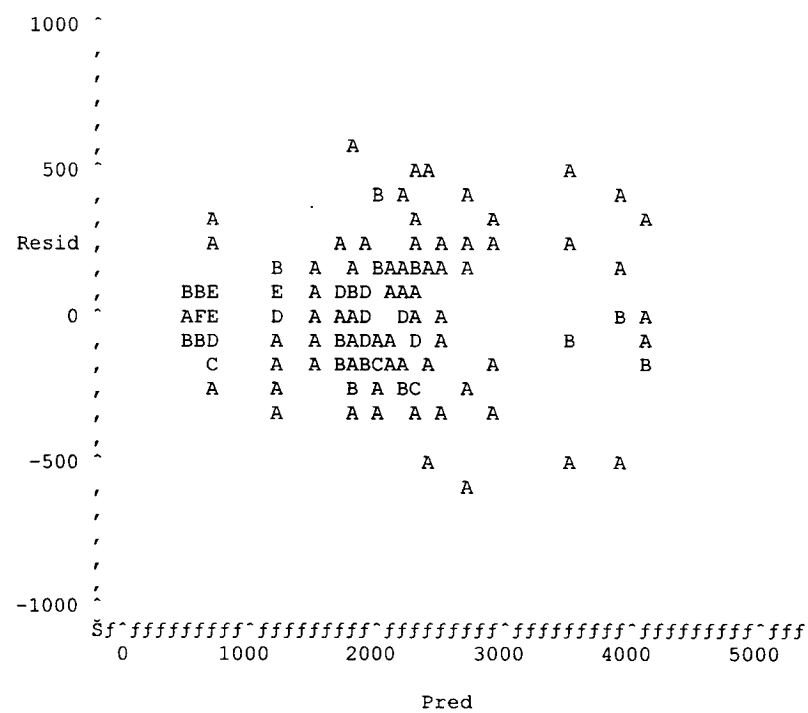
Test		--Statistic---		-----p Value------	
Shapiro-Wilk	W	0.984248	Pr < W	0.0631
Kolmogorov-Smirnov	**D**	**0.058717**	**Pr > D**	**>0.1500**
Cramer-von Mises	**W-Sq**	**0.086602**	**Pr > W-Sq**	**0.1743**
Anderson-Darling	A-Sq	0.700932	Pr > A-Sq	0.0697

Stem	Leaf	#	Boxplot
5	9	1	0
5	01	2	0
4	57	2	0
4	4	1	|
3	6899	4	|
3	013	3	|
2	5	1	|
2	01112223	8	|
1	5556667788	10	|
1	0000111111122222334	19	+-----+
0	555667778889	12	| |
0	111122223333344444	18	*--+--*
-0	44443333221000	14	| |
-0	9999888866666665555	19	| |
-1	433322221100	12	+-----+
-1	9998887776555	13	|
-2	4433321100	10	|
-2	665	3	|
-3	321	3	|
-3	555	3	|
-4			
-4			
-5	430	3	0
-5	8	1	0

Multiply Stem.Leaf by 10**+2



Plot of Resid*Pred. Legend: A = 1 obs, B = 2 obs, etc.



NOTE: 3 obs had missing values

The SAS System

POLE C REPEATED MEASURES (OXFORD)

The Mixed Procedure

Model Information

Data Set	WORK.POLEOXFORD
Dependent Variable	conc
Covariance Structure	Compound Symmetry
Subject Effect	subject
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Between-Within

Class Level Information

Class	Levels	Values
Block	11	1 2 3 4 5 6 7 8 9 10 11
subject	15	1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Ring	3	1 2 3
rep	5	1 2 3 4 5

Dimensions

Covariance Parameters	2
Columns in X	48
Columns in Z	0
Subjects	15
Max Obs Per Subject	11
Observations Used	162
Observations Not Used	3
Total Observations	165

Fit Statistics

Res Log Likelihood	-908.1
Akaike's Information Criterion	-910.1
Schwarz's Bayesian Criterion	-910.8
-2 Res Log Likelihood	1816.2

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
Block	10	117	43.40	**<.0001**
Ring	2	12	697.89	**<.0001**
Block*Ring	20	117	28.10	**<.0001**

Least Squares Means

Effect	Block	Ring	**Estimate**		Standard Error	DF	t Value	Pr >|t|
Block	1		**1562.74**	fg	58.1993	117	26.85	<.0001
Block	2		**1890.97**	cd	60.5701	117	31.22	<.0001
Block	3		**1767.68**	de	58.1993	117	30.37	<.0001
Block	4		**1971.51**	c	58.1993	117	33.88	<.0001
Block	5		**1679.72**	efg	60.5701	117	27.73	<.0001
Block	6		**1705.30**	ef	58.1993	117	29.30	<.0001
Block	7		**1604.99**	efg	58.1993	117	27.58	<.0001
Block	8		**1504.65**	g	58.1993	117	25.85	<.0001
Block	9		**1741.56**	de	58.1993	117	29.92	<.0001
Block	10		**2485.02**	b	60.5696	117	41.03	<.0001
Block	11		**2706.27**	a	58.1993	117	46.50	<.0001
Ring		1	**2529.81**	a	33.5804	12	75.34	<.0001
Ring		2	**2213.80**	b	33.2575	12	66.57	<.0001
Ring		3	**880.15**	c	32.9412	12	26.72	<.0001

The SAS System

POLE C REGRESSION

The CORR Procedure

4 Variables: length D1 D2 D3

Simple Statistics

Variable	N	Mean	Std Dev	Sum	Minimum	Maximum
length	55	6.00000	3.19142	330.00000	1.00000	11.00000
D1	53	2540	674.66509	134619	1432	4305
D2	54	2201	705.14400	118858	1461	4418
D3	55	880.14709	340.55429	48408	386.73000	1673

Pearson Correlation Coefficients
Prob > |r| under H0: Rho=0
Number of Observations

	length	D1	D2	D3
length	1.00000	**0.42479**	**0.61439**	**-0.34109**
		0.0015	**<.0001**	**0.0108**
	55	53	54	55
D1	0.42479	1.00000	0.60019	-0.47266
	0.0015		<.0001	0.0004
	53	53	52	53
D2	0.61439	0.60019	1.00000	-0.16131
	<.0001	<.0001		0.2439
	54	52	54	54
D3	-0.34109	-0.47266	-0.16131	1.00000
	0.0108	0.0004	0.2439	
	55	53	54	55

Obs	_TYPE_	_NAME_	length	D1	D2	D3
1	MEAN		6.0000	2539.98	2201.07	880.147
2	STD		3.1914	674.67	705.14	340.554
3	N		55.0000	53.00	54.00	55.000
4	CORR	length	1.0000	0.42	0.61	-0.341
5	**CORR**	D1	**0.4248**	1.00	0.60	-0.473
6	**CORR**	D2	**0.6144**	0.60	1.00	-0.161
7	**CORR**	D3	**-0.3411**	-0.47	-0.16	1.000

The SAS System
The REG Procedure
Model: MODEL1
Dependent Variable: **Depth 1**

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	4270986	4270986	11.23	0.0015
Error	51	19398009	380353		
Corrected Total	52	23668995			

Root MSE	616.72775	R-Square	**0.1804**
Dependent Mean	2539.98434	Adj R-Sq	0.1644
Coeff Var	24.28077		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	**1994.20214**	183.58663	10.86	**<.0001**
length	1	**89.55559**	26.72527	3.35	**0.0015**

The SAS System
The REG Procedure
Model: MODEL1
Dependent Variable: **Depth 2**

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	9947532	9947532	31.53	<.0001
Error	52	16405556	315491		
Corrected Total	53	26353087			

Root MSE	561.68626	R-Square	**0.3775**
Dependent Mean	2201.06796	Adj R-Sq	0.3655
Coeff Var	25.51881		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	**1392.03955**	163.09849	8.53	**<.0001**
length	1	**136.52355**	24.31329	5.62	**<.0001**

The SAS System
The REG Procedure
Model: MODEL1
Dependent Variable: **Depth 3**

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	728646	728646	6.98	0.0108
Error	53	5534124	104417		
Corrected Total	54	6262770			

Root MSE	323.13688	R-Square	**0.1163**
Dependent Mean	880.14709	Adj R-Sq	0.0997
Coeff Var	36.71396		

