

**The Limnology and Remediation
of Two Proximal Pit Lakes
in Northwestern Ontario**

by

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of the requirements for the degree of
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Abstract

Two adjacent pit lakes, Caland and Hogarth, were formed after the closure and subsequent flooding of the Steep Rock Iron Mines near Atikokan, Ontario, Canada. They were examined to predict flooding patterns, outflow location, and water quality of the pit lakes when they eventually flow into an adjacent river system. The use of wetlands to remediate of the pit lakes was also examined.

Models generated using ArcView v. 3.0 accurately predicted the joining of two pit lakes (Hogarth and Roberts). It also projects the most likely location at which outflow into the Seine River system will occur. While water chemistry varies over time, Cr, and Cu were predicted to reach levels exceeding the guidelines for the preservation of aquatic life in Canada before outflow occurs. Also, Mn, S, SO₄, and TDS will likely exceed the levels defined as safe for human consumption. A model incorporating the past and present depths of the oxygenated freshwater lens present on the surface of Caland pit lake predicted that as the lake fills, the depth of this lens will decrease logarithmically. This will seriously impact the operation of a commercial rainbow trout farm situated in Caland.

Wetlands may be a practical means of remediation of the water contained within these pit lakes. Of the four plant species examined, *Carex sp.* was able to concentrate the greatest amounts of S, as well as Al, Cu, Fe, Ni, Sr and Zn. The former west arm of Steep Rock Lake is a likely location for treatment wetlands to be established. This is because it is strategically located between the Seine River and the predicted flood out

point. In addition, its large surface area enables it to treat a sufficiently large volume of water to make it practical.

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i. General Introduction

i.i History of the Steep Rock Mine

In Canada, the majority of base-metal mining occurs in the boreal forest region through open pit mining, a method designed specifically to exploit large ore bodies situated near the surface (Ripley et al. 1996, EPA 2000). Although Canada lacks an accurate inventory of the quantity or type of waste stored in abandoned tailings sites, or even how many of these sites exist, an estimate of the total land area disturbed by open pit mining up to 1970 was 18 000 ha, with 4 000 ha of this resulting from the draining of Steep Rock lake (Ripley et al. 1996). The Steep Rock mining operation had its start in 1938 when the richest hematite deposit in North America to date was discovered beneath Steep Rock Lake. During World War II, mining of the Steep Rock ore deposit was authorized under Canada's War Measures Act in an attempt to combat the decreasing supply of South American iron ore reaching North American steel mills. In order to gain access to the ore deposit, a massive water diversion project was undertaken. This project included the diversion of the Seine River by the construction of numerous dams, weirs, and tunnels, as well as the draining of the Middle, East and Southeast arms of Steep Rock Lake (5.7x 10¹¹ L of water) and the removal of 2.15x 10⁸ m³ of overburden (Sowa 2002). The ore body was mined from 1944 to 1979 and returned to the Province of Ontario in 1985 (McNaughton 2001). Before the mining lease was relinquished, the Crown required that Steep Rock Iron Mines Inc. provide an abandonment plan, an assessment of the condition of the dams, weirs, and tunnel systems, and a study on the impact of the dredging and overburden disposal. It was shown that the Seine River could not be returned to its original course as it would then be flowing over the translocated overburden. This

overburden would resuspend in the current of the river and the subsequent increase in sediment load would have serious negative effects on fish and fish habitat downstream. In addition, some of the dams had been occupied by Ontario Power Generation. As these pit lakes descend to depths below regional water tables, ground water seeping is a continual problem. During mining, pumping removed the water that accumulated in the bottom of the pits, but with the abandonment of the mine in 1979, pumping also ceased and consequently, the mine pits (some as deep as 300m below lake level) slowly began to fill with water.

Although the Federal Fisheries Act states that no person shall carry on any work or undertaking that results in the harmful alteration, disruption, or destruction of fish habitat (Bardecki 1984), the Steep Rock pit mining operation was allowed to occur without the careful environmental planning that would normally have been mandatory. The reasons for this are twofold: first, mining began in the 1940's before such legislation existed, or the environmental impacts of such actions were clearly known; and second, because the war effort required more iron from the richest and most secure source of ore available. The Steep Rock pit lakes are, unfortunately, far from being the only contaminated site of its kind in North America. In the United States alone, it was estimated in 1996 by the US EPA that there were approximately 217 000 contaminated sites and that it would cost approximately \$190 000 000 000 (US) to clean them up (EPA 2000).

i.ii Characteristics of Pit Lakes

Pit lakes are formed when open pit mining operations cease and ground water fills the abandoned pits. These lakes are generally small but very deep. Because of the influx of saline ground water, and/or the accumulation of inorganic salts, it is possible for a pit lake basin to become meromictic (Page et al 1984, Axler et al 1996). The Steep Rock pit lakes exist in a state of meromixis (McNaughton 2001). Although mixing depth is an important feature of all lakes, it is especially so in meromictic systems because of the permanence of the layers and the many factors contributing to layer and mixing depths (McGuire and Currie 1993). It is therefore difficult to predict whether mixing will occur in deep pit lakes, because the stability of the water column depends on the concentrations of dissolved solids (TDS), as well as climate and pit morphology (Cloern et al 1983, McGuire and Currie 1993, Miller et al 1996). It is important to understand the factors controlling mixing of pit lakes as well as the input of chemicals into the system because it is probable that the pit lake will contain high levels of dissolved metals (Stevens and Lawrence 1998) and it is vital that the movement and fate of these metals be understood.

Pit lakes contain higher concentrations of dissolved substances than natural lakes due to previous mining processes. When rock is exposed to the atmosphere, as during open pit mining, reduced constituents in that rock can become oxidized to form soluble metal-bearing salts (Miller et al 1996). When mining ceases and water seeps through the rock walls and into the pit, these salts dissolve and enter the newly formed lake. In the case of the Steep Rock pit lakes, there is a variety of dissolved elements and compounds, but the major cause for concern is the high level of sulfate salts. The high concentration of

sulfate is one of the principal causes of the meromictic conditions observed in these two lakes (McNaughton 2001). High levels of sulfates, such as those found in the Steep Rock pit lakes, can be harmful to organisms as it can increase the amount of minerals excreted, resulting in the loss of biomass (Andres and Cline 1989).

Although pit lakes do not generally have as deep a sediment layer as natural lakes (Stevens and Lawrence 1998), a thin layer of accumulated sediment may be a significant source of contaminants contributing to generally poor water quality in pit lakes. The sediment layer in pit lakes comes generally from the erosion of tailings piles left around the pit area by rising waters. Metal mine tailings are generally characterized by being chemically reactive and as such may lead to changes acidity, alkalinity, high metal concentrations, and low nutrient contents (Ripley et al 1996, McCabe and Otte 2000). For these reasons, tailings piles often remain free of vegetation, even long after mining operations have ceased. Furthermore, the lack of vegetation further facilitates their erosion as rising water levels contact these tailings piles (McCabe and Otte 2000). In the case of the Steep Rock Pits, both fine and coarse tailings piles are present. In either case however, they generally support very little vegetation –some herbaceous plants and an occasional stunted tree. Those tailing piles that are currently in contact with water are ringed to a diameter greater than one meter with fine suspended silt that has been eroded away by wave action. These rings, which are bright red-orange in color, are in evidence even in calm water. As water levels continue to increase in these pit lakes, an increasing number of eroded tailings piles will compound an already serious problem.

i.iii Effect on Organisms

As was discussed earlier, when rock is exposed to the atmosphere, reduced substances get oxidized and form soluble, metal-bearing salts (Miller et al 1996). When mining operations cease, and water levels in the pits begin to rise, many of the oxidized substances dissolve readily as they are submerged (Miller et al 1996). In addition to naturally occurring metals, such as Ca, Cu, Fe, K, Mg etc., which are required by plants (Raskin 1996), other substances may enter the water column—including those that may be toxic to plants and animals in the area. Even beneficial metals may become toxic if their levels reach toxicity thresholds. Aluminum (Al), also found in high concentrations within the study area, is normally tied up in mineral compounds, but, under acid conditions, it is released as Al^{3+} ions which can enter plant roots causing the cells to become rigid and stunting plant growth or even causing death (Moffat 1999). Al has also been shown to be toxic to fish and other aquatic organisms (Playle and Wood 1989, Gensemer and Playle 1999) and can be toxic to organisms drinking from contaminated water or feeding on contaminated plants. Axler et al (1996) have looked at aquaculture operations as a possible means of increasing the amount of dissolved organic carbon (DOC) and N in pit lakes as a means of remediation. They have found that N is excreted primarily as unionized ammonia—which is potentially toxic to aquatic organisms. Much of the rest of the N is excreted as ammonium, however, and this is readily available to algae and is being considered as a possible means of increasing algae growth in an N-deficient system (Axler et al 1996). Although the P load resulting from net-pen aquaculture was 70-80% solids and as such precipitated out of solution rather quickly,

significant amounts may be resuspended should mixing events occur, especially if the bottom water is anoxic (Axler et al 1996).

Because water that accumulates in the pits of former mine sites is of poor quality, there is a risk of ground water contamination (Miller et al 1996). Also, as most of these pits connect with aquifers, often making them attractive to animals in search of drinking water and migratory birds, these pits can pose potential hazards for both public health and conservation efforts alike (Castro and Miller 2000). These conservation concerns can affect every aspect of an ecosystem. McCabe and Otte (2000) discuss how poor growth of plants on tailings piles of abandoned silver mines is a result of high salt ($MgSO_4$) content and an associated high conductivity. Cu and Cd also pose a threat to plants in that they create free radicals which damage cells and can displace other ions (i.e. Zn) essential to the functioning of certain enzymes (Moffat 1999). Some plants such as Indian Mustard (*Brassica juncea*) and Sunflower (*Helianthus annuus*) are able to acquire and concentrate large amounts of heavy metals in their roots before a critical threshold is reached and the plants suffer from the high concentrations of metals (Rugh et al 1998). This, and other, findings have lead to studies of plants as possible tools in the remediation of metal contaminated sites, such as abandoned mines in the area of Sudbury, Ont. Additionally, studies by Mitsch and Wise (1998) and Palmeri and Trepel (2002) have examined these properties of plants and determined that wetlands could be viable alternatives in the treatment of waters contaminated by mining activities. This principle has lead to the development of various bioremediation techniques. Bioremediation is based on the natural biological and physical principles that have been developing in some species for

millions of years in which some organisms such as plants or microbes can take up metals and in doing so effectively remove them from the ecosystem (Moshiri 1993, Mistch and Wise 1998, Palmeri and Trepel 2002). For example, the use of *Typha latifolia*, *Phragmites australis*, and *Scirpus acutus* in the revegetation of mine tailings under wetland conditions (McCabe and Otte 2000). The benefits of revegetation of mine tailings include the reduction of erosion as well as the possible removal of hazardous substances.

In freshwater fish, the principal receptor site for toxic metals are the gill filaments where Na^+ and Ca^{2+} are transported from the water to the bloodstream (Chapman et al 1998). Sulfates can enter the organism through this portal and result in increased mineral excretion and weight loss in fish (Andres and Cline 1989). Metals can also enter the same way, but unlike organic compounds, they are not biomagnified in fish tissues (Chapman et al 1998).

i.iv Termination of Mining Operations

The termination of an open-pit mining operation results in two problems- the rehabilitation of the site and surrounding ecosystem, as well as the containment of any hazardous materials and elements released during the mining operation (Stevens and Lawrence, 1998). The sheer size of many pit lakes means that remediation may be very expensive and not very realistic (Miller et al 1996). This is, however, no reason not to try and remediate these systems. In this paper, the remediation of the Steep Rock pit lakes through the use of wetlands will be examined.

i.v GIS as a Tool in Remediation

Although Geographic Information System (GIS) is a relatively recent technology, it is becoming more accessible and important in the field of remediation and conservation biology. GIS is capable of storing, georeferencing, manipulating and displaying vast amounts of spatially variable information (Palmeri and Trepel 2002) and as such is an ideal tool for the complex analyses required in pollution and risk assessment models (Hendriks et al 1998). It has also been shown by Mattikalli and Richards (1996) that GIS systems are successful in hindcasting changes in surface water quality. As a system capable of hindcasting should also be able to forecast change, GIS (specifically ArcView 3.0 with 3D Analyst and Spatial Analyst, also versions 3.0) was selected for use in this study of changes and predictions of the Steep Rock pit lakes -two flooding meromictic pit lakes in Northwestern Ontario.

i.vi Objectives

This thesis has the following objectives:

1. To monitor the water quality of the Steep Rock pit lakes and predict the changes in concentration of the elements in the waters over time.
2. To construct a predictive model, using GIS, which estimates the depth of the oxygenated, fresh water lens in Caland pit lake as it changes over time.
3. To develop a model that describes the flooding pattern of the Steep Rock pit lakes over time.

4. To compare plant tissue concentrations from controlled experiments with that of representative plant species gathered from naturally occurring wetlands both in impacted and unimpacted areas of the former Steep Rock mine site.
5. To determine which of the four test species was the most effective in the remediation of specific elements and what combination of the species would provide optimal remediation of the Steep Rock pit waters.
6. To determine whether wetland remediation is a viable remediation alternative.

The first three of these objectives are addressed in Chapter 1 while the final three are discussed in Chapter 2 of this thesis. Appendix 1 contains a complete list of the equations used to predict the future concentrations of the elements in the pit lakes, while Appendix 2 describes a proposed *in situ* experiment that was performed in Hogarth pit lake during the summer of 2003 along with recommendation to improve its methodology (Appendix 2). Appendix 3 compares the predicted water chemistry values, with the Canadian Water Quality Guidelines (TWFQCCREM 1987).

1. Monitoring and the Use of GIS in Predictive Water Quality Models of an Abandoned Open Pit Iron Mine in Northwestern Ontario

1.1 Introduction

Pit lakes, formed when open pit mining operations cease and ground water fills the abandoned pits, are a new phenomenon – most pit lakes, in North America at least, are less than 25 years old (Miller et al 1996). Unlike most natural lakes which are usually much wider than they are deep, pit lakes are often quite deep (>300m) and have a small surface-area-to-depth ratio. Pit lakes, like crater lakes, often have high surrounding walls that result in the formation of a microclimate within the pit (Stevens and Lawrence 1998). Other characteristics of pit lakes are the lack of an extensive sediment layer, and often high concentrations of dissolved material, particularly metal complexes in the water column (Ripley et al 1996). Finally, pit lakes may experience quick and radical changes in water levels.

Because of the influx of saline ground water, and/or the accumulation of inorganic salts, mixing of the upper strata (less dense layer) with the lower portion (more saline water) is inhibited and a pit lake basin can become meromictic (Page et al 1984; Axler et al 1996). Predicting whether mixing will occur is difficult in deep pit lakes, because the stability of the water column is such that these density layers may, to varying degrees, resist mixing (Cloern et al 1983; McGuire and Currie 1993). Often mixing only occurs in the upper layer, called the mixolimnion, which overlies the more saline water, or monimolimnion (Jorgensen et al 1979).

Although the sediment layer in pit lakes is generally not as deep as in natural lakes (Stevens and Lawrence 1998), the accumulated sediment may release contaminants resulting generally in poor water quality in pit lakes. The sediment layer in pit lakes comes generally from the erosion of tailings piles around the pit area by rising waters. Metal mine tailings are often characterized by being chemically reactive and as such, their oxidation may lead to increased acidity, and metal release (Ripley et al 1996). Furthermore, the texture of tailings can affect water retention leading to poor water retention and high evaporation rates (in the case of coarse tailings). At the other extreme, it can result in poor water infiltration (in the case of fine tailings). In either case, the tailings piles are often free of vegetation long after mining operations have ceased (McCabe and Otte 2000). For the preceding reasons as the tailings piles come into contact with rising flood waters, erosion is often amplified.

This study examines the water quality in two adjacent pit lakes at the abandoned Steep Rock Lake mine site previously described by McNaughton (2001). These pit lakes are both meromictic due primarily to high concentrations of sulfates (leading to saline water) coupled with their great depth. They differ, however, in their individual water quality. Caland, one of the pit lakes, supports life as it consists of a freshwater lens resting on a layer of denser, mineral enriched, water. A commercial fish farm (Snow Lake Fish Farm) operates within this lens. There are both fine and coarse tailings piles, supporting only sparse vegetation around both lakes. Eventually, these two pit lakes will join and discharge into the Seine River system. If the pit lakes are allowed simply to fill and flood without any remediation, the poor water quality of these lakes may adversely impact

areas downstream of the flood out point. Since the Seine River system feeds lakes on both sides of the Canadian-American border, this can become a matter of international concern.

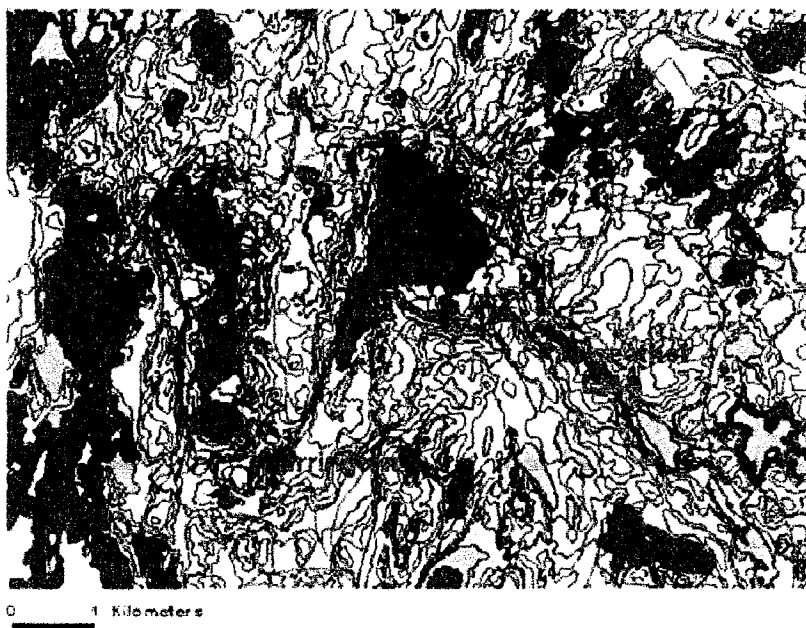
The objectives of this chapter are: to monitor the changes in depth and water chemistry of the Steep Rock pit lakes area in order to predict the flooding sequence of the pit lakes over time; and to develop models which will allow for the estimation of the concentrations of major elements in the pit lakes when flood-out occurs.