Parameter Estimates

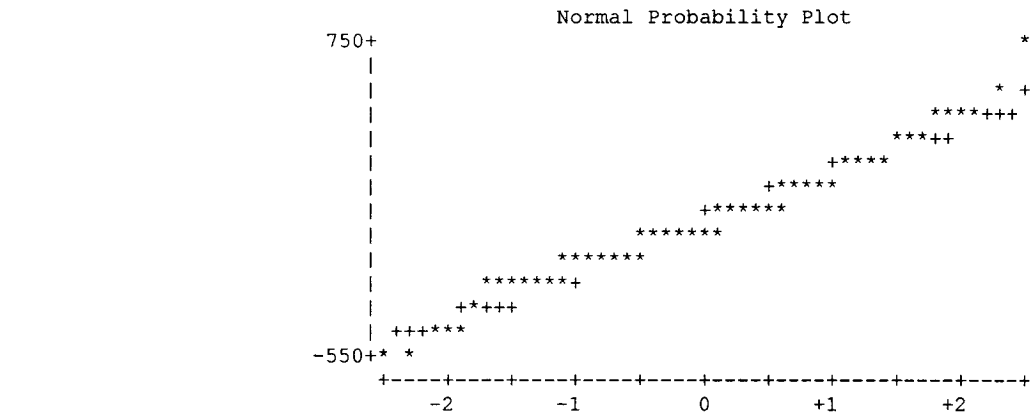
Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	**1098.53476**	93.45103	11.76	**<.0001**
length	1	**-36.39795**	13.77860	-2.64	**0.0108**

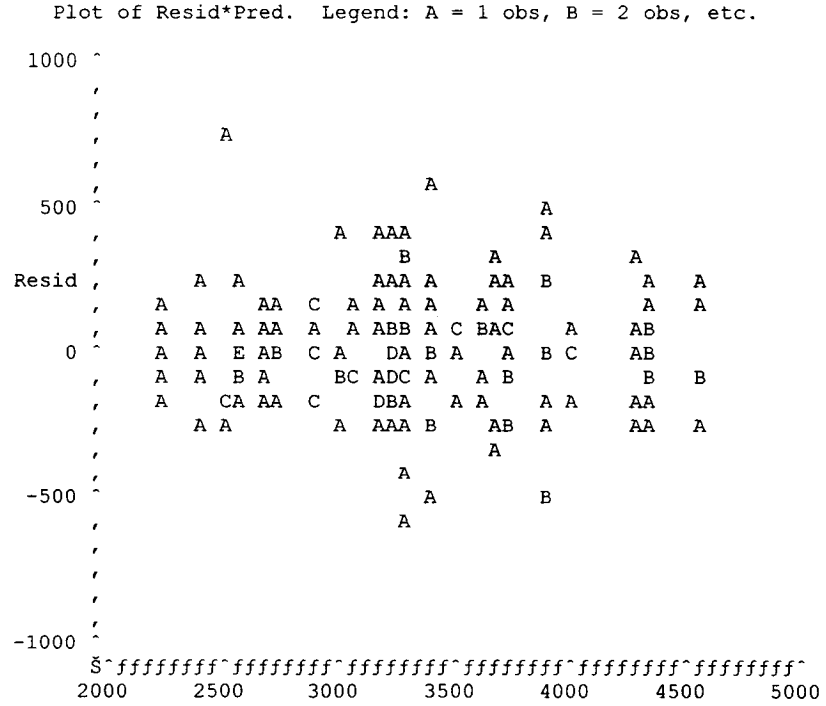
Figure A.5: Statistical analysis output for pole B

The UNIVARIATE Procedure
Variable: Resid

Tests for Normality

Test		--Statistic---		-----p Value------	
Shapiro-Wilk	**W**	**0.983757**	**Pr < W**	**0.0508**
Kolmogorov-Smirnov	**D**	**0.053273**	**Pr > D**	**>0.1500**
Cramer-von Mises	**W-Sq**	**0.09224**	**Pr > W-Sq**	**0.1442**
Anderson-Darling	**A-Sq**	**0.626**	**Pr > A-Sq**	**0.1015**





The SAS System

POLE B REPEATED MEASURES (OXFORD)

The Mixed Procedure

Model Information

Data Set	WORK.POLEBDEGOXFORD
Dependent Variable	B
Covariance Structure	Compound Symmetry
Subject Effect	subject
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Between-Within

Class Level Information

Class	Levels	Values
length	11	1 2 3 4 5 6 7 8 9 10 11
subject	15	1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
depth	3	1 2 3
rep	5	1 2 3 4 5

Dimensions

Covariance Parameters	2
Columns in X	48
Columns in Z	0
Subjects	15
Max Obs Per Subject	11
Observations Used	165
Observations Not Used	0
Total Observations	165

Iteration History

Iteration	Evaluations	-2 Res Log Like	Criterion
0	1	1864.79132946	
1	1	1863.59380240	0.00000000

Convergence criteria met.

Covariance Parameter Estimates

Cov Parm	Subject	Estimate
CS	subject	-1987.79
Residual		55463

Fit Statistics

Res Log Likelihood	-931.8
Akaike's Information Criterion	-933.8
Schwarz's Bayesian Criterion	-934.5
-2 Res Log Likelihood	1863.6

Null Model Likelihood Ratio Test

DF	Chi-Square	Pr > ChiSq
1	1.20	0.273

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
length	10	120	46.77	**<.0001**
depth	2	12	313.40	**<.0001**
length*depth	20	120	9.18	**<.0001**

Least Squares Means

Effect	block	ring	Estimate	Standard Error	DF	t Value	Pr > |t|
length	1		**3792.03 a**	59.7076	120	63.51	<.0001
length	2		**3349.82 c**	59.7076	120	56.10	<.0001
length	3		**3676.62 ab**	59.7076	120	61.58	<.0001
length	4		**3529.91 b**	59.7076	120	59.12	<.0001
length	5		**3337.49 c**	59.7076	120	55.90	<.0001
length	6		**2848.13 d**	59.7076	120	47.70	<.0001
length	7		**2785.61 d**	59.7076	120	46.65	<.0001
length	8		**2873.25 d**	59.7076	120	48.12	<.0001
length	9		**2795.99 d**	59.7076	120	46.83	<.0001
length	10		**3669.38 ab**	59.7076	120	61.46	<.0001
length	11		**3799.64 a**	59.7076	120	63.64	<.0001
depth		1	**3807.40 a**	24.7155	12	154.05	<.0001
depth		2	**3163.31 b**	24.7155	12	127.99	<.0001
depth		3	**2972.34 c**	24.7155	12	120.26	<.0001

POLE B REGRESSION (OXFORD)

The CORR Procedure
4 Variables: length D1 D2 D3

Pearson Correlation Coefficients, N = 55
Prob > |r| under H0: Rho=0

	length	D1	D2	D3
length	1.00000	**-0.37605** **0.0047**	**-0.22890** **0.0928**	**0.15282** **0.2653**
D1	-0.37605 0.0047	1.00000	0.68415 <.0001	0.29281 0.0300
D2	-0.22890 0.0928	0.68415 <.0001	1.00000	0.41443 0.0017
D3	0.15282 0.2653	0.29281 0.0300	0.41443 0.0017	1.00000

Obs	_TYPE_	_NAME_	length	D1	D2	D3
1	MEAN		6.0000	3807.40	3163.31	2972.34
2	STD		3.1914	543.42	587.20	399.43
3	N		55.0000	55.00	55.00	55.00
4	CORR	length	1.0000	-0.38	-0.23	0.15
5	**CORR**	D1	**-0.3761**	1.00	0.68	0.29
6	**CORR**	D2	**-0.2289**	0.68	1.00	0.41
7	**CORR**	D3	**0.1528**	0.29	0.41	1.00

The REG Procedure
Model: MODEL1
Dependent Variable: **Depth 1**

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	2255069	2255069	8.73	**0.0047**
Error	53	13691305	258327		
Corrected Total	54	15946374			

Root MSE	508.25831	R-Square	**0.1414**
Dependent Mean	3807.40055	Adj R-Sq	0.1252
Coeff Var	13.34922		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	**4191.59385**	146.98806	28.52	<.0001
length	1	**-64.03222**	21.67221	-2.95	0.0047

The REG Procedure
Model: MODEL1
Dependent Variable: **Depth 2**

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	975551	975551	2.93	**0.0928**
Error	53	17644060	332907		
Corrected Total	54	18619611			

Root MSE	576.98075	R-Square	0.0524
Dependent Mean	3163.31145	Adj R-Sq	0.0345
Coeff Var	18.23977		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	3416.00538	166.86256	20.47	<.0001
length	1	-42.11565	24.60254	-1.71	0.0928