1.2 Methods

1.2.1 Site Description

The study site (Fig. 1.1) was previously described in detail by McNaughton (2001). The Steep Rock iron mines operated from 1944 to 1979 and impacted an area of 4000 ha by its activities (Ripley et al. 1996, Rabbitts et al. 1971). These activities included the diversion of the Seine River by the construction of numerous dams, weirs and tunnels, as well as the draining of the Middle, East and Southeast arms of Steep Rock Lake (5.7×10^{11} L of water) and the removal of 2.15×10^8 m³ of overburden (Steep Rock Resources Inc., 1986) to expose the two major ore bodies (found in Caland and Hogarth pits) as well as two smaller deposits (Errington and Roberts). The Southeast arm became isolated as a result of this draining and formed a separate lake (Fairweather Lake). As with nearly all open pit mining operations, cessation of mining resulted in the termination of the pumping of seepage water out of the pits (Sowa 2002). This led to the gradual filling of the pit lakes and the erosion of tailings piles within the pit basins.

Figure 1.1 Water Quality Sampling Sites at the Former Steep Rock Mine Site



In total, four pit lakes have formed, in addition to Fairweather Lake: two major lakes (Caland and Hogarth) as well as two minor lakes (Roberts and Errington). The major pit lakes are both meromictic due primarily to an abundance of sulfates coupled with incomplete mixing caused by their great depth, but differ considerably in their individual water quality (McNaughton 2001). At present, Caland supports a diverse community of organisms while Hogarth is apparently devoid of life. Continued flooding will greatly affect the operation of the Snow Lake Fish Farm which raises Rainbow trout (*Onchorhynchus mykiss*) in a net pen culture system in Caland (McNaughton 2001). This culture system is dependent in large part upon the volume of the oxygenated freshwater lens on the surface of the lake. As water levels increase, Caland will flood into a large area to the south with a relatively low slope. The effect of this will be a progressive decrease in the depth of the fresh water lens which will subsequently affect the fish farm. Both fine and coarse tailings piles, supporting only sparse vegetation, are evident around the two pit lakes. Eventually these two pit lakes will fill with water, join and discharge into the west arm of Steep Rock Lake and from there into the Seine River system. If the pit lakes are allowed simply to fill and flood without any remediation, their poor quality water may severely impact areas downstream of the point of discharge. As the Seine River system feeds lakes on both sides of the Canadian-American border, is a matter of international concern.

1.2.2 Field Procedures

1.2.2.1 Water Quality Monitoring

Water samples were collected using a Kemmerer bottle on a calibrated rope and placed in polyethylene bottles from two locations at Caland Lake (Figure 1.1). The first site, (Site A, N 48° 48' 984", W 091° 38' 613") was located at the Northwest end of the lake, behind the only island. The second site (Site B, N 48° 49' 090", W 091° 36' 333") was located near the eastern end of the lake, below a trailer located on the shore. Water samples (500ml each) were taken at both sites at depths of 2m, 18m and 1m off the bottom. These depths were chosen so as to get a sample from each of the mixolimnion, chemocline, and monimolimnion as well as to coincide with water samples taken in previous studies of the same pit lakes (McNaughton 2001). Dissolved oxygen and temperature profiles were obtained to a depth of 40m for both sites A and B (YSI model 57 dissolved oxygen/temperature probe). Water samples, temperature and DO profiles were also collected from two sites on Hogarth, (Figure 1.1) labeled A and B (N 48° 48' 753", W 091° 38' 647" and N 48° 49' 083", W 091° 38' 699" respectively) at three depths (2m, 18m, and 1m off bottom). The water samples were not filtered.

1.2.2.2 Laboratory Procedures

Water samples were analyzed at the Lakehead University Environmental Laboratory (LUEL) in Thunder Bay, Ont. adhering to strict Quality Assurance/Quality Control (QA/QC) guidelines. A blank sample was run for each test, followed by a standardized QA/QC sample and then a repeat of a field sample. LUEL standard operating procedures were followed for all tests (LUEL 2003). These protocols were modified from Standard

Methods for the Examination of Water and Wastewater 18th ed. by Greenberg et al (1992). Table 1.1 lists the parameters determined for in the water samples collected from both Caland and Hogarth Pit Lakes.

Table 1.1 Water Chemistry Parameters Determined at each Sampling Site in Caland and Hogarth Pit Lakes

Alkalinity	pH
Aluminum	Potassium
Calcium	Sulfate
Chlorine	Sodium
Conductivity	Strontium
Copper	Sulfur
Dissolved Organic Carbon	Total Dissolved Solids
Free Ammonium	Total Nitrogen
Iron	Total Phosphorus
Magnesium	Total Suspended Solids
Manganese	Vanadium
Nickel	Zinc
Nitrate	

1.2.2.3 Data Analysis

Data gathered in 1998, 1999, 2002, 2003, and 2004 were separated into two subsets –one representing Caland, the other for Hogarth. Repeated measures ANOVA’s were performed for each of the parameters for which there were sufficient data (at least ½ of all samples showing above detection limits) in order to test for significant differences ($p < 0.05$) over time. In those cases where the ANOVA showed significant differences, Paired-comparison tests determined which years differed from the others.

1.2.3 Predicting Water Level Changes

Mattikalli and Richards (1996) demonstrated that GIS systems can successfully hindcast changes in surface water quality. As a system capable of hind-casting should also be able

to forecast change, GIS was selected for use in this study of changes and predictions for the Steep Rock pit lakes. The GIS analysis was performed on a 10m Digital Elevation Map (DEM) file obtained from the Ontario Ministry of Natural Resources (OMNR), using ESRI's ArcView v. 3.0, with the spatial analyst, 3D analyst, geoprocessing, and Xtools extensions enabled (Mattikalli and Richards 1996).

1.2.3.1 Flooding Prediction Model

In order to predict the extent of areas within the pit lakes that would be flooded at any given time, a physical model, based upon surface filling of a basin, was created using ArcView. The DEM file was clipped to include only those points contained within the predicted flood boundary of Caland (those points bounded by 380m contour), and for those points contained within the flood boundary for Hogarth (again bounded by 380m contour). As filling would occur separately for each pit until just prior to flood out (in the year 2030), the eastern (Caland and Errington) pits were treated separately from the western (Hogarth and Roberts) ones. Polygons were created for each of the four pits at 10m intervals (approximately 3 year intervals). Using these polygons, visual records of flooding at each point in time were generated. As flooding progressed, the pit lakes joined and these new lakes were treated as single pits. In order to include flood out in the prediction, a new dataset was created by clipping the DEM to include all points bounded by the 390m contour line.

1.2.3.2 Change in Oxygenated Freshwater Lens Depth over Time

The DEM file was clipped to include only those points contained within the predicted flood boundary of Caland (those points bounded by 380m contour). This newly clipped file created a Triangular Irregular Network (TIN) for the computation of volumes. The volume of water contained in the fresh water lens was calculated by subtracting the volume of water contained below an elevation of 270m from that contained below 289m (the water level as of 2003 was at an elevation of 289m with the fresh water lens extending to a depth of 19m). Using historical data on water level elevations of Caland over time provided by OMNR (2003), the following equation was created which estimated future elevations in water level:

$$\text{Lens Depth (in m)} = 9192.9527 * (\ln(x)) - 69586.2043$$

Where:

$$x = \text{year}$$

Using this equation, the predicted elevation for Caland was computed for every third year from 1998 to 2030. Water volumes were then calculated from the predicted elevations between 1998 and 2030. Using these predicted values and the volume of the fresh water lens previously calculated, the proportion of the volume which consisted of fresh water was calculated over time. The proportions were applied to the estimated depths of Caland at each associated year in order to obtain an estimate of the depth of the freshwater lens at any point in time.

1.2.4 Predicted Water Quality

Water chemistry data gathered in 1992, 1998, 1999, 2002, 2003, and 2004 were employed in regression equations (using SigmaPlot 8.0) that estimated the levels of each element or variable for the monimolimnion that showed significant variation over time. Only the monimolimnion levels were used because as flooding continues, the lakes will spill into larger basins, the mixolimnion will then thin out to become proportionally less prevalent, and eventually, negligible. The type of regression equation used for each variable was chosen to represent the best fit to the data. For Caland, a 2-parameter logarithmic regression was most appropriate for Cu, while DOC and TSS equations were determined by linear regression. The equations for NO₃, Sr, and Zn were determined by third order logarithmic, 4 parameter sigmoidal, and first order inverse regressions, respectively. For Hogarth, Ca, conductivity, DOC, Ni, SO₄ and Zn equations were calculated using linear regression while 4-parameter sigmoidal regressions provided the equations for Cl and Sr. The equations for alkalinity and pH were calculated using 3-parameter power and first order inverse regressions, respectively. Since other variables did not change significantly, the means and standard deviations were used as the predictors of future levels. These equations can be found in Appendix 1. From these equations, the predicted concentrations for Caland and Hogarth at 380m elevation (approximately in the year 2027) were calculated. In ArcView (v. 3.0), the volume of water contained within the lake basins below 380m and above 390m elevations was calculated (in m³ and then converted to L) using a TIN created from the 10m contour layer. The volume difference between these two elevations was also computed. Using the volume of water (in L) below 380m, the mass of each element present was calculated

for both pits, converted to mg, and summed up to provide the total predicted mass of elements present in water below 380m elevation. Next, the volume of water present between 380 and 390m was used to convert the concentrations of each element into the mass (in mg) estimated to be present in this volume of water. The total mass present below 380m was then added to the mass predicted between 380 and 390m to give the total predicted mass of elements in the pit lake waters at flood out (390m elevation). Using the total volume of water in the pits at 390m (in L), the total predicted mass (in Kg) was reverted back into concentrations (mg/L). For example, in 2027, Al will have a concentration of 0.091 mg/L in Caland, which at an elevation of 380m contained 4.237×10^{11} L of water, yielding a total of 38.555 tonnes Al. The concentration in Hogarth in 2027 will be 0.112 mg/L and the volume will be 2.180×10^{11} L, giving a total of 24.414 tonnes Al. Between 380m and 390m elevation, an additional 1.071×10^{11} L of water will enter the system. Since at this point the two pit lakes have joined, the average concentration estimate (0.1015 mg/L) was used to calculate the mass of Al present in this volume (10.873 tonnes Al). These three masses were then added together and divided by the total volume of water present at an elevation of 390m (7.4879×10^{11} L) to get an estimated concentration at flood out of 0.099 mg/L of Al.

1.3 Results

1.3.1 Water Chemistry Analysis

Table 1.2 shows the mean annual levels of chemicals from the monimolimnion of Caland between 2002 and 2004. When comparisons were made over time (1998-2004) using repeated measures ANOVA's, it was found that Alkalinity, Conductivity, DOC, K, NO₃, pH, SO₄, TDS, and TKN (total Keldjal Nitrogen) showed significant differences ($p < 0.05$) for Caland. Figure 1.2 shows the mean trends for a selection of these variables in Caland. Conductivity showed a fluctuating pattern in the mixolimnion with significant increases between 1999 and 2002 and between 2002 and 2004. In the monimolimnion, conductivity decreased from 1999 to 2003. DOC, for both mixolimnion and monimolimnion, had significantly lower concentrations in 2002 and 2003 compared to 1999. In the mixolimnion, K showed a significant decrease from 1999 to 2002, then a significant increase from 2002 to 2004. The K in the monimolimnion exhibited a significant decreasing trend from 1998 to 2003. In both layers, NO₃ exhibited a significant decrease in concentrations between 1999 and 2004. SO₄ in the mixolimnion only exhibits a significant decrease from 1999 to 2002. Monimolimnion SO₄ decreased from 1999 to 2002 and then increased. SO₄ levels between 2002 and 2004 were significantly different (Table 1.2). TDS in the mixolimnion decreased between 1999 and 2002 while in the monimolimnion there were no significant differences.

Table 1.2: Annual Means of Parameters Measured in the Monimolimnion of Caland Pit Lake

		2002	2003	2004
Alkalinity α	Mean	163.75	169.97	178.35
	Std Dev	11.42	11.93	3.46
Conductivity α	Mean	981.67	962.5	1092
	Std Dev	71.32	84.58	19.8
DOC α	Mean	1.58	1.92	2.28
	Std Dev	0.29	0.25	0.07
Ca	Mean	116.17	108.02	126.25
	Std Dev	12.2	22.15	1.63
Cl	Mean	9.31	12.01	7.63
	Std Dev	0.72	5.16	2.89
K α	Mean	4.83	4.6	5.05
	Std Dev	0.56	0.48	0.13
Mg	Mean	59.34	51.5	64.22
	Std Dev	6.28	9.8	1.44
Na	Mean	16.7	14.29	16.84
	Std Dev	2.47	3.22	0.35
NO₃ α	Mean	2.11	1.77	1.36
	Std Dev	0.35	0.29	0.19
Al	Mean	0.01	0.13	0.07
	Std Dev	0	0.24	0.03
Fe	Mean	0.02	0.18	0.16
	Std Dev	0.01	0.38	0
Mn	Mean	0.03	0.13	0.38
	Std Dev	0.03	0.25	0.21
Ni	Mean	0.01	0.01	0.01
	Std Dev	0	0.01	0
S	Mean	128.12	97.2	208.03
	Std Dev	16.46	56.87	88.49
Sr	Mean	0.92	0.93	1.43
	Std Dev	0.09	0.05	0.61
Zn	Mean	0	0	0
	Std Dev	0	0	0
SO₄ α	Mean	342.08	379.55	387.15
	Std Dev	28.03	37.21	12.52
pH	Mean	7.16	6.71	6.52
	Std Dev	0.3	0.21	0.04
TDS α	Mean	708.8	748.35	769.4
	Std Dev	56.99	52.31	8.77
TKN α	Mean	0.16	0.19	0.12
	Std Dev	0.06	0.06	0.04
TSS	Mean	3.53	43.8	6.05
	Std Dev	0.6		3.46

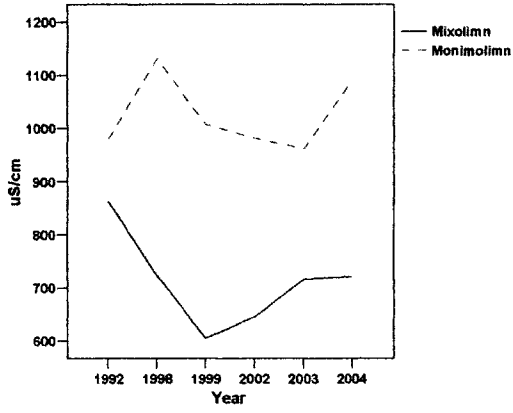
α = significant difference ($p < 0.05$) noted over time

Results shown in table 1.2 are given in mg/L except for alkalinity

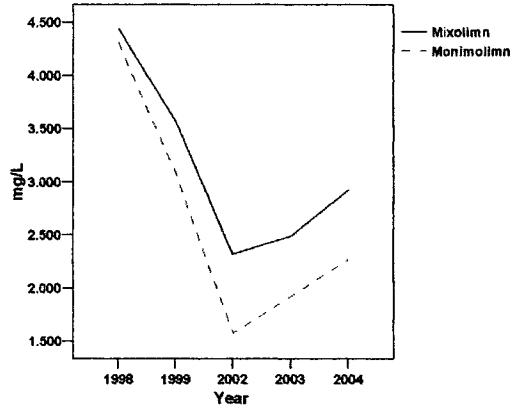
(mgCaCO₃/L), conductivity (μ S/cm), and pH.

Figure 1.2: Mean Concentrations over Time for Caland Pit Lake

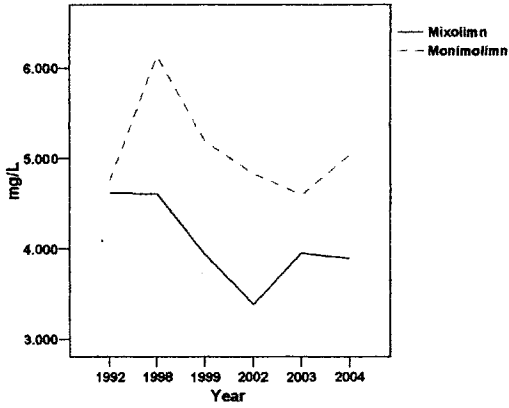
Conductivity



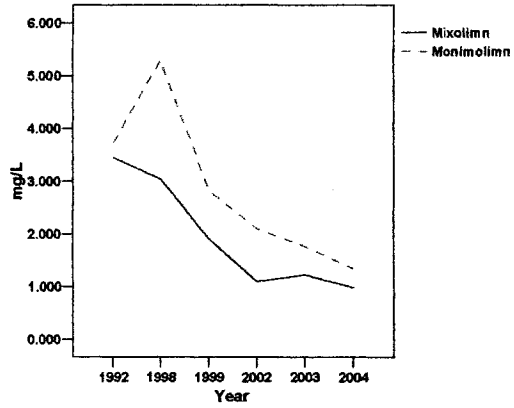
DOC



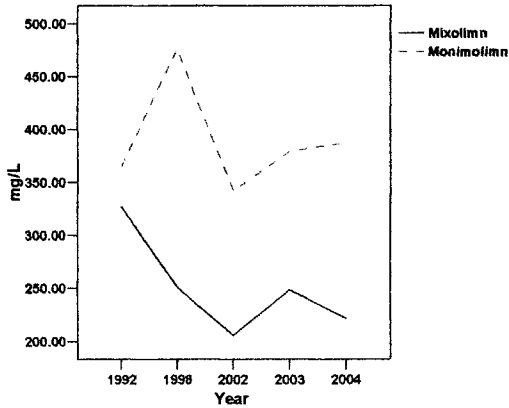
K



NO₃



SO₄



TDS

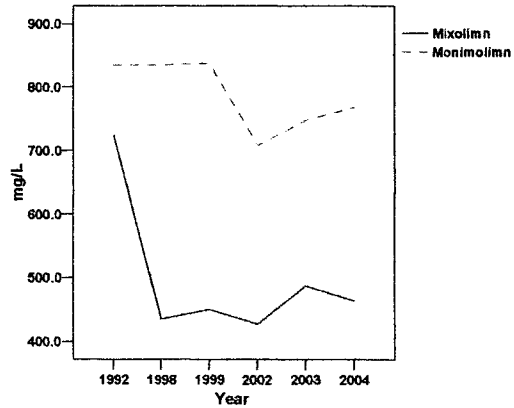


Table 1.3 shows the annual means of parameters from the monimolimnion of Hogarth between 2002 and 2004. When comparisons were made over time, repeated measures ANOVA's found that Ca, Cl, Conductivity, DOC, K, Mg, NO₃, pH, SO₄, Sr, and Zn exhibited significant differences for Hogarth from 1998 to 2004. Figure 1.3 shows the same variables as in Fig. 1.2, changing over time in Hogarth. In the mixolimnion, a significant decrease in conductivity levels of the mixolimnion was noted between 2002 and 2003 followed by a rapid significant increase in 2004. The opposite trend was noted for DOC, with an increase between 2002 and 2003 followed by a decrease to 2004. A significant decrease was noted in DOC, K, and Mg between 1999 and 2002, and to 2003 for NO₃ and SO₄. NO₃ and SO₄ both experienced significant increases between 2003 and 2004. K and Mg exhibited a significant increase between 2002 and 2004, with Mg showing an overall decrease compared to its levels in 1999. In the monimolimnion, there was no significant difference in conductivity or K, although there seems to be an increasing trend for conductivity. Levels of Mg and NO₃ decreased significantly between 1999 and 2002 and, although Mg then experienced an increase in 2004, the net change was still a decrease. Between 1999 and 2002, SO₄ concentrations increased significantly. Although the monimolimnion did not yield sufficient data points above detection limits to permit a paired comparison test of DOC to be performed, it appeared that the situation was one of decreasing concentrations.