The REG Procedure
Model: MODEL1
Dependent Variable: **Depth 3**
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	201206	201206	1.27	0.2653
Error	53	8414092	158756		
Corrected Total	54	8615297			

Root MSE	398.44253	R-Square	0.0234
Dependent Mean	2972.34400	Adj R-Sq	0.0049
Coeff Var	13.40499		

Parameter Estimates

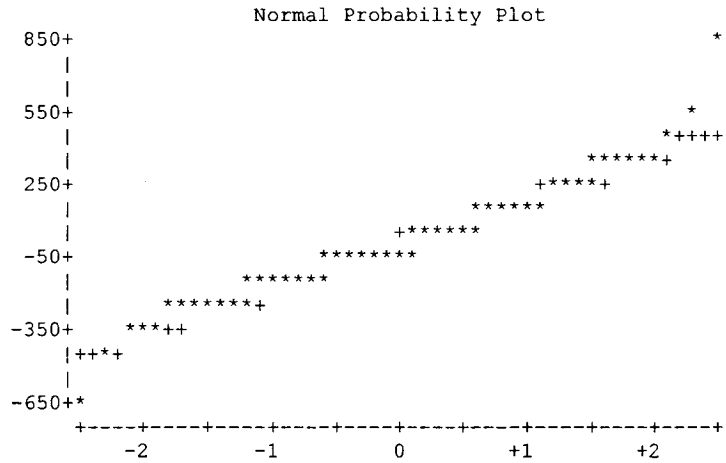
Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	2857.58418	115.22939	24.80	<.0001
length	1	19.12664	16.98965	1.13	0.2653

Figure A.6: Statistical analysis output of pole D.

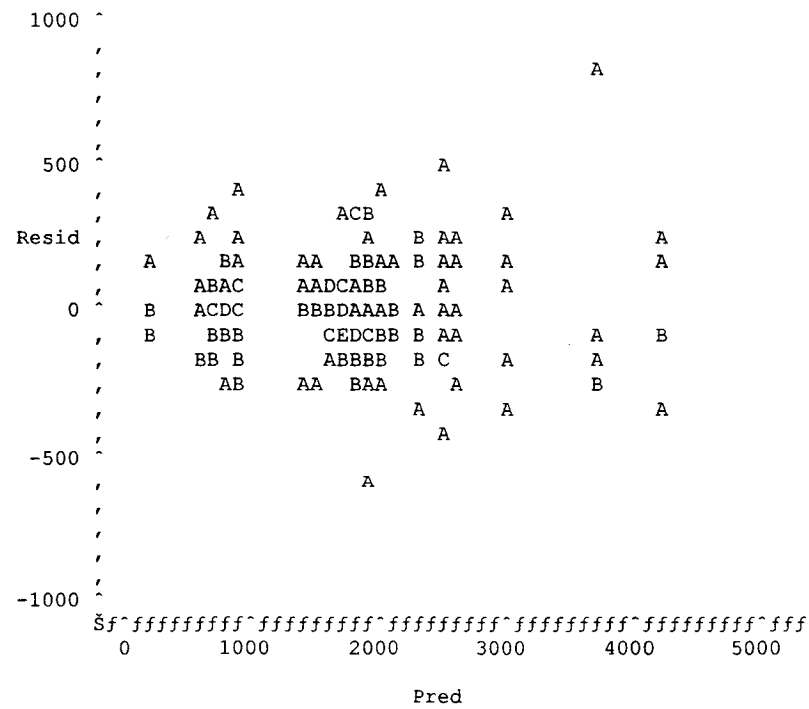
The UNIVARIATE Procedure
Variable: Resid

Tests for Normality

Test	--Statistic---		-----p Value------	
Shapiro-Wilk	W	0.974611	Pr < W	0.0040
Kolmogorov-Smirnov	**D**	**0.052569**	**Pr > D**	**>0.1500**
Cramer-von Mises	W-Sq	0.111253	Pr > W-Sq	0.0827
Anderson-Darling	A-Sq	0.686029	Pr > A-Sq	0.0759



Plot of Resid*Pred. Legend: A = 1 obs, B = 2 obs, etc.



The SAS System

POLE D REPEATED MEASURES (OXFORD)

The Mixed Procedure

Model Information

Data Set	WORK.POLEBDEGOXFORD
Dependent Variable	D
Covariance Structure	Unstructured
Subject Effect	subject
Estimation Method	REML
Residual Variance Method	None
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Between-Within

Class Level Information

Class	Levels	Values
length	11	1 2 3 4 5 6 7 8 9 10 11
subject	15	1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
depth	3	1 2 3
rep	5	1 2 3 4 5

Dimensions

Covariance Parameters	66
Columns in X	48
Columns in Z	0
Subjects	15
Max Obs Per Subject	11
Observations Used	165
Observations Not Used	0
Total Observations	165

Iteration History

Iteration	Evaluations	-2 Res Log Like	Criterion
0	1	1835.91188079	
1	1	1704.24690558	0.00000000

Convergence criteria met.

Fit Statistics

Res Log Likelihood	-852.1
Akaike's Information Criterion	-918.1
Schwarz's Bayesian Criterion	-941.5
-2 Res Log Likelihood	1704.2

Null Model Likelihood Ratio Test

DF	Chi-Square	Pr > ChiSq
65	131.66	<.0001

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
length	10	12	724.42	**<.0001**
depth	2	12	731.89	**<.0001**
length*depth	20	12	498.48	**<.0001**

Least Squares Means

Effect	block	ring	Estimate	Standard Error	DF	t Value	Pr > |t|
length	1		**2695.10 a**	51.5885	12	52.24	<.0001
length	2		**1894.50 cd**	67.9460	12	27.88	<.0001
length	3		**1766.06 d**	39.3636	12	44.87	<.0001
length	4		**1378.63 f**	36.5494	12	37.72	<.0001
length	5		**1219.44 g**	36.9968	12	32.96	<.0001
length	6		**1381.10 f**	43.2695	12	31.92	<.0001
length	7		**1493.43 e**	46.2232	12	32.31	<.0001
length	8		**1585.16 e**	44.3204	12	35.77	<.0001
length	9		**1625.62 e**	54.3583	12	29.91	<.0001
length	10		**2332.06 b**	72.7301	12	32.06	<.0001
length	11		**1995.67 c**	75.8903	12	26.30	<.0001
depth		1	**2335.15 a**	24.9745	12	93.50	<.0001
depth		2	**1930.43 b**	24.9745	12	77.30	<.0001
depth		3	**1016.26 c**	24.9745	12	40.69	<.0001

POLE D REGRESSION (OXFORD)

The CORR Procedure

4 Variables: length D1 D2 D3

Pearson Correlation Coefficients, N = 55
Prob > |r| under H0: Rho=0

	length	D1	D2	D3
length	1.00000	**0.56399** **<.0001**	**-0.56945** **<.0001**	**-0.50019** **0.0001**
D1	0.56399 <.0001	1.00000	-0.03206 0.8162	0.05574 0.6861
D2	-0.56945 <.0001	-0.03206 0.8162	1.00000	0.58261 <.0001
D3	-0.50019 0.0001	0.05574 0.6861	0.58261 <.0001	1.00000

Obs	_TYPE_	_NAME_	length	D1	D2	D3
1	MEAN		6.0000	2335.15	1930.43	1016.26
2	STD		3.1914	843.23	484.62	656.80
3	N		55.0000	55.00	55.00	55.00
4	CORR	length	1.0000	0.56	-0.57	-0.50
5	**CORR**	D1	**0.5640**	1.00	-0.03	0.06
6	**CORR**	D2	**-0.5694**	-0.03	1.00	0.58
7	**CORR**	D3	**-0.5002**	0.06	0.58	1.00

The REG Procedure
Model: MODEL1
Dependent Variable: **Depth 1**
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	12212943	12212943	24.72	<.0001
Error	53	26182707	494013		
Corrected Total	54	38395650			

Root MSE	702.86082	R-Square	**0.3181**
Dependent Mean	2335.14945	Adj R-Sq	0.3052
Coeff Var	30.09918		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	**1441.06185**	203.26701	7.09	<.0001
length	1	**149.01460**	29.97009	4.97	<.0001

The REG Procedure
Model: MODEL1
Dependent Variable: **Depth 2**
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	4112390	4112390	25.43	<.0001
Error	53	8569641	161691		
Corrected Total	54	12682032			

Root MSE	402.10862	R-Square	**0.3243**
Dependent Mean	1930.43309	Adj R-Sq	0.3115
Coeff Var	20.82997		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	**2449.25353**	116.28962	21.06	<.0001
length	1	**-86.47007**	17.14597	-5.04	<.0001

The REG Procedure
Model: MODEL1
Dependent Variable: **Depth 3**
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	5828263	5828263	17.68	0.0001
Error	53	17466893	329564		
Corrected Total	54	23295156			

Root MSE	574.07667	R-Square	**0.2502**
Dependent Mean	1016.25745	Adj R-Sq	0.2360
Coeff Var	56.48929		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	**1633.90324**	166.02270	9.84	<.0001
length	1	**-102.94096**	24.47871	-4.21	0.0001

Figure A.7: Statistical analysis output for pole E.

The UNIVARIATE Procedure
Variable: Resid

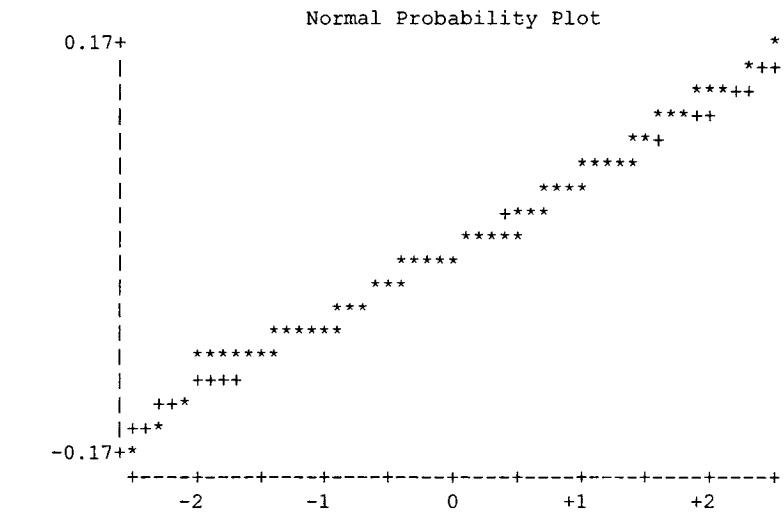
Tests for Normality

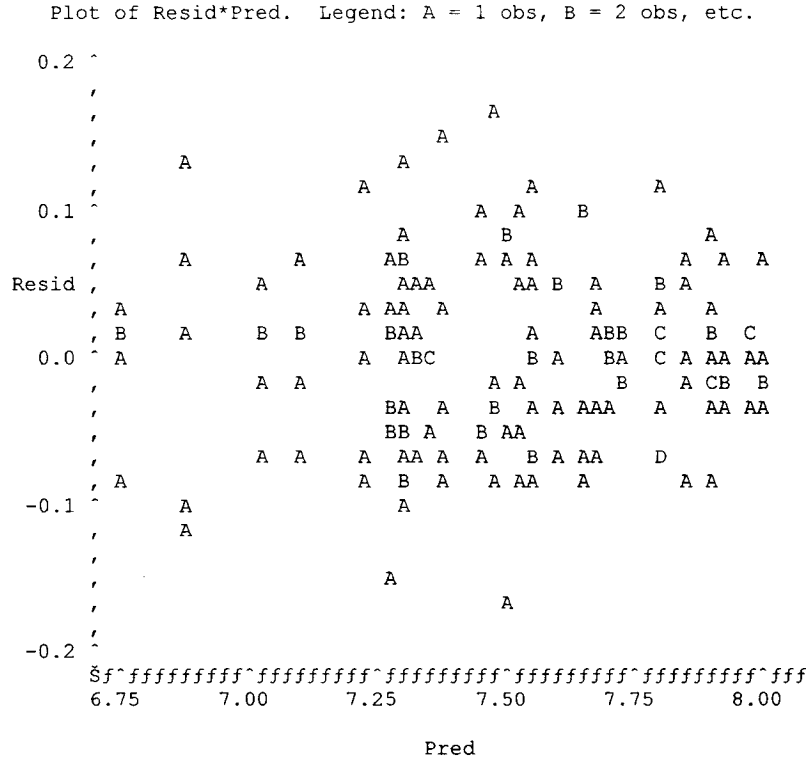
Test		--Statistic---		-----p Value------	
Shapiro-Wilk	**W**	**0.990585**	**Pr < W**	**0.3511**
Kolmogorov-Smirnov	D	0.065106	Pr > D	0.0879
Cramer-von Mises	**W-Sq**	**0.076783**	**Pr > W-Sq**	**0.2323**
Anderson-Darling	**A-Sq**	**0.50912**	**Pr > A-Sq**	**0.2044**

Transformation used: natural log

Stem	Leaf	#	Boxplot
16	9	1	0
14	9	1	|
12	428	3	|
10	12577	5	|
8	904	3	|
6	166711224579	12	|
4	013456667256788	15	|
2	11344712259	11	+-----+
0	133344889000111111223455677888	28	| |
-0	98854311199888876544422211	26	*--+--*
-2	96665553298766620	17	| |
-4	7643098860	10	+-----+
-6	9875443110973322100	19	|
-8	4208776532	10	|
-10			|
-12	4	1	|
-14	5	1	|
-16	4	1	0

Multiply Stem.Leaf by 10**-2





NOTE: 1 obs had missing values.

The SAS System

POLE E REPEATED MEASURES (OXFORD)

The Mixed Procedure

Model Information

Data Set	WORK.POLEBDEGOXFORD
Dependent Variable	lE
Covariance Structure	Unstructured
Subject Effect	subject
Estimation Method	REML
Residual Variance Method	None
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Between-Within

Class Level Information

Class	Levels	Values
length	11	1 2 3 4 5 6 7 8 9 10 11
subject	15	1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
depth	3	1 2 3
rep	5	1 2 3 4 5

Dimensions

Covariance Parameters	66
Columns in X	48
Columns in Z	0
Subjects	15
Max Obs Per Subject	11
Observations Used	164
Observations Not Used	1
Total Observations	165

Iteration History

Iteration	Evaluations	-2 Res Log Like	Criterion
0	1	-287.85019549	
1	2	-397.14177738	0.00046752
2	1	-397.33552486	0.00028405
3	1	-397.43686530	0.00018375
4	1	-397.51187288	0.00009773
5	1	-397.54575284	0.00004745
6	1	-397.56399426	0.00001258
7	1	-397.56847599	0.00000183
8	1	-397.56910746	0.00000005
9	1	-397.56912211	0.00000000

Convergence criteria met.

Covariance Parameter Estimates

Cov Parm	Subject	Estimate
UN(1,1)	subject	0.006287
UN(2,1)	subject	0.004301
UN(2,2)	subject	0.009550
UN(3,1)	subject	-0.00091
UN(3,2)	subject	0.001060
UN(3,3)	subject	0.003869
UN(4,1)	subject	0.000845
UN(4,2)	subject	0.002155
UN(4,3)	subject	0.001831
UN(4,4)	subject	0.005409
UN(5,1)	subject	0.001167
UN(5,2)	subject	-0.00030
UN(5,3)	subject	-0.00105
UN(5,4)	subject	0.001585
UN(5,5)	subject	0.004097
UN(6,1)	subject	-0.00109
UN(6,2)	subject	0.001356
UN(6,3)	subject	0.001378
UN(6,4)	subject	0.002388
UN(6,5)	subject	0.000622
UN(6,6)	subject	0.004303
UN(7,1)	subject	0.000629
UN(7,2)	subject	0.002616
UN(7,3)	subject	0.002103
UN(7,4)	subject	0.002125
UN(7,5)	subject	-0.00099
UN(7,6)	subject	0.002644
UN(7,7)	subject	0.004560
UN(8,1)	subject	0.001235
UN(8,2)	subject	-0.00019
UN(8,3)	subject	-0.00002
UN(8,4)	subject	0.000858
UN(8,5)	subject	-0.00153
UN(8,6)	subject	-0.00061