Table 1.3: Annual Means of Parameters Measured in the Monimolimnion of Hogarth Pit Lake

		2002	2003	2004
Alkalinity	Mean	103.53	114.67	115.2
	Std Dev	5.65	1.29	
Conductivity α	Mean	2383.33	2400	2460
	Std Dev	21.6	52.92	0
DOC α	Mean	0.78	0.67	
	Std Dev	0.18	0.21	
Ca α	Mean	316.37	306.1	317.95
	Std Dev	11.38	8.31	1.06
Cl α	Mean	13.42	13.94	13.73
	Std Dev	1.48	0.69	0.06
K α	Mean	6.15	7.14	6.67
	Std Dev	0.48	0.06	0.02
Mg α	Mean	183.52	201.01	196.3
	Std Dev	16.88	2.15	0.42
Na	Mean	23.44	25.97	23.55
	Std Dev	0.85	0.59	0.17
NO3 α	Mean	0.97	0.94	0.82
	Std Dev	0.11	0.1	0.01
Al	Mean	0.19	0.04	3.11
	Std Dev	0.4	0.03	3.68
Fe	Mean	0.98	0.21	19.45
	Std Dev	2.29	0.22	22.66
Mn	Mean	0.21	0.03	1.61
	Std Dev	0.18	0.01	2.11
Ni	Mean	0.06	0.04	0.09
	Std Dev	0.01	0	0.06
S	Mean	530.2	483.66	452
	Std Dev	41.5	13.93	5.66
Sr α	Mean	1.41	1.13	1.26
	Std Dev	0.09	0.13	0.06
Zn α	Mean	0.01	0	0.02
	Std Dev	0	0	0.02
SO4 α	Mean	1436.17	1437.91	1473.92
	Std Dev	80.7	99.47	16.02
pH α	Mean	6.81	6.46	6.32
	Std Dev	0.29	0.14	0.01
TDS	Mean	2259.97	2359.93	2274.5
	Std Dev	48.91	40.8	10.89
TKN	Mean	0.11	0.04	0.05
	Std Dev	0.08	0.02	
TSS	Mean	27.34	35.5	523.4
	Std Dev	22.65	26.07	671.33

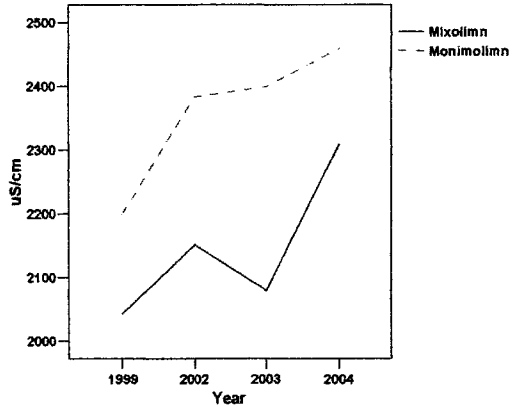
α = significant difference ($p < 0.05$) noted over time

Results shown in table 1.2 are given in mg/L except for alkalinity

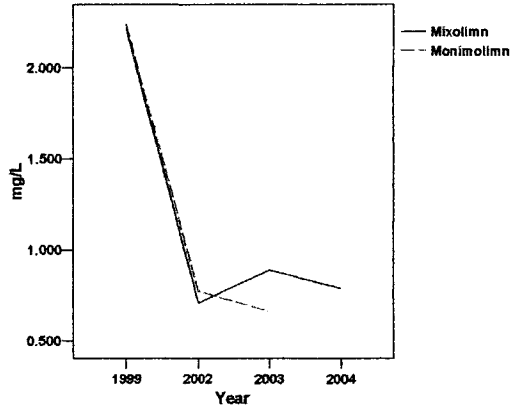
(mgCaCO₃/L), conductivity (μ S/cm), and pH.

Figure 1.3: Mean Concentrations over Time for Hogarth Pit Lake

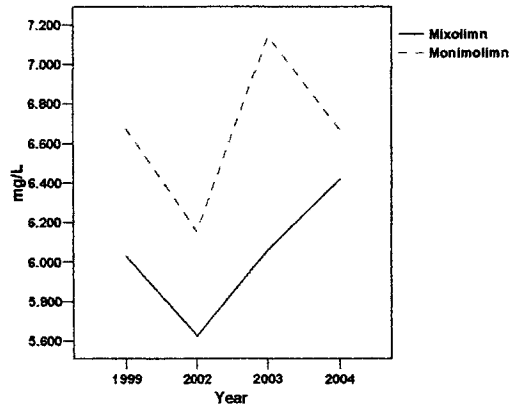
Conductivity



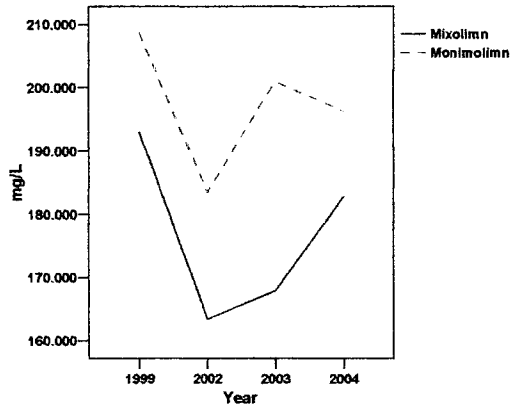
DOC



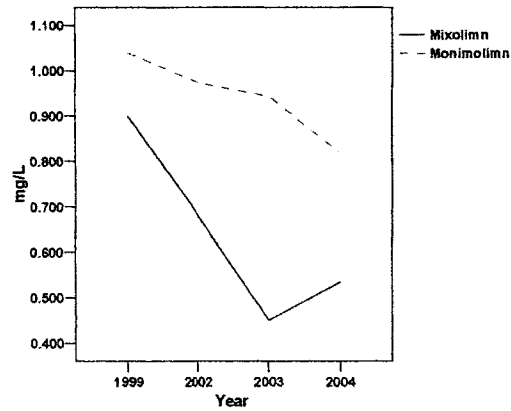
K



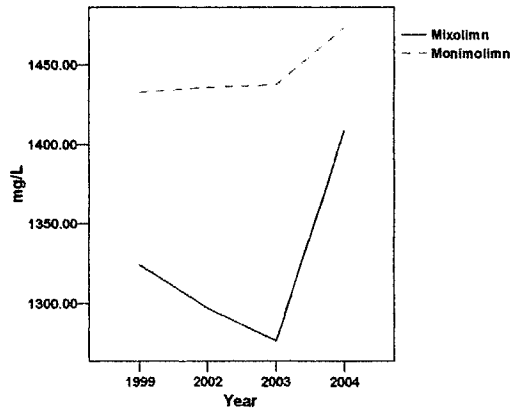
Mg



NO₃



SO₄



1.3.2 Flooding Prediction Model

Using ArcView 3.0, polygons were created to represent the increases in water levels over time in 10m increments. Figure 1.4 shows that Hogarth and Roberts pit lakes (Northwestern and Southwestern lakes respectively) join sometime between the years 2000 and 2003. Caland is predicted to join with Errington Pit Lake (Northeastern and Southeastern respectively) between 2015 and 2018. At this point, there will be two visible lakes (Western and Eastern), each with two basins. This situation is expected to continue until the two lakes finally join and the entire area is submerged sometime between 2027 and 2030. Flood out is expected to occur sometime between 2027 and 2030 as well. The red zone in the upper left side of the polygon for 2030 represents the point at which flood out is expected to occur.

Figure 1.4: Predicted Flooding Sequence within the Steep Rock Pit Lakes Basin

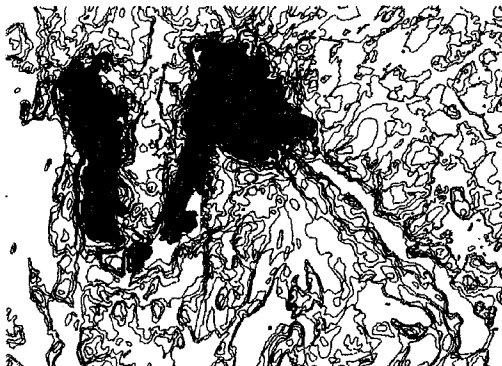
290m elevation (2000)



300m elevation (2003)



340m elevation (2015)



350m elevation (2018)



380m elevation (2027)



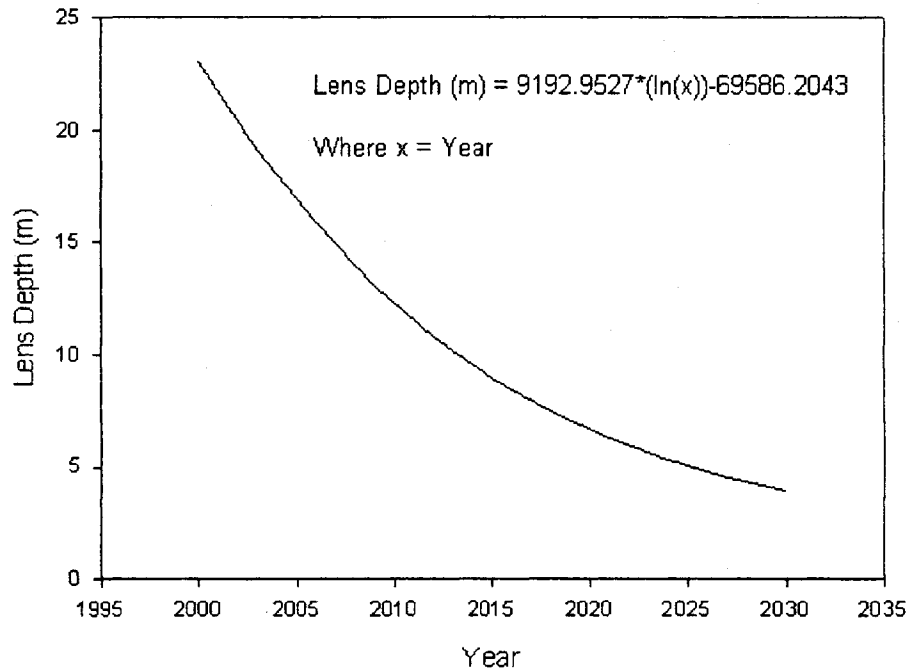
390m elevation (2030)



1.3.3 Change in Oxygenated Freshwater Lens Depth over Time

Figure 1.5 shows the predicted depth of oxygenated water contained within the Caland basin represented by the layer of water exceeding 6 ppm DO. The volume of the fresh water lens is assumed to be static over time. The depth of the oxygenated lens shows a logarithmic decrease over time.

Figure 1.5: Predicted Depth of Freshwater Lens in Caland Pit Lake over Time



1.3.4 Estimated Concentrations at Flood out

Equations were calculated for all chemical factors that changed significantly over time (Appendix 1). If no significant trend was observed over time for an element, the mean and standard deviation were used as the predictor. The estimations of the concentrations present in Caland and Hogarth pit lakes in 2027 were calculated separately as they will join just prior to flooding (estimated to be in the year 2030). Table 1.4 shows the estimated concentrations of various constituents and variables for Caland and Hogarth prior to joining (2027) and at flood out (2030). In 2027, Ca, K, Mg, Na, Mn, Ni, S, SO₄, Sr, V, and TDS show significantly higher levels in Hogarth when compared to Caland. The predicted pH in Hogarth is also significantly different from that in Caland, showing a steady decline over time. Conversely, alkalinity, DOC, NO₃, Ba, and TKN show significantly higher concentrations in Caland than in Hogarth.

Table 1.4: Predicted Future Concentrations of Hogarth and Caland Pit Lakes and the Combined Steep Rock Pit Lake at Flood Out

	Caland in 2027	Hogarth in 2027	Flood out (2030)
Al	0.091 ± 0.199	0.112 ± 0.281	0.099
Alkalinity	166.957 ± 10.671	152.782 ± 9.3531	161.816
Ca	115.818 ± 17.610	173.649 ± 9.6525	136.79
Cl	11.081 ± 3.494	21.761 ± 1.2492	14.954
Conductivity	985.721 ± 78.527	3043.3476 ± 67.9201	1731.913
Cr	0.006	0.011	0.008
Cu	0.113 ± 0.001		0.072
DOC			
Fe	0.078 ± 0.227	0.635 ± 1.593	0.28
K	4.845 ± 0.59	6.461 ± 0.627	5.431
Mg	57.611 ± 9.295	190.623 ± 17.331	105.847
Mn	0.095 ± 0.172	0.171 ± 0.153	0.123
Na	16.083 ± 2.936	24.282 ± 1.327	19.056
NH4	0.093 ± 0.088	0.102 ± 0.103	0.096
Ni	0.009 ± 0.006	0.0018 ± 0.0113	0.006
NO3		1.036 ± 0.204	0.376
pH	7.054 ± 0.363	4.875 ± 0.2515	6.264
S (total)	112.663 ± 43.057	514.687 ± 40.821	258.456
SO4	367.656 ± 47.001	1729.1885 ± 23.1153	861.411
Sr	0.937 ± 0.0909	1.3429 ± 0.1813	1.084
TDS	750.390 ± 68.913	2305.153 ± 98.570	1314.22
TKN	0.198 ± 0.088	0.086 ± 0.066	0.157
Total P	0.012 ± 0.013	0.009 ± 0.002	0.011
TSS	1010.4001 ± 0.5965	28.170 ± 22.061	654.198
V	0.271 ± 0.167	0.631 ± 0.243	0.402
Zn			0

Results shown in table 1.2 are given in mg/L except for alkalinity

(mgCaCO₃/L), conductivity (µS/cm), and pH.

Those spaces that are left blank are predicted to fall below instrument detection limits

1.4. Discussion

1.4.1 Variations in Chemical Composition

Figure 1.2 showed the concentrations of six variables for Caland. The majority of the variables in Caland exhibited different trends in the mixolimnion compared to the monimolimnion. This is not surprising as the density gradient inhibits mixing (Cloern et al 1983; Stevens and Lawrence 1998), allowing the layers to behave differently. The stagnant monimolimnion (Fry 1986) does not mix and as a result, the concentration of suspended matter decreases leading to a decline in conductivity. Conductivity and TDS in the mixolimnion increased consistently from 2002 to 2004. This may have been due to erosion as rises in water levels and wave action erodes more tailings piles adding more particulate matter to the system. SO_4 was shown to be decreasing in the monimolimnion, likely due to its reduction to sulfides. Bottom waters of pit lakes are often rich in S and sulfidic compounds (Fry 1986). It is important to note that the process of SO_4 reduction, as carried out by anaerobic, sulfur-reducing bacteria, results not only in the increase of sulfides, but also of alkalinity (Last 1993). Alkalinity did indeed increase significantly between 2002 and 2004. Although no significant trend was observed, the levels of S compounds in the monimolimnion of Caland (Table 1.2) appears to have increased between 2002 and 2004. The combination of these two trends implies the activity of sulfur-reducing bacteria in Caland. The mixolimnion also exhibited a decrease in SO_4 , but, for unknown reasons, only during the period between 1999 and 2002.

Fig. 1.3 showed, in detail, the concentrations of six variables in Hogarth. Of the six variables examined (conductivity, DOC, K, Mg, NO_3 , and SO_4) only DOC and Mg

behaved similarly in both the mixolimnion and monimolimnion. In both cases, Mg decreased over time. While conductivity in the isolated monimolimnion did not change significantly over time, that of the mixolimnion displayed a net increase, perhaps due to increased input from erosion as a result of heavy flooding in the spring of 2002. DOC in the mixolimnion was shown to decrease rapidly between 1999 and 2002 only to rebound slightly in 2003. In the monimolimnion the same behavior was observed. As Hogarth is devoid of life (McNaughton 2001), the source of this organic carbon is unknown. It may be composed of pollen and other organic matter blown or eroded into this pit lake such as hummic substances from the surrounding soil. Input of vegetation resulting from erosion of the surrounding areas may be responsible for the input of organic carbon. The tailings piles, many of which support at least some plants, are continually contacting the rising water levels. Surrounding those tailings piles that have come into contact with water are rings of eroded and suspended sediment. These rings, bright red-orange in color, are present even in calm water. As water levels continued to rise in these pit lakes, an increasing number of tailings piles began to erode which resulted in elevated concentrations of many constituents, including SO_4 (Razowska 2001). In Hogarth, the trend in concentration of SO_4 mimicked that found in Caland, although the concentrations were roughly doubled, possibly due to deposits of sulfidic ore (Eary 1998; Knoller et al 2004) in the catchment of the Hogarth basin, or possibly due to greater erosion of tailings.

1.4.2 Flooding Prediction Model

Fig. 1.4 showed that, since the two major basins (Hogarth and Caland) do not join until 2027 - 2030, they can be considered separately until then. The flooding model predicts the location of the outfall of the Steep Rock pit lakes into the west arm of Steep Rock Lake and into the rest of the Seine river system which may assist in the planning of remedial action to minimize the effects that this flooding will have on the Seine river system. The model accurately predicted that Hogarth and Roberts would join between 2000 and 2003. The two lakes actually connected in the spring of 2002 (Jackson pers comm. 2002).

1.4.3 Change in Oxygenated Freshwater Lens Depth over Time

Fig. 1.5 depicted a progressive decline in the depth of the oxygenated freshwater lens present in Caland. Based upon data collected between 1998 and 2003, this model has been shown to be accurate in predicting the depth of the lens. The observed decrease in depth is likely due to the presence of the fish farm in the pit lake. Axler et al (1996) were able to prove that intensive aquaculture results in decreased concentrations of dissolved oxygen when compared to the condition of the pit lakes prior to any aquaculture operations and compared to unused pit lakes. This prediction is limited since it assumes that freshwater inputs and evaporation are equal which may not be the case. However, despite this limitation, the model predicted a lens depth of 19.036m in 2003 compared to the actual measurement of this depth which was 19m.

1.4.4 Predicted Water Quality

Currently significantly different concentrations occur in 18 of the 29 variables monitored in the water within each of the two pit lakes (Figs 1.2 and 1.3). Hogarth showed significantly higher ($p < 0.05$) concentrations of Ca, K, Mg, Na, Mn, Ni, S, Sr, V, SO₄, Conductivity and TDS when compared to Caland. The pH in Hogarth is significantly lower ($p < 0.05$) than that of Caland as is the levels of alkalinity, DOC, NO₃, Ba, and TKN. The relatively elevated levels of dissolved organic carbon (DOC) found in Caland is at least partially due to the presence of the Snow Lake fish farm and its associated inputs of organic matter (Axler et al 1996). The elevated sulfate levels in Hogarth are most likely due to the high S content of ore deposits in the area (Mitsch and Wise 1998; McNaughton 2001). These two water bodies behave independently in terms of their water quality changes over time.

As flooding connects the pits, the water quality will also change (Table 1.4) so that at flood out Cr, and Cu levels will exceed the guidelines for the preservation of aquatic life in Canada. Also, Mn, S, SO₄, and TDS will exceed the safe levels for drinking water in Canada (0.05mg/L, 0.05mg/L, 500mg/L, and 500mg/L respectively) (TFWQCCREM 1987). SO₄ concentrations will also exceed the United States EPA guidelines (Castro and Moore 2000), by more than a factor of 3. Fe is predicted to attain levels only slightly lower than the limits set for the preservation of aquatic life and human consumption. Cr, although exhibiting a stimulatory effect on plant life, has negative and bioaccumulatory effects on fish, more so in bottom feeders than in those that live in the upper layers (Jordao et al, 1997). Cu toxicity produces gill damage that disrupts ion regulation,

causing an acid-base imbalance, and decreases oxygen transfer from water to blood (Carvalho et al 2004). In Atlantic salmon (*Salmo salar*) LC₅₀ toxicity concentrations for Cu can be as low as 0.036 mg/L (Gray 1998). Fe toxicity in fish clogs and damages the gills leading to suffocation (Dalzell and MacFarlane 1999; Henry et al 2001). Mn toxicity is of concern as it bioaccumulates readily (Adam et al 1997). In humans, toxicity to sulfur-compounds occurs once threshold levels have been exceeded (Komarnisky et al 2003). The effects of TDS toxicity cannot be predicted since it is the effect of additive, antagonistic, or synergistic interactions of all the chemical components that are a part of the dissolved loading of the water (Chapman et al 2000; Goodfellow et al 2000; LeBlond and Duffy, 2001), but TDS of mine effluent typically causes toxicity at the parts per million (ppm) level (LeBlond and Duffy, 2001). The metals and metal compounds previously stated would have negative impacts on aquatic life if allowed to enter the Seine River system without treatment. Also, as many people live, at least part time, or camp along the Seine River and the lakes it feeds, drinking the waters in the process, (Quetico Provincial park, and the White Otter Wilderness in Canada, and the Boundary Waters Canoe Area Wilderness in Minnesota) there is potential for impacts to human health as well.

1.5 Implications and Conclusions

Section 1.4.4 discussed water quality after flood out and compared contaminants with the Canadian Water Quality Guidelines for the preservation of aquatic life as well as those for human water consumption (TFWQCCREM 1987). The results show exceedance of several parameters. Cr, and Cu will reach levels exceeding the guidelines for the preservation of aquatic life in Canada (2.0 ug/L and 4 ug/L respectively), while Mn, S, SO₄, and TDS will exceed the levels defined as safe for human consumption (0.05 mg/L, 0.05 mg/L, 500 mg/L, and 500 mg/L respectively). This is important when considered in the context of what will happen in the years after flooding. The Seine river system flows South beyond Atikokan, Ont. before turning West, eventually reaching Rainy Lake near Fort Frances Ont. It also influences water quality in many lakes along this course, some contained partially or entirely within the United States. Therefore, any input of contaminated water could have serious impacts as far west as Rainy Lake and, through a network of lakes, South into the United States.

An important effect of the pit lake water will be its high salinity. When the Steep Rock pit lakes flood into the Seine River, the inflow of dense, saline water may, instead of mixing, force the fresh water of the Seine River to ride over it thus preventing mixing and dilution (Cloern et al 1983; McGuire and Currie 1993). Hence, this anoxic, saline bottom layer will adversely impact aquatic flora and fauna far downstream of the Steep Rock pit lakes.

Another concern is the unknown cause of extreme toxicity in Hogarth (McNaughton 2001). To remediate this pit, the exact cause of this toxicity must be identified so that it can be rectified prior to flood out. A future study should identify the cause(s) of this toxicity in Hogarth.

As mentioned in section 1.4.3, the implications of flooding to the Snow lake fish farm are severe. Likely, within 10 years, the freshwater lens will be less than 10 m deep. As the Snow lake fish farm utilizes net pen aquaculture and as these pens descend to a depth of 20m, a 10m lens of oxygenated fresh water may be insufficient to sustain a viable operation.

In conclusion, detailed water chemistry data gathered over several years, were used to develop models predicting the water chemistry of the pit lakes as they fill and flood out into the Seine River System. GIS technology was used to predict the flooding sequence of the pit lakes based on the regional topography and known rates of flooding.

2. Wetlands as a Means of Remediation of an Abandoned Open Pit Iron Mine in Northwestern Ontario.

2.1. Introduction.

In North America, the majority of base-metal mining occurs in the boreal forest region through open pit mining, a method designed specifically to exploit large ore bodies situated near the surface (EPA 2000). Although Canada lacks an accurate inventory of the quantity or type of waste stored in abandoned tailings sites, or even how many of these sites exist, an estimate of the total land area disturbed by open pit mining up to 1970 listed 18 000 ha as affected, with 4 000 ha of this resulting from the draining of Steep Rock lake (Rabbitts et al. 1971). With the closure of a mine come two main problems: the rehabilitation of the mine site and the containment of any pollutants generated by the mining operation (Stevens and Lawrence 1998). Today, mining companies retain responsibility for their mine sites after operations have been completed and are required to remediate these sites. Some sites, however, were abandoned before such legislation existed. These “orphaned” sites pose a significant problem in that an effective, long-term, low cost remediation technique must be found in order to treat these polluted sites (Ripley et al. 1996). Remediation efforts at these contaminated sites are often hindered and complicated by the presence of acid mine drainage (AMD) and high concentrations of toxic substances found in the tailings and waste piles which affect both surface and ground water supplies (Kadlec and Knight, 1996). In order to minimize the damage to the surrounding environment, these wastes must first be contained and protected from such environmental factors as wind and precipitation. Tailings piles often remain free of vegetation even years after mining operations cease (McCabe and Otte,

2000). Bare, dry mine wastes are highly prone to wind erosion. Also, the outer walls of tailings impoundment areas and piles are very susceptible to rainfall and snowmelt. This makes it easy for many contaminants they contain to enter adjacent land areas and infiltrate water systems (Ripley et al., 1996).

Submerging or revegetating these waste piles under wetland conditions can drastically reduce the effects of wind and water erosion (McCabe and Otte, 2000). Wetlands remove contaminants from the water and/or soil (Palmeri and Trepel 2002), as well as mediate the negative impacts of low pH and high concentrations of metals and SO_4 in acid mine drainage (AMD) (Moshiri 1993; Mitsch and Gosselink 2000; Palmeri and Trepel 2002). The mitigating effect of wetlands results from the ability of wetland plants to concentrate metals and other substances in their tissues (Peterson et al 1991; Raskin 1996).

While the uptake rates of metals varies across plant species, it also depends upon other factors such as: pH, exposure time, the concentration of metals in the environment, water and air temperature, water flow, and the depth to which removal occurs (Peterson et al 1991; Moshiri 1993; Manios et al 2003). Understanding these factors allows us to construct or modify existing wetlands to serve as remediation devices.

This study continues the investigations of McNaughton (2001) into the water chemistry of the former Steep Rock Iron Mines site near Atikokan, Ontario. In addition to investigation of the water chemistry using GIS methodology discussed in the first chapter of this thesis, this study examines the effectiveness of four local wetland species to

improve the water quality of Caland pit lake. This chapter had three objectives: (1) To quantify the effectiveness of metal uptake of each of the four species so as to determine if wetland treatment of the on-site tailings is a viable option; (2); To compare the plant tissue concentrations taken from the experimental plants with that of representative plant species (gathered from naturally occurring wetlands both in impacted and unimpacted areas of the former Steep Rock mine site) in order to determine the effectiveness of the plant species located outside of the controlled experiment and (3); To determine what combinations of the experimental plant species optimize remediation of the Steep Rock pit waters.

2.2. Methods:

2.2.1 Site Description:

The west arm of Steep Rock Lake (Fig 2.1), situated between the Steep Rock Pit Lakes and the Seine River system, was determined to be the most likely spot for the establishment of a treatment wetland. During the operation of the Steep Rock Iron Mines, the west arm of Steep Rock Lake was partially filled with overburden, decreasing its average depth from approximately 30m to closer to 3m (Jackson, pers comm. 2003). The shallower parts of this lake quickly became wetlands and were only eliminated by the installation of an overflow weir in 1992 (Jackson, pers comm. 2003) which increased water depth beyond that required for most aquatic macrophytes. This weir is still in place and adjustments to flow rates would drop the water level creating a site, approximately 620 ha in size. This would be suitable for the establishment of a treatment wetland to intercept contaminated water as flooding occurs. Figure 2.1 shows the Steep Rock pit lakes area at flood out (approximately 2030), with the proposed wetland (Steep Rock lake's west arm) highlighted in purple.

Figure 2.1: Steep Rock pit lakes at flood out

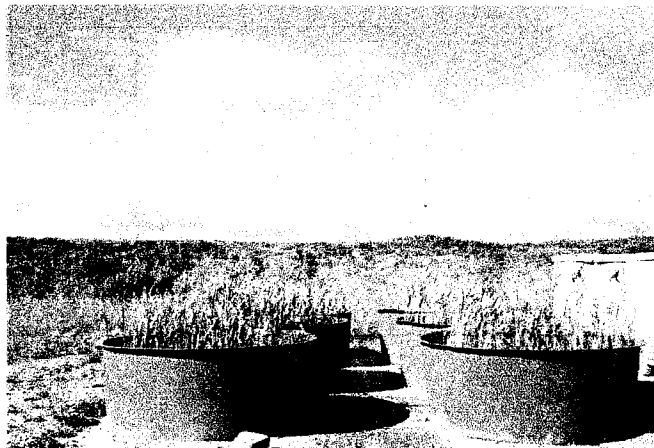


2.2.2 Experimental procedure:

Six round, plastic microcosms (180 centimeters diameter, and 1m tall) were used in the experiment (Fig 2.2). Thirty centimeters of sediment taken from the original lake bottom (from the north end of Fairweather Lake (Fig 1.1)) was placed in the tubs and gently hand packed. Two microcosms were filled with 20 centimeters of water from the mixolimnion (surface), two from the monimolimnion (> 24m deep) of Caland, and two from the head pond of the drinking water supply of the Snow Lake Fish Farm, which acted as the control water treatment. Each microcosm was divided into four quadrants into each of which 10 plants from one of the four test species (*Phragmites australis*, *Typha latifolia*, *Eleocharis smallii*, and *Carex sp.*) were placed. The water level in the microcosms was monitored and water was added from the appropriate source (mixolimnion,

monimolimnion, or control) whenever evaporation had noticeably lowered its level (approximately 250L every two weeks). Plant tissue and soil samples were collected in the fall of 2002 and 2003, dried, and analyzed for various chemical constituents.

Figure 2.2: Microcosms



2.2.3 Laboratory Analysis:

All the analytical methods followed the standard operating procedures of the Lakehead University Environmental Laboratory (LUEL 2003) which were adapted from Standard Methods for the Examination of Water and Wastewater 18th ed. (Greenberg et al 1992).

2.2.3.1 Plant Tissue Analysis

Plant samples were air-dried for three weeks at room temperature (approximately 20°C). These dried samples were ground to a fine powder, and 0.5g of each was then placed into 50 ml microwave vessels and digested with 3 ml concentrated HNO₃ (1.5 ml aliquots separated by 5 minutes) and 1 ml concentrated HCl (added three hours later). This

solution was allowed to sit overnight before 1 ml H₂O₂ was added in 0.5ml aliquots, waiting for bubbling to stop between aliquots. Replicates were run for each sample series (2002, and 2003), as were quality control samples. Solutions were slowly heated to 90°C (over the course of one hour) in a MARS 5 CEM microwave digester and then digested for 4 hours. When cooled, the samples were brought to 50 ml with double distilled water (DDW). The newly diluted samples were centrifuged at 1875 times the force of gravity for 10 minutes and then filtered in order to remove any particulate material left after digestion. The solutions were analyzed for metals in a Vista Pro CCD Simultaneous Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES).

2.2.3.2 Soil Analysis

Pore water was extracted from 35 ml of the collected soil samples by centrifuging at 1875 times the force of gravity for 40 minutes. This pore water was then analyzed for metals at the Lakehead University Environmental Laboratory (LUEL). A blank sample was run for each test, followed by a repeat of a field sample. Replicate samples were also run to ensure consistency. Soil metals were extracted from samples after they had been dried overnight at 35 to 37 °C. Ca, K, Mg, and Na were extracted by dissolving 5 g of the dried soil sample in 50ml Ammonium acetate solution. The samples were then mixed and filtered and 10ml of the filtrate was analyzed using a Vista Pro CCD Simultaneous ICP-OES. SO₄ was extracted in a similar fashion, with KCl as the extraction solution. 10 ml of the filtrate was measured into a scalar tube for colorimetric analysis. Metals (Fe, Mn, Cu, and Zn) were extracted from the soil by dissolving 1.0 g in 50 ml 0.1N HCL, mixing it and filtering into test tubes for analysis using a Vista Pro CCD Simultaneous ICP-OES.

Total K was analyzed by first digesting 1.0g of soil in 7.5 ml of a H₂SO₄ digestion mixture with 3 boiling beads in calibrated 75 ml test tubes. This solution was placed in a block heater where it was held at 150°C for 60 minutes, followed by 200°C until boiling stopped. The tubes were then heated to 380°C until the solution became transparent or yellow-straw at which point the samples were removed from the heat and allowed to cool for 3 to 5 minutes before 10 ml of DDW was added. After the samples had cooled completely, they were brought to the mark with DDW and mixed by inversion. The final solution was analyzed in a Vista Pro CCD Simultaneous ICP-OES.

2.2.4 Field Samples:

In order to compare the experimental plant tissue results with levels occurring at the mine site, 5 naturally occurring wetland sites were sampled (Fig. 2.3). Wetlands 1-4 occurred under altered conditions within the mine site, while wetland 5 was established in a more natural, unaffected setting outside the area where mining took place.

Figure 2.3: Natural wetland sampling sites



Site 1 consisted of a meadow marsh composed primarily of *P. australis*, *T. latifolia*, and *Carex sp.* and was situated in a shallow pan of water on a tailings field. The tailings were extremely fine in texture and as such water infiltration was slowed to the point that surface water existed throughout the growing season. Site 2 was a wetland found along the northern shore of a small pond formed by surrounding tailings piles and consisted primarily of *P. australis* and *T. latifolia*. Site 3 was similar to site 2 in that it consisted of a wetland surrounding a small pond formed in a low spot between tailings piles. The flora of site three was primarily *T. latifolia* and *P. australis*. Site 4 was a *T. latifolia* stand growing in a settling pond while the natural wetland site (site 5) was primarily a *T. latifolia* marsh, with an outer fringe of *Equisetum fluviatile*, growing in an area of the

southeast arm of the former Steep Rock Lake known as Fairweather Lake. The wetland of site 5 was established on a substrate consisting of the original lake bottom and as such was not impacted by mine tailings or effluent. Each of these 5 sites were sampled in the fall of 2002 using transects. At every 2m (starting at 0m), samples were taken from representative plant species within 1m on either side of the transect line. This procedure was repeated for 10m, or until open water was reached. Thus, one composite sample was collected for every 2m of transect. These samples were then compared to each other and to the microcosm samples in order to get a better understanding of the effect of substrate on plant tissue concentrations.

2.2.5 Data Analysis

Means were calculated for the metal concentrations in the plant tissue of the microcosms. Univariate ANOVA's determined the significance of plant species, treatment, and plant species by treatment on the concentrations found in both the plant tissue and the soil samples. These concentrations were then used to calculate the effectiveness of plant species to remove the metals.