UN(8,7)	subject	0.000618
UN(8,8)	subject	0.003608
UN(9,1)	subject	0.000085
UN(9,2)	subject	-0.00008
UN(9,3)	subject	-9.08E-7
UN(9,4)	subject	-0.00013
UN(9,5)	subject	-0.00040
UN(9,6)	subject	0.000031
UN(9,7)	subject	-0.00043
UN(9,8)	subject	0.000253
UN(9,9)	subject	0.001042
UN(10,1)	subject	-0.00034
UN(10,2)	subject	0.000715
UN(10,3)	subject	0.001523
UN(10,4)	subject	0.001400
UN(10,5)	subject	0.000464
UN(10,6)	subject	0.000532
UN(10,7)	subject	0.000578
UN(10,8)	subject	-0.00054
UN(10,9)	subject	-0.00009
UN(10,10)	subject	0.001185
UN(11,1)	subject	-0.00007
UN(11,2)	subject	-0.00026
UN(11,3)	subject	0.001266
UN(11,4)	subject	0.001152
UN(11,5)	subject	-0.00051
UN(11,6)	subject	0.001047
UN(11,7)	subject	0.003089
UN(11,8)	subject	0.000529
UN(11,9)	subject	0.000379
UN(11,10)	subject	0.000931
UN(11,11)	subject	0.006125

Fit Statistics

Res Log Likelihood	198.8
Akaike's Information Criterion	132.8
Schwarz's Bayesian Criterion	109.4
-2 Res Log Likelihood	-397.6

Null Model Likelihood Ratio Test

DF	Chi-Square	Pr > ChiSq
65	109.72	0.0004

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
length	10	12	700.89	**<.0001**
depth	2	12	311.81	**<.0001**
length*depth	20	12	110.87	**<.0001**

Least Squares Means

Effect	block	ring		Trans Estimate	Standard Error	DF	t Value	Pr > |t|
length	1	**1371.692**	**h**	7.2238	0.02047	12	352.84	<.0001
length	2	**1430.100**	**h**	7.2655	0.02546	12	285.35	<.0001
length	3	**1534.408**	**g**	7.3359	0.01606	12	456.77	<.0001
length	4	**1785.225**	**f**	7.3803	0.01899	12	388.63	<.0001
length	5	**2049.805**	**c**	7.6255	0.01653	12	461.41	<.0001
length	6	**2296.634**	**a**	7.7392	0.01694	12	456.93	<.0001
length	7	**1835.184**	**d**	7.5149	0.01744	12	431.02	<.0001
length	8	**2048.985**	**c**	7.6251	0.01551	12	491.63	<.0001
length	9	**2146.942**	**b**	7.6718	0.008334	12	920.56	<.0001
length	10	**2330.178**	**d**	7.7537	0.008887	12	872.48	<.0001
length	11	**1604.071**	**d**	7.4873	0.02021	12	370.54	<.0001
depth		1 **2343.967**	**a**	7.7596	0.01420	12	546.54	<.0001
depth		2 **1836.653**	**b**	7.5157	0.01423	12	528.24	<.0001
depth		3 **1419.699**	**c**	7.2582	0.01420	12	511.23	<.0001

POLE E REGRESSION (OXFORD)

The CORR Procedure

4 Variables: length D1 D2 D3

Simple Statistics

Variable	N	Mean	Std Dev	Sum	Minimum	Maximum
length	55	6.00000	3.19142	330.00000	1.00000	11.00000
D1	55	2386	442.22925	131256	1511	3200
D2	55	1914	559.59038	105260	774.48000	2970
D3	55	1447	277.76929	79582	858.56000	2058

Pearson Correlation Coefficients, N = 55
Prob > |r| under H0: Rho=0

	length	D1	D2	D3
length	1.00000	**0.89361** **<.0001**	**0.80521** **<.0001**	**-0.13491** **0.3261**
D1	0.89361 <.0001	1.00000	0.84179 <.0001	0.09617 0.4849
D2	0.80521 <.0001	0.84179 <.0001	1.00000	0.20971 0.1244
D3	-0.13491 0.3261	0.09617 0.4849	0.20971 0.1244	1.00000

Obs	_TYPE_	_NAME_	length	D1	D2	D3
1	MEAN		6.0000	2386.47	1913.81	1446.94
2	STD		3.1914	442.23	559.59	277.77
3	N		55.0000	55.00	55.00	55.00
4	CORR	length	1.0000	0.89	0.81	-0.13
5	**CORR**	D1	**0.8936**	1.00	0.84	0.10
6	**CORR**	D2	**0.8052**	0.84	1.00	0.21
7	**CORR**	D3	**-0.1349**	0.10	0.21	1.00

The REG Procedure
Model: MODEL1
Dependent Variable: **Depth 1**

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	8433063	8433063	210.08	<.0001
Error	53	2127539	40142		
Corrected Total	54	10560602			

Root MSE	200.35531	**R-Square**	**0.7985**
Dependent Mean	2386.46673	Adj R-Sq	0.7947
Coeff Var	8.39548		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	**1643.51160**	57.94266	28.36	<.0001
length	1	**123.82585**	8.54318	14.49	<.0001

The REG Procedure
Model: MODEL1
Dependent Variable: **Depth 2**

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	10963697	10963697	97.73	<.0001
Error	53	5945938	112188		
Corrected Total	54	16909635			

Root MSE	334.94403	**R-Square**	**0.6484**
Dependent Mean	1913.81491	Adj R-Sq	0.6417
Coeff Var	17.50138		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	**1066.68811**	96.86565	11.01	<.0001
length	1	**141.18780**	14.28206	9.89	<.0001

The REG Procedure
Model: MODEL1
Dependent Variable: **Depth 3**

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	75831	75831	0.98	**0.3261**
Error	53	4090580	77181		
Corrected Total	54	4166412			

Root MSE	277.81426	R-Square	0.0182
Dependent Mean	1446.94291	Adj R-Sq	-0.0003
Coeff Var	19.20008		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	1517.39513	80.34375	18.89	<.0001
length	1	-11.74204	11.84604	-0.99	0.3261

Figure A.8: Statistical analysis output of pole G.

The SAS System
The UNIVARIATE Procedure
Variable: Resid

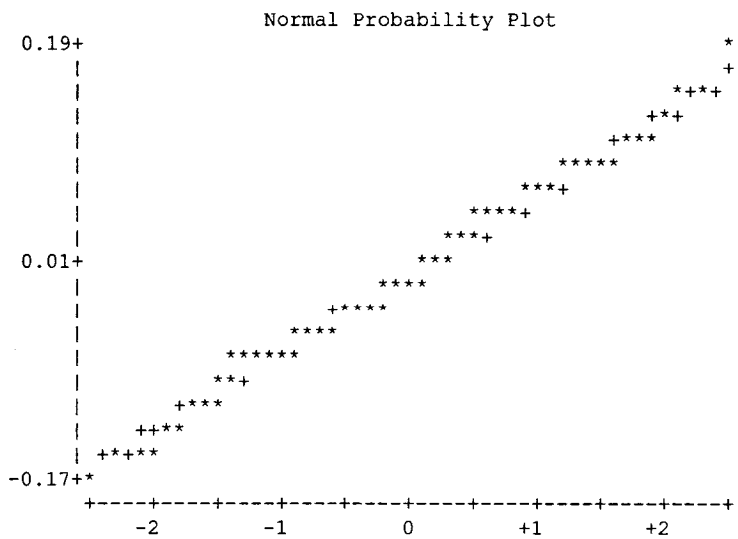
Tests for Normality

Test		--Statistic---		-----p Value------	
Shapiro-Wilk	**W**	**0.994682**	**Pr < W**	**0.8208**
Kolmogorov-Smirnov	**D**	**0.052872**	**Pr > D**	**>0.1500**
Cramer-von Mises	**W-Sq**	**0.064894**	**Pr > W-Sq**	**>0.2500**
Anderson-Darling	**A-Sq**	**0.378297**	**Pr > A-Sq**	**>0.2500**