2.3 Results:

2.3.1 Plant Tissue Analysis

Mean tissue concentrations in the microcosms for 2002 are shown in Table 2.1. and Fig. 2.4. Fig. 2.4 compares the concentrations of seven constituents in plant tissue from the treatments in 2002. These constituents were selected as they are the only micronutrients which showed significant differences due either to treatment or plant species. In 2002, the plant species had significantly different ($p < 0.05$) concentrations of Al, Cr, Cu, Fe, Mn, S, and Sr. *Carex sp.* tissues contained consistently higher concentrations ($p < 0.05$) of Al, Cu, S, and Sr than any of the other three species, followed by *T. latifolia*, *P. australis* and *E. smallii* respectively. *P. australis* was shown to contain significantly higher concentrations of Cr than all other test species in all treatments. While *Carex sp.* showed the greatest concentrations of Fe in the control and surface microcosms, *P. australis* contained the highest concentrations in the deep treatment microcosms. In the case of Mn, *T. latifolia* and *Carex sp.* exhibited the greatest concentrations ($p < 0.05$) while neither *E. smallii* nor *P. australis* accumulated it to any degree. S exhibited significantly different concentrations ($p < 0.05$) in species, treatment, and treatment by species. In all treatments, *Carex sp.* exhibits the greatest concentration of S followed by *T. latifolia*, with *E. smallii* showing greater concentrations than *P. australis* in the deep treatment, but not in the control or surface treatments.

Mean tissue concentrations in the microcosms for 2003 are shown in Table 2.2 and Fig. 2.5. The five variables depicted in Fig. 2.5 are the only ones that showed significant differences. In 2003, Mn revealed significantly different levels ($p < 0.05$) among plant species, while Ca and S exhibited differences ($p < 0.05$) among both species and treatment and Zn among treatment by species. Also, significantly greater concentrations ($p < 0.05$) of Ca, Mn, and Sr were found in the tissues of *T. latifolia* as well as in the deep treatment for Zn. S concentrations were highest in *E. smallii* followed by *T. latifolia* and *P. australis*, except in the control where *T. latifolia* exhibited the greatest concentration of S.

During the winter of 2002-2003, *T. latifolia* and *Carex sp.* in the microcosms experienced a dramatic die-off. By the fall of 2003, no *Carex sp.* was present and only two of the six microcosms contained any *T. latifolia*.

Table 2.3 summarizes the results of mean tissue concentrations for the naturally occurring wetlands and the microcosms (data from 2002). Significant differences ($p < 0.05$) exist across the five natural wetlands and three treatment microcosms for Al, Ba, Cu, Fe, Mn, Na, Ni, P, S, Sr, and Zn. Fig. 2.6 shows that Al and Fe tissue concentrations from three experimental wetlands were significantly higher (< 0.05) than those from on-site wetlands. Ni, S, and Sr by contrast showed significantly higher concentrations ($p < 0.05$) in the natural wetlands than the microcosms with the exceptions of wetland 5 for S and Ni, and wetland 4 for Sr.

Table 2.1: Mean microcosm tissue concentrations (in mg/Kg) for the Surface, Deep, and Control water treatments for 2002

Plant	Surface				Deep				Control				
	Carex	Eleo	Phrag	Typha	Carex	Eleo	Phrag	Typha	Carex	Eleo	Phrag	Typha	
Al α	Mean	94.83	34.89	53.87	65.53	151.2	83.41	160.91	85.12	414.6	269.19	268.6	146.7
	Std Dev	54.69	8.46	37	24.15	159.53	106.2	181.15	26.42	108.89	331.51	137.18	40.31
Ca (%) β	Mean	1.17	0.09	0.11	0.76	1.18	0.18	0.18	0.83	1.08	0.25	0.32	0.97
	Std Dev	0.05	0.05	0.03	0.27	0.32	0.22	0.13	0.13	0.25	0.32	0.01	0.35
Cr β	Mean	0.77	0.27	2.16	0.42	0.84	1.3	3.69	0.42	1.99	2.03	5.48	0.69
	Std Dev	0.45	0.01	1.41	0.06	0.82		3.37	0.22	0.17	2.65	2.1	0.29
Cu β	Mean	13.51	1.35	3.43	6.85	9.77	2.18	3.53	3.99	15.62	3.75	4.32	5.23
	Std Dev	1.21	1.35	0.24	0.59	7.88	2.75	1.19	0.81	7.76	4.45	2.59	0.67
Fe α	Mean	181.39	67.46	124.18	122.94	246.79	144.63	329.74	169.19	712.99	449.79	528.59	265.24
	Std Dev	64.21	19.3	68.18	23.12	192.47	182.1	343.3	30.83	146.09	550.84	238.15	79.41
K (%) β	Mean	2.48	0.46	1.2	1.84	2.74	0.62	1.21	1.42	2.65	0.72	0.62	1.82
	Std Dev	0.13	0.41	0.16	0.4	1.39	0.65	0.66	0.29	0.75	0.83	0.11	0.58
Mg (%) β	Mean	0.27	0.03	0.06	0.15	0.27	0.06	0.08	0.12	0.23	0.09	0.1	0.15
	Std Dev	0.01	0.02	0.01	0.02	0.03	0.07	0.02	0.02	0	0.11	0	0.03
Mn β	Mean	1540.73	50.07	63.45	1185.48	1776.23	160.17	111.48	2009.23	1594.73	100.04	169.93	1892.73
	Std Dev	451.13	25.5	8.8	443	289.21	181.95	70.51	242.54	841.46	114.83	1.7	592.56
P (%) β	Mean	0.21	0.04	0.15	0.22	0.32	0.05	0.16	0.15	0.24	0.09	0.13	0.22
	Std Dev	0.06	0.05	0.01	0.04	0.02	0.04	0.03	0.01	0.08	0.1	0.05	0.07
S $\alpha\beta\gamma$	Mean	6987.35	785.5	1076.85	2130.85	6132.85	1781.4	1301.85	1920.35	1583.35	617.39	882.55	1397.15
	Std Dev	45.96	618.51	25.46	888.13	420.02	2266.21	36.77	341.53	744.58	784.13	390.75	682.64
Sr β	Mean	23.83	1.98	2.63	11.19	24.16	4.7	4.12	12	13.84	4.89	6.39	11.57
	Std Dev	0.13	1.06	0.16	0.8	6.45	5.45	3.36	0.57	3.03	6.21	0.45	3.61
Zn	Mean	15.51	6.01	9.12	8.38	15	8.62	8.95	9.7	18.37	11.4	7.42	10.17
	Std Dev	2.06	4.12	0.76	1.51	8.99	9.84	1.11	0.66	2.88	13.68	3.42	1.08
α	Significant difference ($p < 0.05$) noted due to treatment												
β	Significant difference ($p < 0.05$) noted due to species												
γ	Significant difference ($p < 0.05$) noted due to treatment*species												

Table 2.2: Mean microcosm tissue concentrations (in mg/Kg) for the Surface, Deep, and Control water treatments for 2003

Plant		Surface		Deep			Control			
		Eleo	Phrag	Eleo	Phrag	Typha	Eleo	Phrag	Typha	
Al	Mean	128.4	131.65	128.9	127.6	126.1	134.65	129.55	125.1	
	St Dev	2.98	2.47	2.83	0.28		2.19	7.42		
Ca (%) $\alpha\beta$	Mean	0.47	0.41	0.45	0.40	0.71	0.45	0.38	0.79	
	St Dev	0.02	0.06	0.02	0.03		0.09	0.04		
Cr	Mean	0.07	0.28	0.2	0.12		0.11	0.17	0.06	
	St Dev	0.03	0.13		0.09		0	0.04		
Cu	Mean	0.27	1.92	0.19		1.1	1.82	1.48	1.16	
	St Dev	0.19		0.02			0.08	0.87		
Fe	Mean	43.86	48.4	140.19	47.75	41	102.64	63.07	63.15	
	St Dev	7.66	2.86	140.5	4.43		68.74	25.56		
K (%)	Mean	1.65	1.03	1.94	7.46	2.39	1.74	0.95	2.25	
	St Dev	0.08	0.16	0.04	0.07		0.33	0.40		
Mn α	Mean	227.44	178.84	200.89	176.19	1529.64	198.99	151.14	1301.64	
	St Dev	2.81	20.22	40.94	35.85		0.07	6.93		
Ni	Mean	0.65	0.7	0.32	0.93	0.35	0.48	6.1	0.71	
	St Dev	0.7	0.15		0.03		0.22	7.88		
S $\alpha\beta$	Mean	3362.3	1594.97	3270.47	1240.97	2473.97	1711.97	780.97	2594.97	
	St Dev	83.01	649.12	497.1	299.81		545.89	364.87		
Sr β	Mean	12.8	12.22	15.52	13.75	17.88	9.54	7.45	11.76	
	St Dev	0.58	1.2	2.56	5.34		0.73	2.18		
Zn γ	Mean	6.36	10.76	7.35	4.83	11.59	8.69	7.1	8.43	
	St Dev	0.74	7.29	0.52	0.08		1.81	1.48		
	α	Significant difference ($p < 0.05$) noted due to species								
	β	Significant difference ($p < 0.05$) noted due to treatment								
	γ	Significant difference ($p < 0.05$) noted due to treatment by species								

Table 2.3: Mean tissue concentrations (in mg/Kg) for field and microcosm wetlands in 2002

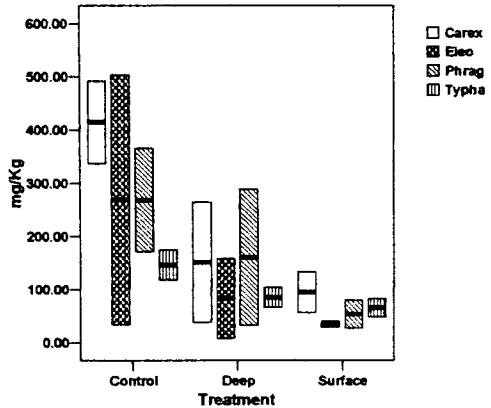
		Wetland					Microcosm		Control
		1	2	3	4	5	Surface	Deep	
Al α	Mean	14.45	8.95	9.09	32.45	5.09	62.28	120.16	274.77
	Std Dev	6.49	5.09	4.73	11.23	1.02	35.45	107.34	174.95
As	Mean	0.80					2.02	0.73	0.91
	Std Dev	0.35							0.32
Ba α	Mean	12.12	1.81	9.31	0.33	1.70	9.85	14.29	18.05
	Std Dev	6.44	1.26	2.61	0.06	1.01	5.12	9.05	11.49
Be	Mean			0.10			0.08		0.07
	Std Dev								
Ca (%)	Mean	0.54	0.77	0.80	0.31	1.05	0.54	0.59	0.66
	Std Dev	0.27	0.47	0.19	0.07	0.60	0.50	0.49	0.45
Co	Mean	0.26	1.03	0.21	1.04		0.18	0.18	0.30
	Std Dev	0.25	1.59	0.11	0.45			0.07	0.12
Cr	Mean	0.43	0.14	0.13	0.05		0.90	1.60	2.54
	Std Dev	0.39		0.09			0.98	2.03	2.29
Cu α	Mean	5.03	2.07	2.31	7.29	1.17	6.28	4.87	7.23
	Std Dev	1.37	0.69	0.73	2.59	0.37	4.98	4.46	6.29
Fe α	Mean	66.91	68.00	60.25	105.03	36.80	123.99	222.59	489.15
	Std Dev	27.55	39.56	14.91	11.05	19.57	56.90	181.66	291.42
K (%)	Mean	1.10	1.15	1.32	1.47	0.90	1.50	1.50	1.45
	Std Dev	0.24	0.37	0.27	0.21	0.49	0.84	1.05	1.01
Mg (%)	Mean	0.09	0.14	0.20	0.17	0.07	0.13	0.13	0.14
	Std Dev	0.02	0.07	0.01	0.03	0.04	0.10	0.09	0.07
Mn α	Mean	3569.30	2360.73	3630.40	2548.23	564.39	709.93	1014.28	939.36
	Std Dev	2116.54	2159.29	622.21	626.55	301.65	750.23	956.98	951.85
Na α	Mean	37.25	100.70	140.42	568.59	3220.85	150.34	152.39	142.00
	Std Dev	32.38	42.06	87.06	88.83	2249.84	126.39	100.02	104.71
Ni α	Mean	6.18	4.28	7.26	17.03	0.42	3.27	2.80	2.40
	Std Dev	4.00	4.15	3.49	3.28		4.07	3.26	1.68
P α	Mean	793.84	522.15	663.67	1125.73	1164.12	1540.44	1710.03	1688.04
	Std Dev	160.60	156.42	41.30	217.21	581.65	817.86	1064.89	880.85
Pb	Mean	2.35	4.14	3.77	0.91	1.51	1.72	1.90	0.74
	Std Dev	2.84	5.15	4.51			0.75	1.00	0.64
S α	Mean	3654.14	3929.22	4738.02	5754.85	1722.02	2745.14	2784.11	1120.11
	Std Dev	1706.39	2196.83	1924.17	586.25	1787.24	2703.65	2260.07	653.45
Sr α	Mean	29.58	30.66	20.24	7.23	24.90	9.91	11.24	9.17
	Std Dev	15.97	14.16	2.77	2.87	5.25	9.44	9.30	4.90
Zn α	Mean	20.38	17.75	11.86	11.54	7.38	9.75	10.56	11.84
	Std Dev	8.82	7.71	1.63	2.97	3.39	4.19	5.77	6.96

α Significant difference ($p < 0.05$)

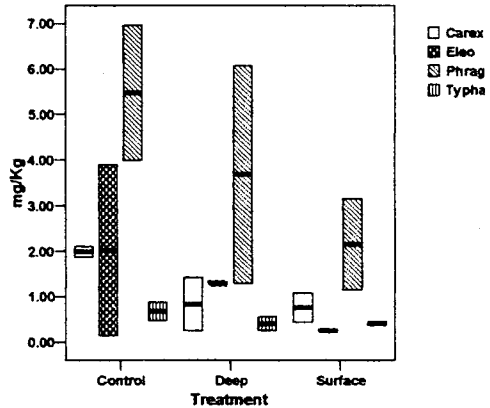
Values are averages of all species sampled

Figure 2.4: Mean microcosm tissue concentrations for the Surface, Deep, and Control water treatments for 2022

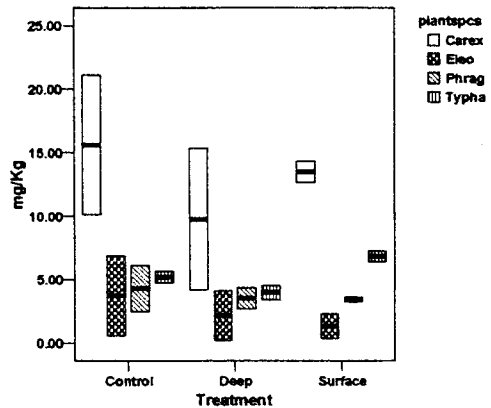
Mean Al (mg/kg) in plant tissue 2022



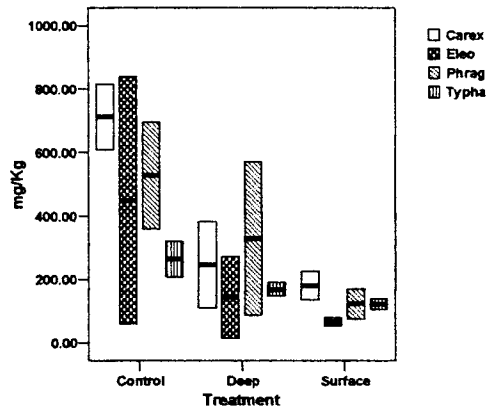
Mean Cr (mg/kg) in plant tissue 2022



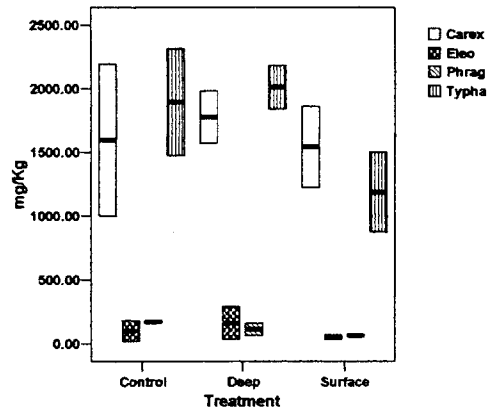
Mean Cu (mg/kg) in plant tissue 2022



Mean Fe (mg/kg) in plant tissue 2022



Mean Mn (mg/kg) in plant tissue 2022



Mean S (%) in plant tissue 2022

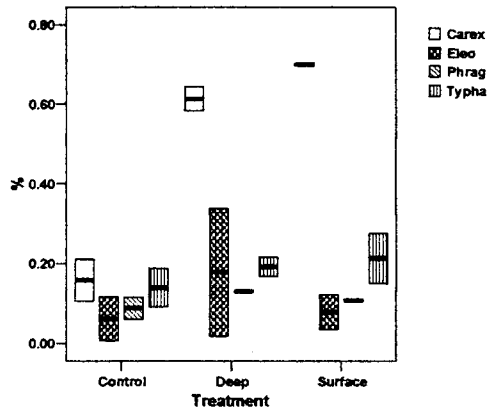


Figure 2.4: Mean microcosm tissue concentrations for the Surface, Deep, and Control water treatments for 2002
(Continued)

Mean Sr (mg/kg) in plant tissue 2002

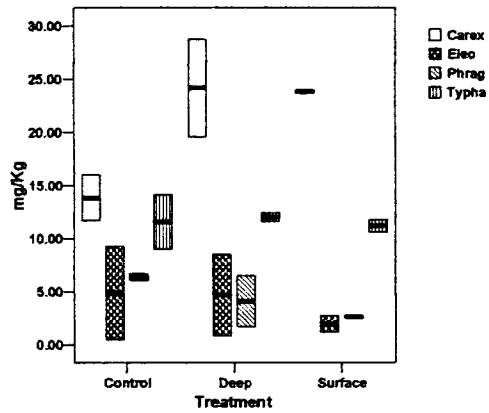
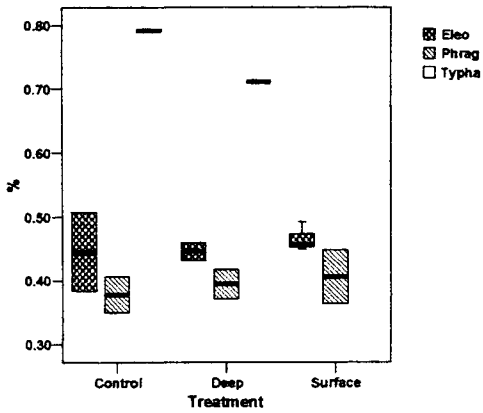
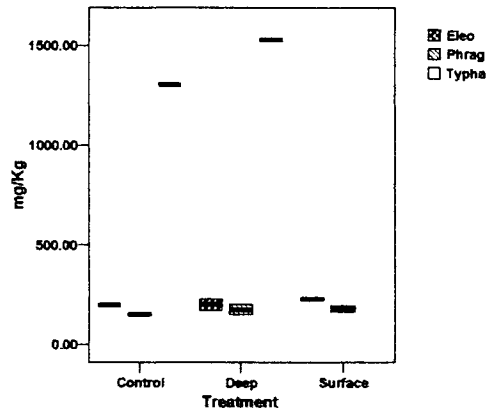