Transformation used: Natural log

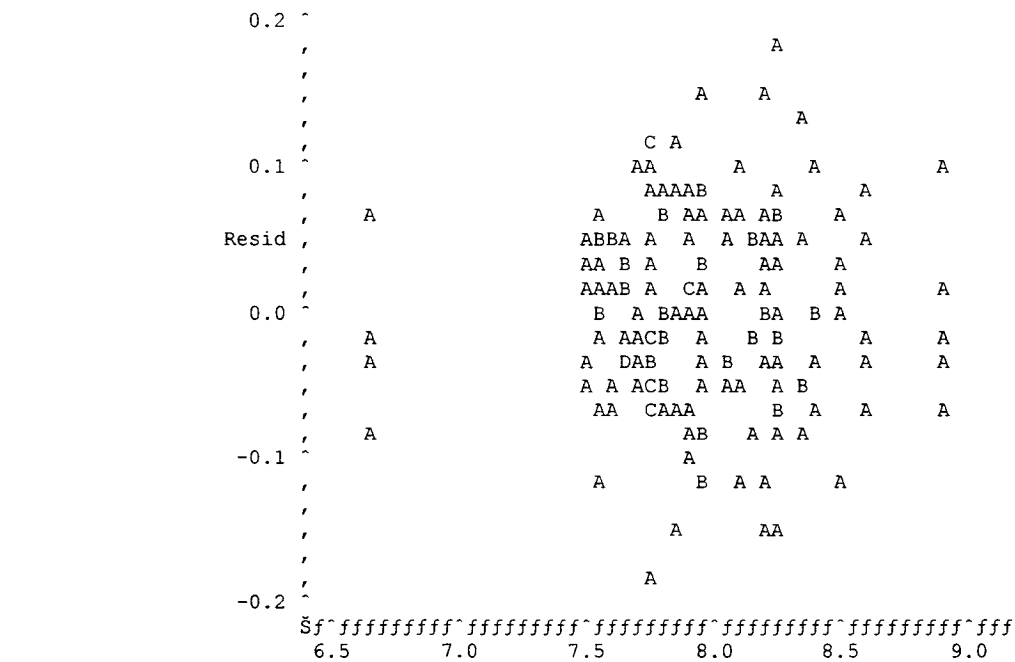
Stem	Leaf	#	Boxplot
18	5	1	
16			
14	32	2	
12	7	1	
10	09059	5	
8	27789902333	11	
6	356671122227	12	
4	13447899002233349	17	
2	1223779901288	13	
0	1122360223345556	16	
-0	9855554418876655 5	18	
-2	75553319887766544330	20	
-4	9888770009997433111	19	
-6	8876639965544222	16	
-8	84	2	
-10	63323	5	
-12	22	2	
-14	332	3	
-16	8	1	

Multiply Stem.Leaf by 10**-2



The SAS System

Plot of Resid*Pred. Legend: A = 1 obs, B = 2 obs, etc.



NOTE: 1 obs had missing values.

The SAS System

POLE G REPEATED MEASURES (OXFORD)

The Mixed Procedure

Model Information

Data Set	WORK.POLEBDEGOXFORD
Dependent Variable	lG
Covariance Structure	Unstructured
Subject Effect	subject
Estimation Method	REML
Residual Variance Method	None
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Between-Within

Class Level Information

Class	Levels	Values
length	11	1 2 3 4 5 6 7 8 9 10 11
subject	15	1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
depth	3	1 2 3
rep	5	1 2 3 4 5

Dimensions

Covariance Parameters	66
Columns in X	48
Columns in Z	0
Subjects	15
Max Obs Per Subject	11
Observations Used	164
Observations Not Used	1
Total Observations	165

Iteration History

Iteration	Evaluations	-2 Res Log Like	Criterion
0	1	-260.06167039	
1	2	-336.94599923	0.00089553
2	1	-337.25610995	0.00016124
3	1	-337.30900827	0.00000981
4	1	-337.31196907	0.00000005
5	1	-337.31198297	0.00000000

Convergence criteria met.

Covariance Parameter Estimates

Cov Parm	Subject	Estimate
UN(1,1)	subject	0.005789
UN(2,1)	subject	0.000366
UN(2,2)	subject	0.005090
UN(3,1)	subject	0.000662
UN(3,2)	subject	-0.00045
UN(3,3)	subject	0.004415
UN(4,1)	subject	0.000231
UN(4,2)	subject	-0.00008
UN(4,3)	subject	-0.00187
UN(4,4)	subject	0.005224
UN(5,1)	subject	0.001685
UN(5,2)	subject	0.000702
UN(5,3)	subject	0.001662
UN(5,4)	subject	-0.00011
UN(5,5)	subject	0.007428
UN(6,1)	subject	0.002267
UN(6,2)	subject	-0.00117
UN(6,3)	subject	0.001383
UN(6,4)	subject	0.000276
UN(6,5)	subject	0.002108
UN(6,6)	subject	0.004614
UN(7,1)	subject	0.000282
UN(7,2)	subject	-0.00007
UN(7,3)	subject	0.000744
UN(7,4)	subject	-0.00276
UN(7,5)	subject	0.001772
UN(7,6)	subject	0.000623
UN(7,7)	subject	0.004971
UN(8,1)	subject	0.000498
UN(8,2)	subject	-0.00109
UN(8,3)	subject	0.000224
UN(8,4)	subject	0.001047
UN(8,5)	subject	0.002839

UN(8,6)	subject	0.002924
UN(8,7)	subject	0.001456
UN(8,8)	subject	0.004575
UN(9,1)	subject	0.002754
UN(9,2)	subject	-0.00062
UN(9,3)	subject	0.003039
UN(9,4)	subject	-0.00281
UN(9,5)	subject	0.001009
UN(9,6)	subject	0.002578
UN(9,7)	subject	0.003897
UN(9,8)	subject	0.000790
UN(9,9)	subject	0.006893
UN(10,1)	subject	-0.00021
UN(10,2)	subject	0.000696
UN(10,3)	subject	-0.00117
UN(10,4)	subject	0.000605
UN(10,5)	subject	-0.00103
UN(10,6)	subject	-0.00134
UN(10,7)	subject	-0.00098
UN(10,8)	subject	-0.00059
UN(10,9)	subject	-0.00134
UN(10,10)	subject	0.004756
UN(11,1)	subject	-0.00078
UN(11,2)	subject	0.001363
UN(11,3)	subject	0.001864
UN(11,4)	subject	-0.00278
UN(11,5)	subject	0.001927
UN(11,6)	subject	0.000688
UN(11,7)	subject	0.002437
UN(11,8)	subject	-0.00006
UN(11,9)	subject	0.002105
UN(11,10)	subject	0.000424
UN(11,11)	subject	0.005395

Fit Statistics

Res Log Likelihood	168.7
Akaike's Information Criterion	102.7
Schwarz's Bayesian Criterion	79.3
-2 Res Log Likelihood	-337.3

Null Model Likelihood Ratio Test

DF	Chi-Square	Pr > ChiSq
65	77.25	0.1421

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
length	10	12	235.12	**<.0001**
depth	2	12	21.41	**0.0001**
length*depth	20	12	450.25	**<.0001**

Least Squares Means

Effect	block	Ring	Trans Estimate	Standard Error	DF	t Value	Pr > |t|
length	1	**2935.109 b**	7.9845	0.01964	12	406.44	<.0001
length	2	**2603.469 e**	7.8646	0.01842	12	426.93	<.0001
length	3	**2451.855 f**	7.8046	0.01716	12	454.94	<.0001
length	4	**2442.067 f**	7.9825	0.01866	12	427.73	<.0001
length	5	**2829.344 d**	7.9478	0.02225	12	357.15	<.0001
length	6	**2585.308 e**	7.8576	0.01754	12	447.99	<.0001
length	7	**2397.304 f**	7.7821	0.01820	12	427.48	<.0001
length	8	**2437.431 f**	7.7987	0.01746	12	446.54	<.0001
length	9	**2903.871 d**	7.9738	0.02144	12	371.97	<.0001
length	10	**5079.154 a**	8.5329	0.01781	12	479.20	<.0001
length	11	**2929.245 c**	7.8006	0.01917	12	407.01	<.0001
depth		1 **2664.575 b**	7.8878	0.01387	12	568.73	<.0001
depth		2 **2747.097 b**	7.9183	0.01387	12	570.94	<.0001
depth		3 **3014.231 a**	8.0111	0.01389	12	576.77	<.0001

The SAS System

POLE G REGRESSION (OXFORD)

The CORR Procedure

4 Variables: length D1 D2 D3

Simple Statistics

Variable	N	Mean	Std Dev	Sum	Minimum	Maximum
length	55	6.00000	3.19142	330.00000	1.00000	11.00000
D1	55	2810	980.73753	154531	1696	5158
D2	55	3001	1533	165044	1674	8035
D3	54	3342	1095	180450	708.97000	5785

Pearson Correlation Coefficients
Prob > |r| under H0: Rho=0
Number of Observations

	length	D1	D2	D3
length	**1.00000**	**0.27257**	**0.46847**	**0.19442**
		0.0441	**0.0003**	**0.1589**
	55	55	55	54
D1	0.27257	1.00000	0.85270	-0.51773
	0.0441		<.0001	<.0001
	55	55	55	54
D2	0.46847	0.85270	1.00000	-0.14463
	0.0003	<.0001		0.2967
	55	55	55	54
D3	0.19442	-0.51773	-0.14463	1.00000
	0.1589	<.0001	0.2967	
	54	54	54	54

Obs	_TYPE_	_NAME_	length	D1	D2	D3
1	MEAN		6.0000	2809.65	3000.80	3341.66
2	STD		3.1914	980.74	1532.79	1095.05
3	N		55.0000	55.00	55.00	54.00
4	CORR	length	1.0000	0.27	0.47	0.19
5	CORR	D1	**0.2726**	1.00	0.85	-0.52
6	CORR	D2	**0.4685**	0.85	1.00	-0.14
7	CORR	D3	**0.1944**	-0.52	-0.14	1.00

The REG Procedure
Model: MODEL1
Dependent Variable: **Depth 1**

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	3858775	3858775	4.25	**0.0441**
Error	53	48080915	907187		
Corrected Total	54	51939690			

Root MSE	952.46369	**R-Square**	**0.0743**
Dependent Mean	2809.64818	Adj R-Sq	0.0568
Coeff Var	33.89975		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	**2307.08044**	275.45204	8.38	<.0001
length	1	**83.76129**	40.61319	2.06	0.0441

The REG Procedure
Model: MODEL1
Dependent Variable: **Depth 2**

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	27843300	27843300	14.90	0.0003
Error	53	99027374	1868441		
Corrected Total	54	126870674			

Root MSE	1366.90929	**R-Square**	**0.2195**
Dependent Mean	3000.79909	Adj R-Sq	0.2047
Coeff Var	45.55151		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	**1650.81000**	395.30951	4.18	0.0001
length	1	**224.99818**	58.28521	3.86	0.0003

The REG Procedure
Model: MODEL1
Dependent Variable: **Depth 3**

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	2402350	2402350	2.04	**0.1589**
Error	52	61151252	1175986		
Corrected Total	53	63553602			

Root MSE	1084.42870	R-Square	0.0378
Dependent Mean	3341.65796	Adj R-Sq	0.0193
Coeff Var	32.45182		

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr > |t|
Intercept	1	2941.87252	316.25285	9.30	<.0001
length	1	67.67528	47.34923	1.43	0.1589

9.0 Appendix B

Patent Template

Patent template as requested by SJI's legal council, Fasken Martineau DuMoulin, for original submission.

This template is issued by patent firms and is the first step in holding rights to an invention for a maximum of 24 months. Alterations and additions are permitted until formal application is made for the patent within the 24 month time frame. Currently, SJI has 8 months left to alter the template. A search is made by the law firm prior to the applicants application to ensure that no other patent is being violated.

Fasken Martineau DuMoulin
Patent Template
Validity 18 months
Strictly Confidential

TITLE OF THE INVENTION

Pentachlorophenol Extraction from Out of Service Utility Poles.
(560800-326063 MTL_LAW#1371538 v.1)

FIELD OF INVENTION

Recycling

BACKGROUND OF THE INVENTION

There is a need for a method of removing pentachlorophenol (PCP) and the carrier oil from out of service utility poles as the chloride ion content makes the burning at regular temperatures breakdown the ozone layer. The current method of disposal involves cutting

the poles off at the groundline and hoping someone takes it away, landfilling or sale as clothesline poles.

OBJECT(S) OF THE INVENTION

A general object of the present invention is therefore to provide a true recycling technology which removes all but trace amounts of PCP and carrier oil from out of service poles, leaving only whitewood behind.

Another object is to provide a dioxin-furan free PCP source as during the lifespan of the pole, photodecomposition has rendered the remaining PCP free of these co-contaminants.

SUMMARY OF THE INVENTION

It is a chemical-physical reaction within our existing systems which converts PCP to water soluble Na-PCP and then causes a phase change from water to steam through the application of a vacuum.

More specifically, it "un-treats' a treated pole.

Advantageously, it uses existing plant equipment and the resulting removed Na-PCP is readily converted back to useable PCP through pH adjustment.

Other objects, advantages and features of the present invention will become more apparent upon reading of the following non restrictive description of preferred embodiments thereof, given by way of example only with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure B.1: Future pole life cycle – (Shows the change in handling and lowering of inputs to landfills).

Figure B.2: Material flow – (Flowchart for material handling).

Figure B.3: Plant equipment – (Specifications for equipment modification).