Figure 2.5: Mean microcosm tissue concentrations for the Surface, Deep, and Control water treatments for 2003

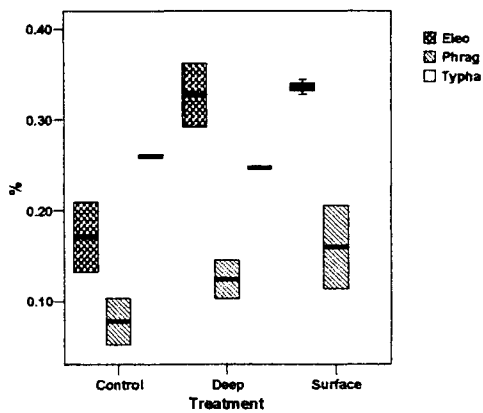
Mean Ca (%) in plant tissue 2003



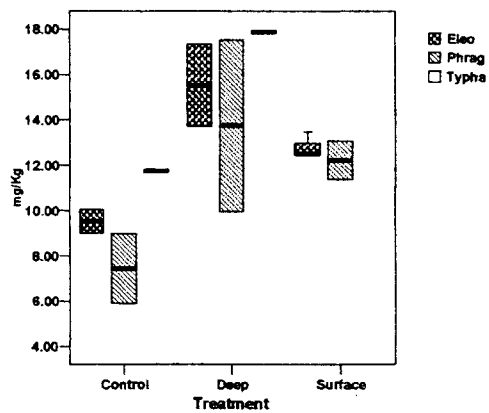
Mean Mn (mg/kg) in plant tissue 2003



Mean S (%) in plant tissue 2003



Mean Sr (mg/kg) in plant tissue 2003



Mean Zn (mg/kg) in plant tissue 2003

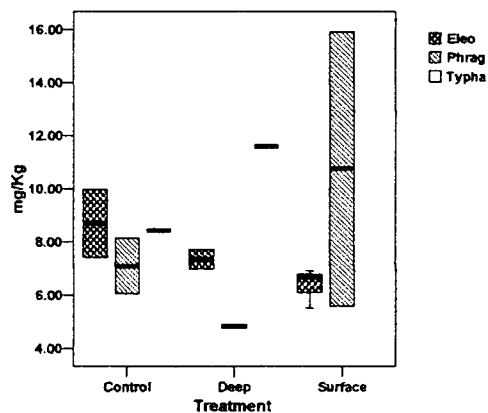
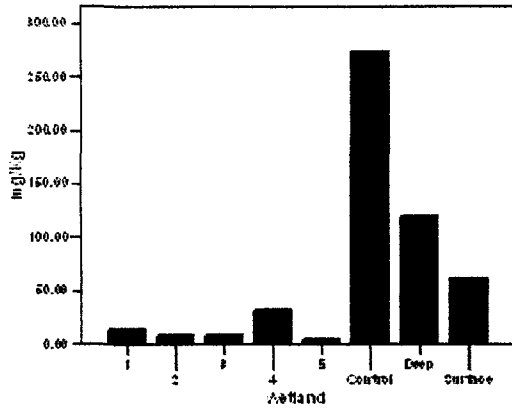
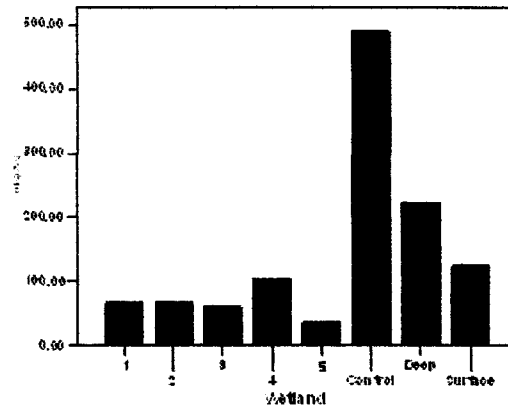


Figure 2.6: Comparison of concentrations between on-site and microcosm wetlands in the Steep Rock Pit Lakes region

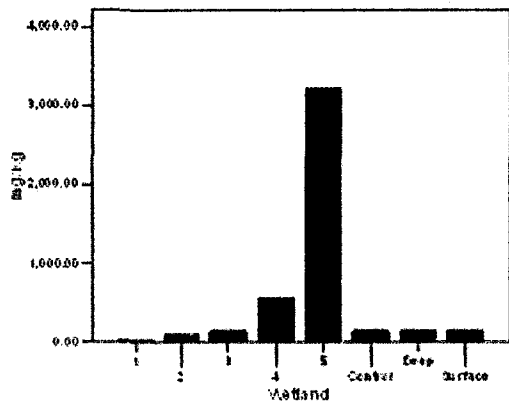
Mean Al (mg/kg) tissue concentrations



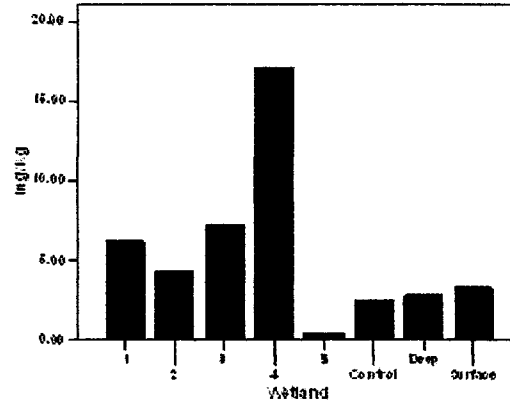
Mean Fe (mg/kg) tissue concentrations



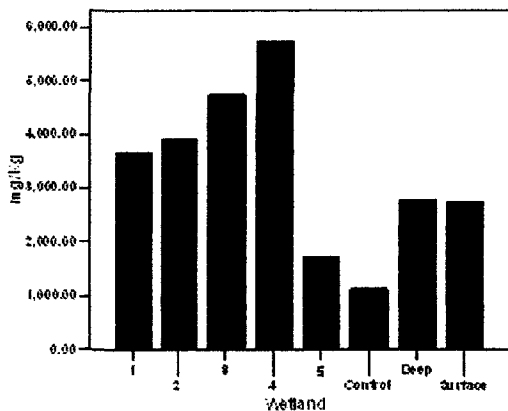
Mean Na (mg/kg) tissue concentrations



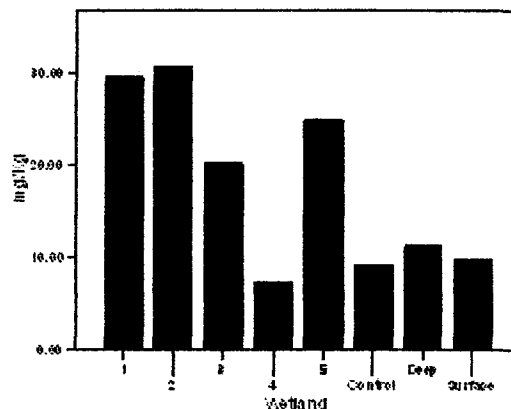
Mean Ni (mg/kg) tissue concentrations



Mean S (mg/kg) tissue concentrations



Mean Sr (mg/kg) tissue concentrations



2.3.2 Soil Analysis

Results of soil analyses for 2002 are shown in Tables 2.4 and 2.5 and Figures 2.7 and 2.8. Those variables described in Figure 2.7 are the only ones that exhibited significant differences in the soil while those in Figure 2.8 consist of all the micronutrients that exhibited significant differences in the porewater. In 2002, the microcosm soils exhibited very high levels of Al, Ca, Fe, K, and Mg while the remaining variables, although high in some cases, were always an order of magnitude less than these five metals. ANOVA analysis showed that, for the soil in 2002, (Table 2.4), plant species had no impact on metal concentrations in the soil; only the treatment had a significant impact ($p < 0.05$) for Cr, Cu, and Sr. Fig. 2.7 further shows the concentrations of three metals (Cr, Cu, and Sr) that exhibited significant differences ($p < 0.05$) across treatment in 2002. Cr levels were found to be higher in the soil of the control microcosms than in either of the two treatments with the highest concentration found in the soil of the quadrant containing *E. smallii* of the control. The soil of the deep treatment contained significantly greater ($p < 0.05$) concentrations of Cu than either the control or surface treatments, while the reverse was true for Sr with the deep treatment showing lower concentrations than either the surface or control.

In 2002, the porewater exhibited significant differences ($p < 0.05$) among treatments for Al, Ca, Cu, Fe, K, Mg, S, Sr, and SO_4 . SO_4 , and S were particularly elevated in the deep treatment. No significant differences were observed in the porewater due to plant species alone, or in combination with treatment. Figure 2.8 describes the relationships of six micronutrients (Al, Cu, Fe, S, SO_4 , and Sr) in the porewater of the microcosms. Al was

shown to have significantly higher ($p < 0.05$) concentrations in the control than in either deep or surface treatments. The control also contained the highest levels of Cu and Fe, followed by the deep treatment and finally the surface treatment microcosms. S and SO_4 levels in the control microcosms were significantly lower than either of the two treatment microcosms, with the surface treatment showing greater concentrations than the deep treatment. Levels of Sr were also significantly lower in the control than in either of the two treatments. In this case, however, the deep treatment exhibited a greater concentration than the surface.

Results of soil analyses for 2003 are shown in Tables 2.6 and 2.7 and Figures 2.9 and 2.10. Those constituents described in Fig. 2.9 include all the micronutrients that exhibited significant differences in the soil, while Fig. 2.10 shows the constituents that exhibited significant differences in the porewater. Table 2.6 shows high levels of Al, Ca, Fe, K, and Mg in microcosm soils in 2003. Al, Ca, Cu, Fe, K, Mg, Mn, S, and Zn showed significant differences ($p < 0.05$) in soil concentration due to treatment. The porewater in 2003 (Table 2.7) showed significant variation ($p < 0.05$) in Ca, K, Mg, S, and Sr, due to treatment while S also differed significantly ($p < 0.05$) due to a combination of treatment and species. Only SO_4 showed a significant difference ($p < 0.05$) due to treatment and plant species.

In 2003 (Fig. 2.9) the concentrations of Al, Cu, Fe, Mn, and Zn in the soils were highest in the control microcosm, followed by the deep treatment and the surface treatment. The deep treatment microcosms showed significantly greater ($p < 0.05$) concentrations of S

than either the control or the surface treatments. Hence, levels of all six constituents were greatest in the deep treatment, followed by the surface and finally the control. S and SO₄ exhibited the greatest variation in concentrations between deep and control treatment microcosms. Figure 2.10 depicts the relationships of six variables (Ca, K, Mg, S, SO₄, and Sr) in the porewater for 2003.

Table 2.4: Mean microcosm soil concentrations (mg/kg) for the Surface, Deep, and Control water treatments for 2002

Plant	Surface				Deep				Control				
	Carex	Eleo	Phrag	Typha	Carex	Eleo	Phrag	Typha	Carex	Eleo	Phrag	Typha	
Al (%)	Mean	2.09	2.15	2.23	2.33	2.18	1.96	2.09	2.08	2.08	2.25	2.25	2.36
	Std. Dev	0.46	0.51	0.24	0.08	0.38	0.43	0.35	0.11	0.13	0.09	0.29	1742.59
Ca (%)	Mean	1.4	1.47	1.5	1.47	1.29	1.13	1.2	1.51	1.33	1.41	1.42	1.49
	Std. Dev	0.28	0.16	0.19	0.2	0.24	0.34	0.24	0.22	0.01	0.13	0.14	0.2
Cr α	Mean	46.89	50.84	54.98	55.37	55.26	48.62	55.68	54.2	52.23	75.96	56.62	54.5
	Std. Dev	9.79	10.34	8.14	1.7	11.6	5.2	16	4.67	8.64	30.96	10.14	5.22
Cu α	Mean	40.11	39.78	42.42	45.31	34497.85	30218.15	33048.58	36267.1	32.55	39.12	40.68	44.43
	Std. Dev	11.5	6.55	3.76	1.69	7089.95	4668.81	5993.46	8027.78	2.47	0.14	3.13	0.91
Fe (%)	Mean	3.35	3.31	3.50	3.95	3.13	2.79	2.89	2.68	3.43	3.68	3.61	3.75
	Std. Dev	0.86	0.58	0.43	0.22	0.03	0.07	0.07	0.01	0.05	0.13	0.28	0.33
K (%)	Mean	0.31	0.34	0.32	0.37	1.34	1.24	1.32	1.31	0.31	0.36	0.35	0.35
	Std. Dev	0.07	0.09	0.04	0.03	0.26	0.32	0.22	0.04	0.02	0.02	0.07	0.05
Mg (%)	Mean	1.38	1.42	1.48	1.52	0.09	0.07	0.07	0.07	1.29	1.45	1.45	1.56
	Std. Dev	0.35	0.29	0.18	0.15	0.03	0.02	0.02	0.01	0.1	0.09	0.12	0.06
Mn	Mean	830.55	771.09	910.61	858.1	1449.6	1248.2	1272.4	1274.4	743.43	855.79	876.46	954.7
	Std. Dev	368.09	150.04	264.35	131.13	228.82	304.76	247.24	20.36	36.73	60.37	135.54	242.22
Ni	Mean	31.1	31.39	36.27	36.09	658	560.6	660.78	623	32.15	45.46	33.98	35.17
	Std. Dev	8.97	5.85	5.72	0.63	153.16	74.39	99.48	73.4	2.22	15.7	3.06	2.97
Pb	Mean	18.5	8.25	7.43	9.15	300.1	242.75	337.8	253.15	8.8	7.95	64.86	9.15
	Std. Dev	13.72	0.07	1.84	2.47	20.08	20.86	70.04	15.91	0	1.77	125.08	0.35
S	Mean	258.2	273.8	270.5	418.25	40.4	35.45	38.25	44.6	237.8	227.7	263.64	232.85
	Std. Dev	44.83	37.62	41.96	159.31	6.65	7.28	7.6	0.85	64.91	0.42	28.5	50.84
Sr α	Mean	43.6	45.95	46.28	50.2	58.01	53.64	60.44	57.86	49	46.2	44.68	46.1
	Std. Dev	6.79	5.59	3.8	4.1	9.29	10.49	13.16	4.87	5.94	0.85	7.36	3.68
Zn	Mean	62.02	63.11	62.71	69.16	6.28	6.39	6.35	6.41	61.96	61.1	65.26	63
	Std. Dev	15.05	13.41	6.98	5.47	0.24	0.22	0.19	0.25	0.61	3.13	3.47	4.99

α Significant difference ($p < 0.05$) observed due to treatment

Table 2.5: Mean microcosm pore water concentrations (mg/L) for the Surface, Deep, and Control water treatments for 2002

Plant	Surface				Deep				Control				
	Carex	Eleo	Phrag	Typha	Carex	Eleo	Phrag	Typha	Carex	Eleo	Phrag	Typha	
Al α	Mean	0.6	0.03	0.24	0.03	0.13	0.11	0.12	0.12	0.73	0.75	0.97	0.75
	Std. Dev	0.77	0	0.12	0.02	0.02	0.03	0.02	0.03	0.65	0.32	0.38	1.02
Ca α	Mean	64.86	61.45	78.73	83.79	0.01	0.01	0.01	0.02	51.8	52.99	42.3	35.84
	Std. Dev	37.86	27.45	7.16	9	0	0	0	0.01	2.94	6.45	13.32	27.52
Cu α	Mean	0.01	0.01	0.01	0.01	0.47	0.15	0.15	0.29	0.01	0.02	0.02	0.02
	Std. Dev	0	0	0	0	0.65	0.08	0.08	0.26	0	0	0	0
Fe α	Mean	0.28	0.05	0.14	0.19	13.17	11.56	10.35	10.14	0.63	0.46	0.48	0.49
	Std. Dev	0.44	0.01	0.12	0.23	2.04	1.9	1.67	2.21	0.74	0.3	0.42	0.74
K α	Mean	5.4	8.37	7.13	8.63	27.74	24.04	25.63	26.73	8.41	10.43	6.75	5.84
	Std. Dev	2.9	4.56	1.22	4.37	3.42	1.68	2.24	2.66	2.07	0.87	2.75	0.57
Mg α	Mean	20.87	20.65	24.53	26.41	1.51	0.9	0.84	1.32	17.31	17.61	13.78	13.13
	Std. Dev	11.46	9.07	2.26	2.87	1.29	1.03	0.89	1.05	2.6	1.74	5.08	9.77
Mn	Mean	0.71	0.59	0.57	1.46	9.41	8.85	10.22	8.04	1.46	1.61	0.43	0.62
	Std. Dev	1.15	0.73	0.74	2.39	3.59	4.09	4.73	1.12	0.83	1.15	0.49	1.04
S α	Mean	38.68	30.39	42.68	50.53	24.51	28.99	43.01	23.3	2.06	1.36	2.98	0.66
	Std. Dev	23.93	15.38	8.83	15.84	19.41	21.1	20.96	17.15	0.96	0.79	2.1	0.06
Sr α	Mean	0.11	0.12	0.13	0.13	0.14	0.13	0.15	0.13	0.09	0.09	0.07	0.09
	Std. Dev	0.06	0.06	0.01	0.02	0.02	0	0.03	0.01	0.01	0.01	0.02	0.01
SO ₄ α	Mean	148.97	110.51	127.5	149.19	72.45	83.91	124.71	69.21	5.03	3.13	7.62	6.36
	Std. Dev	32.07	7.62	25.84	45.36	59.84	59.99	61.54	52.83	2.91	3.13	6.61	9.92

α Significant difference ($p < 0.05$) observed due to treatment

Table 2.6: Mean microcosm soil concentrations (mg/kg) for the Surface, Deep, and Control water treatments for 2003

		Surface			Deep			Control		
		Eleo	Phrag	Eleo	Phrag	Typha	Eleo	Phrag	Typha	
Al (%) α	Mean	1.91	1.81	2.13	2.13	1.92	2.58	2.35	2.46	
	St Dev	0.70	0.43	0.25	0.13	0.16	0.29	0.28	0.06	
Ca (%) α	Mean	1.31	1.20	1.45	1.38	1.26	1.72	1.62	1.80	
	St Dev	0.48	0.28	0.15	0.17	0.17	0.10	0.24	0.24	
Cr	Mean	48.37	43.22	53.17	49.08	46.05	57.91	61.69	56.58	
	St Dev	11.19	10.98	9.96	6.57	4.48	6.88	19.25	2.37	
Cu (%) α	Mean	3.27	2.82	3.55	3.44	3.17	4.25	3.96	3.64	
	St Dev	0.87	0.52	0.72	0.33	0.46	0.57	0.55	0.01	
Fe (%) α	Mean	0.27	0.26	0.33	0.31	0.30	0.37	0.34	0.36	
	St Dev	0.13	0.08	0.03	0.04	0.04	0.03	0.05	0.02	
K (%) α	Mean	1.27	1.20	1.35	1.38	1.21	1.70	1.57	1.75	
	St Dev	0.49	0.30	0.11	0.10	0.12	0.18	0.24	0.09	
Mg (%) α	Mean	0.08	0.07	0.08	0.08	0.07	0.10	0.10	0.09	
	St Dev	233.26	177.97	144.22	253.04	35.76	128.87	133.93	77.23	
Mn α	Mean	31.54	28.29	32.71	31.69	29.47	37.78	39.79	38.08	
	St Dev	9.31	6.82	5.11	4.71	3.22	4.28	8.21	1.07	
Ni	Mean	308.52	224.08	426.03	388.60	336.55	232.10	270.66	203.85	
	St Dev	81.95	59.82	192.30	58.11	47.73	55.93	60.94	9.69	
S α	Mean	41.97	41.15	48.48	44.30	43.80	51.10	50.42	48.55	
	St Dev	11.69	6.37	6.75	4.32	8.49	3.68	9.84	2.47	
Sr	Mean	60.03	52.73	68.25	62.53	62.56	73.31	66.92	73.03	
	St Dev	17.96	9.83	14.36	6.70	1.42	9.69	6.12	6.19	
Zn α	Mean	103.07	108.35	167.11	152.30	152.70	1.14	1.50	3.20	
	St Dev	16.68	18.72	31.96	23.25	6.53	0.93	1.10	4.14	

α Significant difference ($p < 0.05$) observed due to treatment

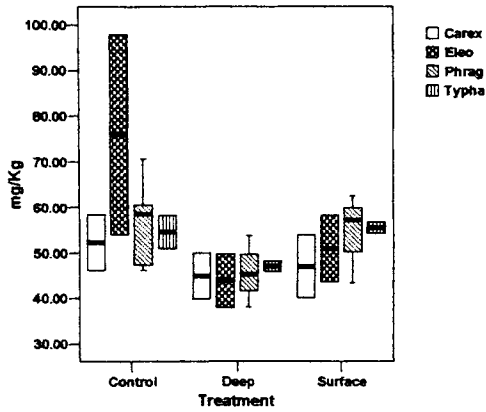
Table 2.7: Mean microcosm porewater concentrations (mg/L) for the Surface, Deep, and Control water treatments for 2003

	Plant	Surface		Deep			Control		
		Eleo	Phrag	Eleo	Phrag	Typha	Eleo	Phrag	Typha
Al	Mean	0.10	0.07	0.06	0.05	0.08	0.09	0.12	0.06
	Std. Dev	0.02	0.02		0.02	0.03	0.02	0.09	0.05
Ca α	Mean	63.16	74.95	107.19	117.04	81.89	64.20	59.34	60.86
	Std. Dev	17.20	8.71	27.88	35.99	12.37	4.93	10.13	5.4
Cu	Mean	0.01	0.01	0.01	0.01		0.01	0.01	0.01
	Std. Dev								
Fe	Mean	0.19	0.08	0.18	0.46	0.56	0.25	0.29	0.1
	Std. Dev	0.10	0.03	0.14	0.39	0.37	0.20	0.25	0.06
K α	Mean	7.88	6.26	9.39	10.2	11.02	6.11	6.14	5.25
	Std. Dev	0.75	1.23	3.64	5	2.93	2.68	1.98	1.11
Mg α	Mean	27.20	26.14	36.55	42.2	28.87	18.53	17.37	18.17
	Std. Dev	4.42	4.17	8.56	12.11	4.8	2.55	3.68	2.66
Mn	Mean	1.40	1.89	2.06	3.02	3.95	1.66	0.94	0.27
	Std. Dev	0.67	0.79	2.89	1.53	0.61	0.80	1.44	0.31
S $\alpha\gamma$	Mean	28.73	36.95	55.94	51.04	51.46	0.62	0.76	2.35
	Std. Dev	7.69	6.42	10.48	7.38	1.7	0.22	0.31	
Sr α	Mean	0.15	0.19	0.32	0.36	0.2	0.11	0.1	0.1
	Std. Dev	0.05	0.05	0.16	0.18	0.01	0.01	0.02	0
SO₄ $\alpha\beta$	Mean	103.07	108.35	167.11	152.3	152.7	1.14	1.5	3.2
	Std. Dev	16.68	18.72	31.96	23.25	6.53	0.93	1.1	4.14

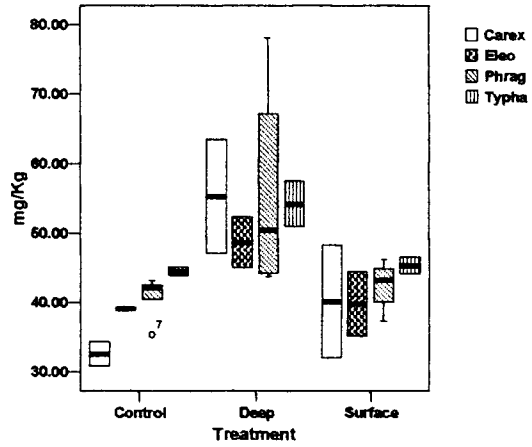
α Significant difference ($p < 0.05$) observed due to treatment
 β Significant difference ($p < 0.05$) observed due to species
 γ Significant difference ($p < 0.05$) observed due to treatment*species

Figure 2.7: Mean microcosm soil concentrations for the Surface, Deep, and Control water treatments for 2002

Mean Cr (mg/kg) in microcosm soil



Mean Cu (mg/kg) in microcosm soil



Mean Sr (mg/kg) in microcosm soil

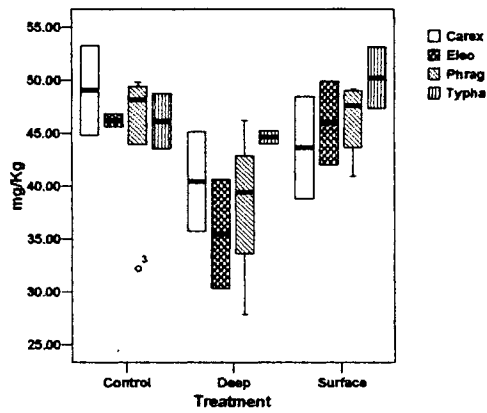
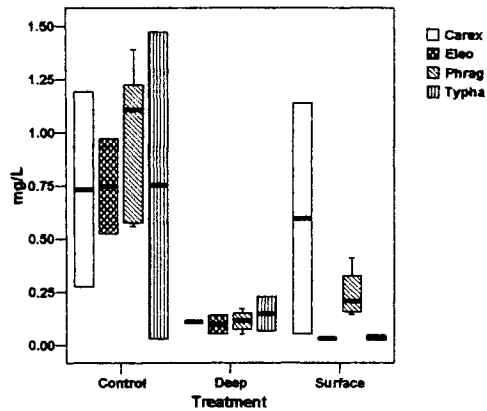
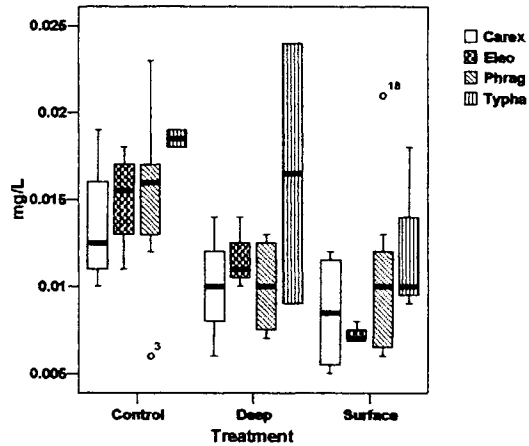


Figure 2.8: Mean microcosm pore water concentrations for the Surface, Deep, and Control water treatments for 2002

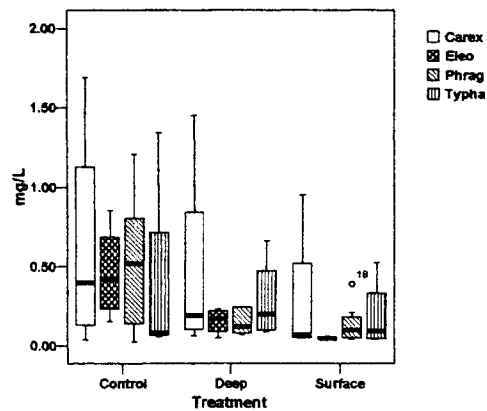
Mean Al (mg/L) in porewater



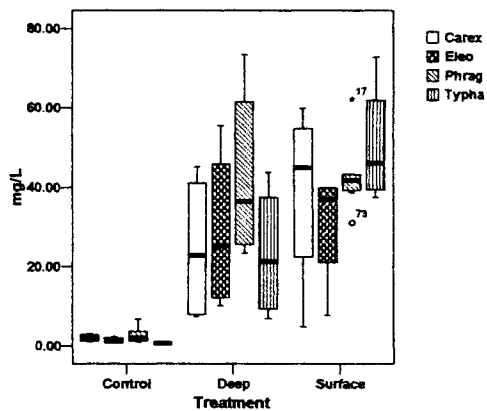
Mean Cu (mg/L) in porewater



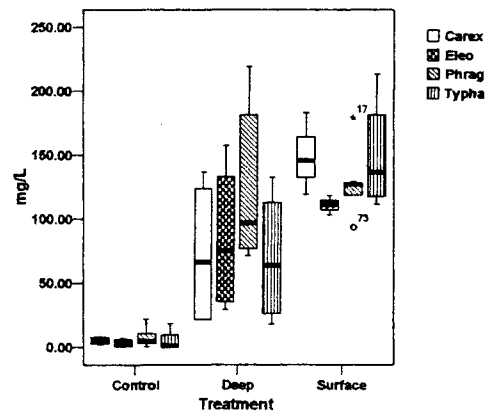
Mean Fe (mg/L) in porewater



Mean S (mg/L) in porewater



Mean SO₄ (mg/L) in porewater



Mean Sr (mg/L) in porewater

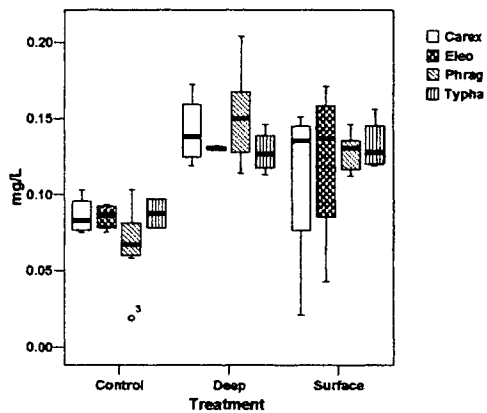
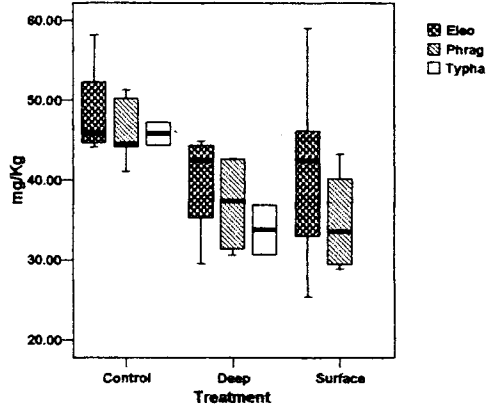
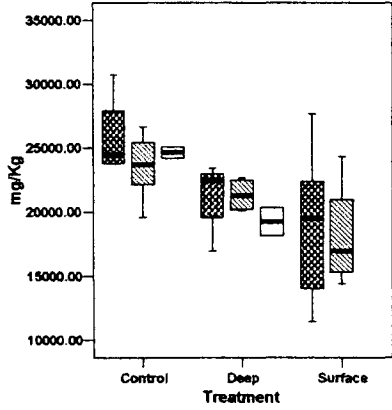


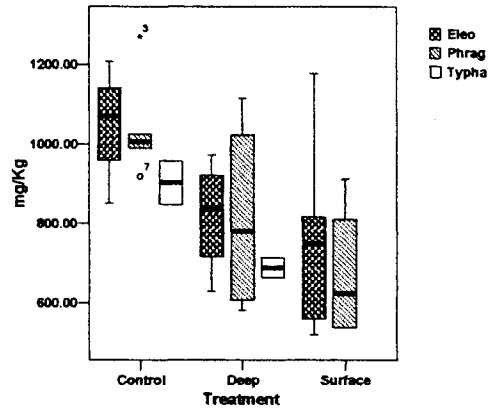
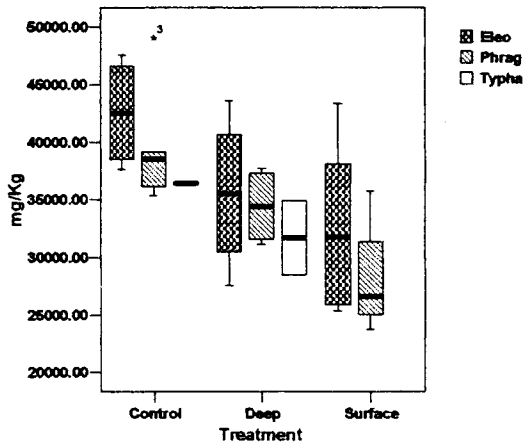
Figure 2.9: Mean concentrations in microcosm soil for 2003

Mean Al (mg/kg) in microcosm soil Mean Cu (mg/kg) in microcosm soil



Mean Fe (mg/kg) in microcosm soil

Mean Mn (mg/kg) in microcosm soil



Mean S (mg/kg) in microcosm soil

Mean Zn (mg/kg) in microcosm soil

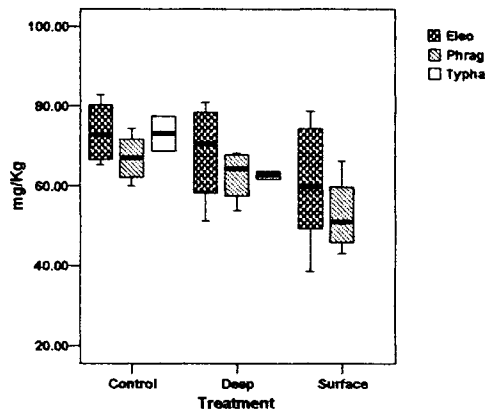
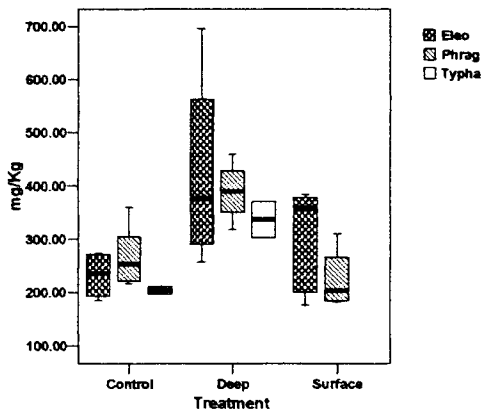
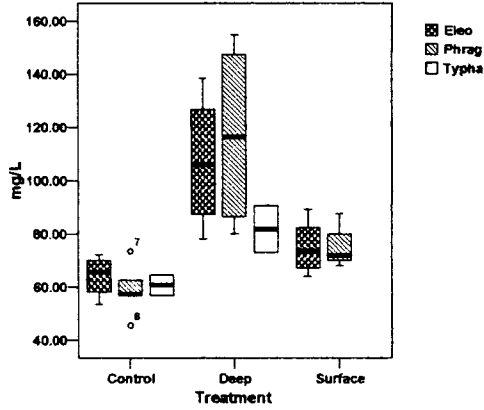
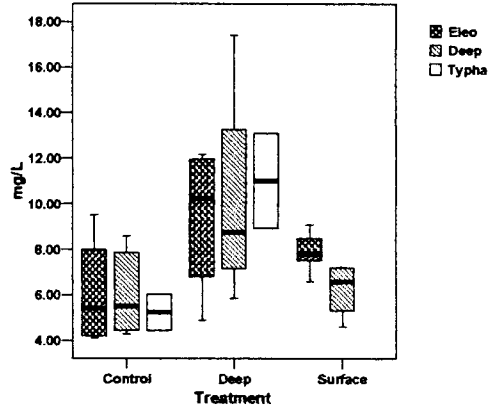


Figure 2.10: Mean concentrations in microcosm porewater for 2003

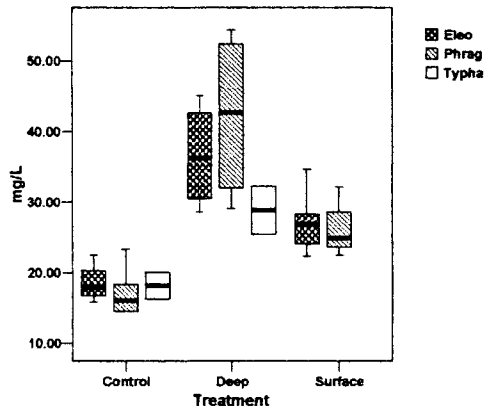
Mean Ca (mg/L) in porewater



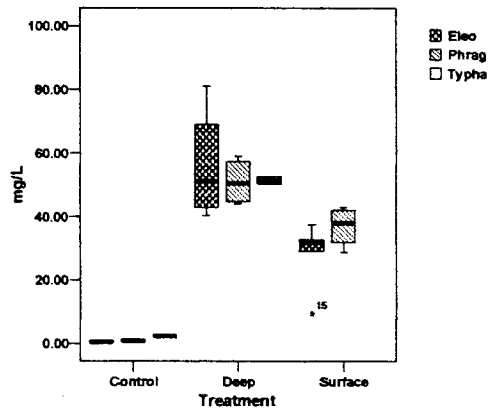
Mean K (mg/L) in porewater



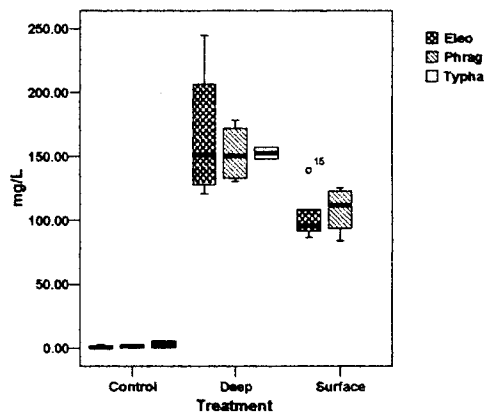
Mean Mg (mg/L) in porewater



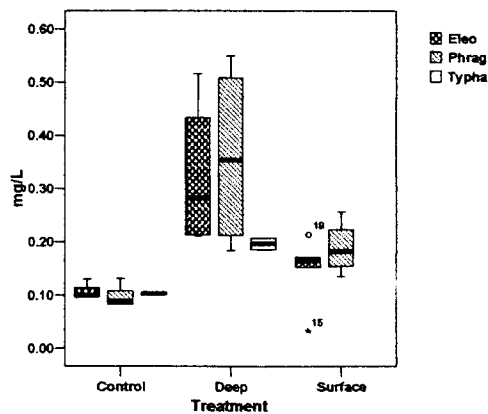
Mean S (mg/L) in porewater



Mean SO₄ (mg/L) in porewater



Mean Sr (mg/L) in porewater



2.3.3 Quantifying the effectiveness of wetland remediation

Based upon the mean metal levels depicted in Table 2.3, calculations were performed in order to quantify the effectiveness of each of the four plant species to remove and accumulate the metals of interest. Only the levels present in the deep water treatment were used since it is this water which will flood into the proposed treatment wetland.