Figure B.4: The wood preserving process

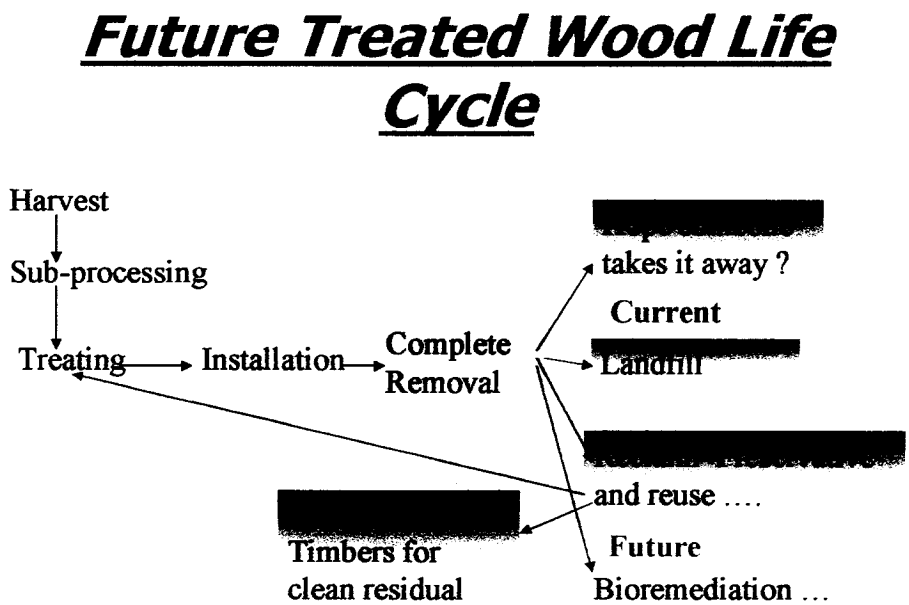


Figure B.1: Future pole life cycle

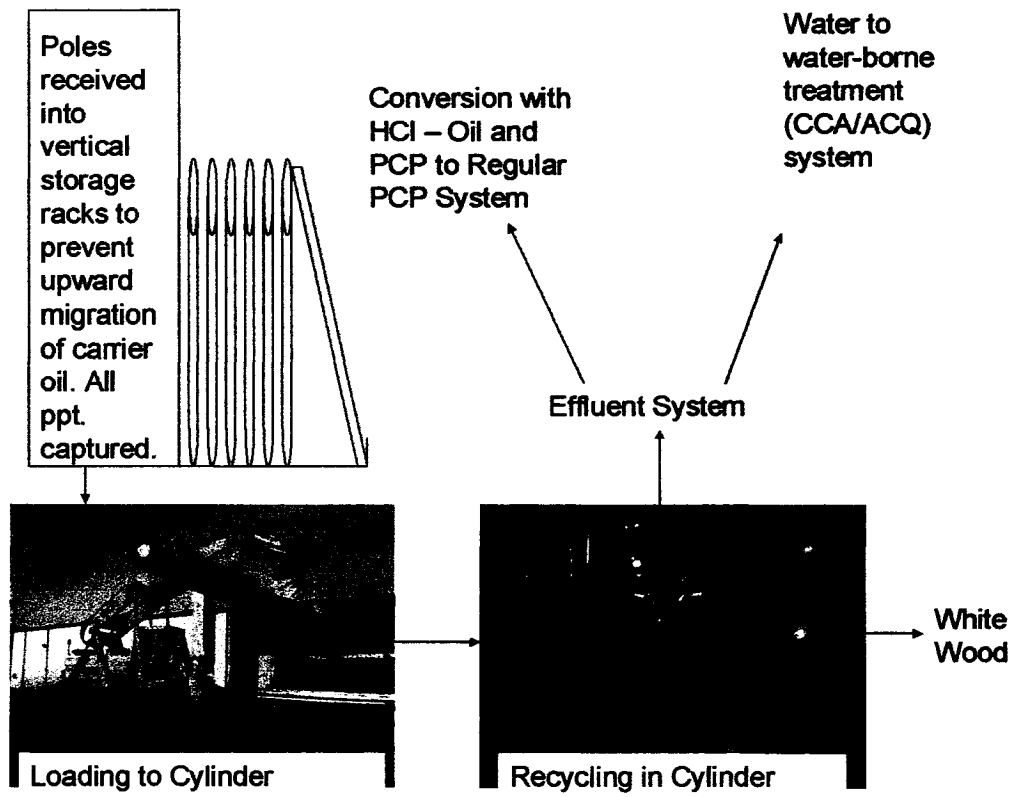


Figure B.2 : Material flow

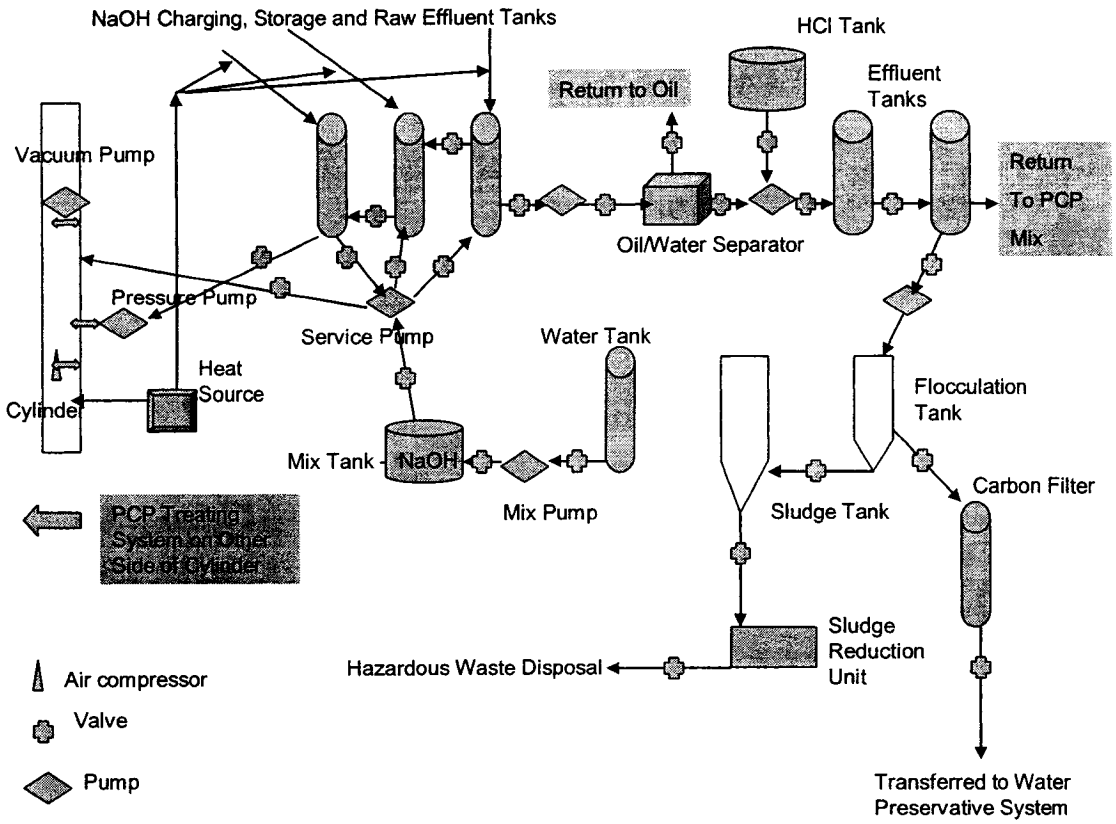


Figure B.3 : Plant equipment

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Definitions – Wood preserving is used to remove wood as a carbon source to decay organisms. Material flow is as follows in Figure B.4 :

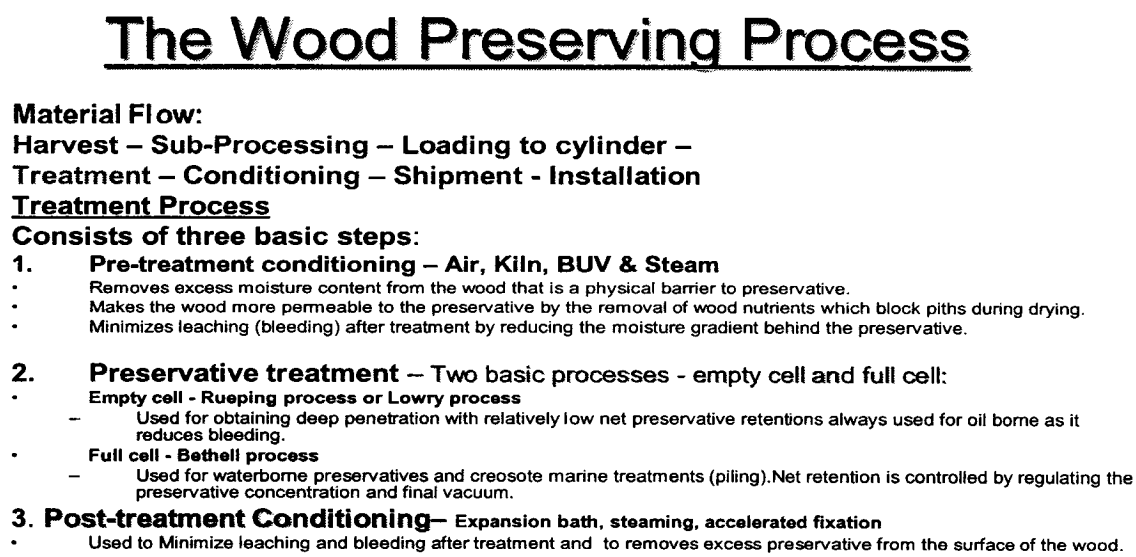


Figure B.4: The wood preserving process

EXPERIMENTAL

1) Development of a non-destructive (radiation based) method to evaluate wood density, moisture content, Cl ion content and the metallic fastener presence in real time. This will determine the type of re-manufacturing, if any, that will take place. The practical implications of this technology are that different types of radiation

will react with specific elements within the wood that relate to specific properties. By reaction, I refer to the collision of the radiation with elements that reflects them back and reduces their energy, or thermalizes, the emissions to the point at which they can be counted by a detector. This count of thermalized radiation is then calibrated by physical sampling to extrapolate for the properties mentioned above. The sphere of influence, which is related to the size of the emission source, will be key to quick scanning.

2) The mapping of PCP, all chlorinated phenolics and carrier oil distribution in the pole with respect to length and depth through high pressure liquid chromatography. This will determine the effective break between chemical extraction and biological remediation of remaining PCP and carrier oil and the issues in point #5 with respect to chemical conversion. These results will also be used to calibrate the radiation source above with respect to Cl content.

3) Determination of optimum solvent extraction systems, remembering that those who attempted this before focused solely on PCP forgetting the carrier oil (95% by volume) and the other chlorinated phenolics which are the partial breakdown components of PCP. This will involve optimizing extraction duration, surface area to volume, solution temperature and hence viscosity, solvent type and strength and ability to separate preservative solution from the extracting solution for reuse in the cylinders.

4) Assessment of the time and depth possible for conversion of pentachlorophenol to the water soluble sodium pentachlorophenate, what catalysts can improve the process, temperatures and pressures required and the ability of the nearly instantaneous phase change of the solution to expel the converted preservative.

RESULTS

Example 1

The mapping and radiation method have been completed and are successful.

Example 2

The conversion process was successful during scale from sawdust through to pole sections with 99% removal of existing PCP carrier oil.

Example 3

The resulting extract was readily converted back to usable PCP of a much higher purity.

Although the present invention has been described hereinabove by way of preferred embodiments thereof, it can be modified without departing from the spirit, scope and nature of the subject invention, as defined in the appended claims.

List of References

The above information has several pending publications and will be completed as a doctoral thesis through Dalhousie's faculty of Biological Engineering.

WHAT IS CLAIMED

1. Almost complete removal of preservative. Values are below any hazardous criteria and have been proven to not be above the levels of PCP naturally occurring in untreated wood.
2. Can be done using existing plant equipment with vacuum system upgrades.
3. PCP extract can be reused.

4. Revenue stream of long duration. If PCP treating stopped tomorrow the next 30 years would see large volumes of PCP poles being removed from service.
5. Reduction in landfilling as a true extraction, not just a minimization of landfilled waste.

ABSTRACT OF THE DISCLOSURE

The present invention relates to a novel method of removing PCP and carrier oil from out of service utility poles. Resulting extract can be reused in the treatment process and is of higher purity. Current wood preserving plant treating equipment can be used and it will result in a reduction in landfill volumes while removing a biocide from a spent piece of wood.