The average concentration of each element (mg/kg) was multiplied by the mean biomass figures (kg/m²) for each of the experimental plant species (2.858 kg/ m² for *Carex sp.* (Mitsch and Gosselink 2000), 0.055 kg/ m² for *Eleocharis sp.* (Smith et al. 2000), 0.980 kg/ m² for *P. australis* (Meyerson et al. 2000), and 0.502 kg/ m² for *T. latifolia* (Mitsch and Wise 1998)) and the total area of the proposed treatment wetland (6182832.937 m²) to give an estimation of the total mass of each element contained within the plants of the proposed wetland in mg/m², assuming the entire wetland was filled with only the one species of interest growing at its average density. This mass was then converted to tonnes. For example, *Carex sp.* exhibited a mean of 151.20 mg/kg Al and has a mean biomass of 2.858 kg/m². When these two numbers are multiplied by 6182832.937 m² (the area of the proposed wetland), the units cancel leaving 2671.697 kg, or 2.672 tonnes of Al. The total removal rate of each of the four plant species based upon full use of the proposed treatment wetland (618.3 ha) was calculated and the results are summarized in Table 2.8.

Table 2.8: Total estimated removal of elements by four wetland plant species for a surface area of 618.3 ha (in Tonnes)

	Carex	Eleocharis	Phragmites	Typha
Al	2.672	0.036	0.874	0.307
Ca	208.564	1.069	17.443	24.607
Cu	0.173	0.000	0.011	0.009
Fe	4.361	0.048	1.144	0.393
K	484.934	4.355	59.380	54.140
Mn	31.387	0.061	0.872	5.740
Ni	0.080	0.000	0.013	0.002
S	108.371	0.859	7.704	6.533
Sr	0.427	0.003	0.054	0.043
Zn	0.265	0.003	0.042	0.032

These estimates of metal removal are based on monocropping of the proposed wetland area using average masses of the plants/m². In order to meet specific requirements, the treatment wetland may need to be established in specific ratios of the four plant species in order to promote optimal removal of elements of concern.

2.4. Discussion:

2.4.1. Species Considered

There were significant differences in metal concentrations in the tissues of the four investigated plant species -*Carex sp.*, *E. smallii*, *T. latifolia*, and *P. australis*- due to treatment and plant species within treatment when they were cultivated under experimental conditions. Although many plant species show promise in remediation, the four test species were chosen for study because they occur in natural, local stands, and because the literature suggests they are effective as remediation tools in a wetland environment (Dunbabin and Bowmer 1992; Moshiri 1993; Ye et al 1997, 1998, 2003; Batty et al 2000; Fediuc and Erdei 2002; Panich-Pat et al 2004; Weis and Weis 2004), and are used to revegetate tailings under wetland conditions (McCabe and Otte 2000).

The results showed that there were significant differences ($p < 0.05$) in concentration across the four test species for Ca, Cr, Cu, K, Mg, Mn, P, Sr, and S for 2002 and Ca, Mn, and S for 2003. There was a dieback of *Carex sp* and *T. latifolia* during the winter of 2002-2003. Reasons for this may include the extreme cold with no insulating snow that led to the complete freezing of the microcosms, or through competition from *E. smallii* and/or *P. australis*. *E. smallii* is allelopathic to aquatic plants (Quayyum et al 1999), and this chemical interaction may have caused the decline.

A comparison of the tissue concentrations of plants grown experimentally in the microcosms with those of plants growing in on-site wetlands located around the Steep Rock pit area (figure 2.2) revealed that many elements (Al, Ba, Cu, Fe, Mn, Na, Ni, P, S,

Sr, and Zn) varied significantly among locations. These differences are generally explainable in the context of the location of each sampled wetland or, in the case of the microcosms, the source of the water supply. Wetland 5, which generally exhibited the lowest concentrations, was situated outside of the area impacted by the mining activities, at the south end of Fairweather Lake (formerly the southeast arm of Steep Rock lake) and as such was exposed to lower concentrations of Al, Fe, Ni, and S than the other wetlands and microcosms which were in the area affected by mining. The microcosm plant tissues generally contained significantly higher levels of Al, Ba, Fe, and P, and lower levels of Mn and Ni from those of the natural wetlands. In the case of S, plants from wetlands 2, 3, and 4 demonstrated significantly higher levels than any of the microcosms. These wetlands have developed either directly on tailings fields, or in pools fed by water flowing over and through, large tailings fields. As such they are exposed to potentially much higher concentrations of many elements than any of the microcosms whose water supplies come from a clean source of water (in the case of the control), or Caland itself, which was shown to contain only moderately high metal concentrations (Chapter 1). Other studies have shown that the waste rock from metal mines often contain elevated concentrations of sulfidic minerals (EPA 2000; Mitsch and Wise 1998) that, in turn increase the concentrations of metals in the wetland plants that are present (Peterson et al 1991; Manios et al 2003).

When comparison were made with the expected average concentrations of plant tissues (Hutchinson, 1975), it was found that only four elements showed variations in expected values. Cr was found to be higher than normal in all the plants in all three treatments,

especially in the deep and control treatments. The exact cause for this is unknown as there is no significant difference ($p < 0.05$) in the concentrations of Cr in the water from any of the three treatments. K is consistently low in all plant species except *Carex sp.* Mn was shown to be lower than average in both *E. smallii* and *P. australis* with the other two species containing average concentrations. Finally, and most importantly, *Carex sp.* exhibited S concentrations twice as high as the average in the deep and surface treatment microcosms, but lower than average in the control. This indicates that *Carex sp.* is capable of extracting and concentrating the S that was available in the treatment water. None of the other three species exhibited greater than expected S concentrations.

2.4.2. Variations in soil concentrations

The results showed (Table 2.4) that in 2002 the significant differences in soil concentrations of Cr, Cu, and Sr in 2002 (Fig 2.7) were due exclusively to the treatment applied to the microcosms and not to the different species present. As the soil in all the microcosms came from the same place, and as the same number and type of plants were placed in each microcosm, it is reasonable to believe that the type of water applied (the only changing variable) would be the only factor to cause significant variations ($p < 0.05$) in the metal concentrations across the microcosms. This was further demonstrated in the porewater for 2002 (Table 2.5) where it was shown that SO_4 , Al, Ca, Cu, Fe, K, Mg, S, and Sr all varied significantly due to the treatment while no other factor that was examined exhibited a significant change in either soil or porewater concentration. This was expected as the porewater derives from the treatment water and any differences across the treatments would be due to differences in the treatment water.

The high levels of S in the water column of the unified pit lakes (see Chapter 1) causing potential meromictic conditions downstream make the results for S particularly important. Significantly higher ($p < 0.05$) levels of S and SO_4 were found in the porewater of the surface and deep treatment microcosms relative to the control. This is most likely due to the higher concentrations of S in the waters of Caland than in the control water taken from Caland's east seep (McNaughton 2001). Another factor could be the extremely high S and SO_4 levels found in the surface and deep treatment waters from Caland. This may have resulted in only a portion of the constituents to be taken up by the plants, thus leaving the excess in the soil (Fitter and Hay 1981; Dunbabin and Bowmer 1992). This is supported by the results of analysis of the plant tissue (2.3.1) which showed very high mean S concentrations in *Carex sp.*, *E. smallii*, and *T. latifolia*. By 2003, SO_4 concentrations in the porewater (Table 2.7) showed significant differences also related to the species of plant present in the quarter of the microcosm from which the soil sample came. The quarters containing *P. australis*, and *T. latifolia* had higher concentrations of SO_4 than the quarter containing *E. smallii*. This concurs with the findings of Kadlec and Knight (1996) and Fitter and Hay (1981) that mineral uptake by plants changes water chemistry, and by association, soil chemistry.

2.4.3. Management potential of wetlands

Which combinations of the four plant species grown in the microcosms would be optimal for the remediation of the Steep Rock pit lakes? Since the concentration of S-compounds is of concern because of their effect on stratification and the resulting potential effects

downstream (McNaughton 2001), this study suggests that the ideal wetland for treatment of Steep Rock pit lake outflow water would consist primarily of species capable of removing S, namely *P. australis*, and *T. latifolia*. If the die off of *Carex sp.* were shown to be due either to freezing in poorly insulated microcosms, or the allelopathic nature of *E. smallii*, not to toxicity caused by the metal concentrations present, *Carex sp.* should also be included in the treatment wetland –indeed, it should constitute the major species present. The *Carex/Phragmites/Typha* wetland provide the maximum removal of S-salts, as well as Al, Cu, Fe, Ni, Sr and Zn.

While the choice of vegetation can vary greatly depending upon the climate, geography and chemistry of the tailings, it is important that indigenous species are selected for treatment wetlands (Kalin 2001). For the last twenty years, *P. australis* has become important for wetland treatment of industrial effluent containing metals (Dunbabin and Bowmer 1992). This is because it is capable of growing in extremely inhospitable conditions such as low pH and elevated metal concentrations (Panich-Pat et al 2004). Also, *P. australis* can tolerate high levels of Cd, Cu, Zn, and Pb (Ye et al 2003) while accumulating Cu (Batty et al 2000; Ye et al 2003), Zn (Batty et al 2000), and Fe (Batty and Younger 2002) as well as other metals, primarily in its root tissues (Weis and Weis 2004). When grown in association with specific periphyton, *P. australis* exhibits enhanced accumulation and retention of metals (Weis and Weis 2004). Finally, no differences in metal tolerance were noted between populations of *P. australis* from metal contaminated and uncontaminated sites –and the same holds true for *T. latifolia* (Ye et al 2003). *T. latifolia* does not appear to exhibit any adaptive tolerance to metals (Dunbabin

and Bowmer 1992; Ye et al 1999). However, it has been shown to accumulate Cu, Ni (Dunbabin and Bowmer 1992), Pb and Zn (Batty et al 2000; Panich-Pat et al 2004) from mine and wastewater, and Cd, Cu and Zn from metal-amended sewage (Dunbabin and Bowmer 1992). Additionally, *T. latifolia* accumulates metals primarily in the roots (Fediuc and Erdei 2002; Weis and Weis 2004). *T. latifolia* is favored for wetland remediation of mining and other industrial wastewater because it grows in extremely inhospitable conditions such as low pH and elevated metal concentrations (Panich-Pat et al 2004) and, along with sedges, alders and willows, has a high evaporation rate which decreases the infiltration of atmospheric precipitation (Kalin 2001).

Kadlec and Knight (1996) found wetlands to be one of the least expensive water quality treatment systems to both establish and to maintain. To establish a wetland consisting primarily of *Carex sp.*, *P. australis*, *T. latifolia*, and *E. smallii*, the water level in the west arm of Steep Rock Lake should be lowered to a depth ranging from 0.1 to 0.5m (Kadlec and Knight 1996). This depth control could easily be facilitated by modifying the existing overflow weir situated at the South end of the West arm of Steep Rock Lake. Removal efficiency of any wetland plant species depends primarily upon the influx rate of the pollutants. Costs are primarily due to earthworks and construction of the bed for the plants. Earthmoving costs in the in Steep Rock pit lakes would be minimized as the treatment wetland would be established within an existing lake basin. The floral community could be established with plants harvested from adjacent wetlands (Dunbabin and Bowmer 1992; Kadlec and Knight 1996).

One of the drawbacks to wetland remediation is that wetlands have a limited extraction capacity and thus require considerable area in order to be effective (Dinges 1982). Size, however, is not an issue in the case of the Steep Rock pit lakes remediation as the proposed wetland consists of approximately 620 ha. However, inflow and residence time must be considered. Moshiri (1993) describes how existing treatment wetlands use a variety of influx rates ranging from 9.5 to 1727.5 L/day/m² (LDM) (mean of 111.8 LDM). Wetlands where influx rates exceed 352.3 LDM often do not meet water quality standards (Moshiri 1993). Hence, while the ideal rate of influx remains undetermined, it should not exceed a rate of 352.3 LDM. With an average flow (111.8 LDM) and a size of the proposed wetland at 618.3 ha, a daily volume of 6.912×10^8 L of water could be accommodated. A residence time averaging 5 (Moshiri 1993) to 10 days is needed for denitrification and the removal of most of the P and TSS (Palmeri and Trepel 2002). Further studies on the rate of uptake of Fe, S, and other elements are needed in order to determine the ideal residence time and exact species composition needed for the treatment of the Steep Rock mines waste water.

2.4.4. Conclusion

In conclusion, this study shows that treatment of the water that will exit the Steep Rock pit lakes employing a wetland may be feasible. Significant differences in tissue concentrations occurred among local species demonstrating that some local species were more efficient than others in the removal of S and metals. These species should be considered as primary candidates for designing a wetland to treat the wastewater of the Steep Rock mine site. The proposed wetland site should be capable of treating a sufficiently large volume of water to make the project feasible. Further work is necessary in order to determine which contaminants pose the greatest risk to local flora and fauna so that the remediation wetland, when created, can be adapted to have the greatest effect.

ii. General Conclusions:

The key findings for all objectives stated in this thesis are grouped into three major points listed below:

ii.i. Water Quality Changes

The water quality of Hogarth and Caland pit lakes was found to differ significantly from each other with Hogarth containing greater concentrations of Ca, K, Mg, Na, Mn, Ni, S, Sr, V, SO₄, conductivity, and TDS compared to Caland. Alkalinity, DOC, NO₃, Ba, TKN, and pH were found to be significantly lower in Hogarth than Caland. Although the exact source of the sulfates in the Steep Rock pit lakes is unknown (suspected to be due to deposits of high sulfur ore located around the region), the levels remained 10 and 70 times higher (for Caland and Hogarth respectively) within the pit lakes than in the surrounding natural systems (Jackson, pers comm., 2003). These sulfates can be reduced by bacterial action to form sulfides which can interfere with the formation of FePO₄, as well as other iron salts, resulting in the release of phosphates, or some other anion (depending upon the salt), and the formation of iron-sulfide compounds while also removing the sulfides (Lamers et al 1998). Such sulfide compounds are often insoluble and result in the effective removal of their component elements from the system (Labrenz et al 2000) and may be the reason for the relatively low Fe concentrations found in the Steep Rock pit lakes.

It was shown that the depth of the oxygenated freshwater lens in Caland pit lake, represented by the layer of water exceeding 6 ppm DO, was decreasing logarithmically

due both to the presence of the fish farm and the flooding of the pit lake into a wider basin. This reduction in depth indicates that there is 10 years or less of viable water quality to support the farming operation at the present rate of decrease.

ii.ii. GIS Modeling

The model developed using GIS illustrated the flooding sequence of the pits in the former Steep Rock mine site and also predicted the location of the eventual merging of the Steep Rock pit lakes with the west arm of Steep Rock Lake and the rest of the Seine River system.

As flooding proceeds, and the pits join, it is predicted that the water quality will change. It was estimated that, at flood out, Cr, and Cu will have reached levels exceeding the guidelines set out for the preservation of aquatic life in Canada, and that Mn, S, SO₄ and TDS will also exceed those levels defined as safe for human consumption. As the Steep Rock pit lakes will eventually flood into the Seine River, any input of contaminated water could have serious impacts as far west as Rainy Lake and, through a network of lakes, south into the United States.

ii.iii. Wetland Remediation

Four species of wetland plants were tested in order to determine their suitability for use in remediation of the Steep Rock pit lakes. It was shown that there were significant differences in the concentrations of many elements across the four species after both one and two years of growth. When these concentrations were compared to expected values,

it was shown that the concentrations of Cr, K, Mn, and S in plants of all species grown in water from Caland pit lake were greater than expected. Thus, the four test species could indeed be used in the remediation of S in the pit lakes under wetland conditions. When the soils of the microcosms were examined, it was shown that significant differences after one year were due solely to the treatment water added while after two years, SO₄ concentrations in the porewater also exhibited significant differences due to plant species.

Based on the findings of this study, the ideal wetland for the treatment of Steep Rock pit lake outflow water would consist primarily of *Carex sp.* with some *P. australis* and *T. latifolia*, assuming that the die-off of *Carex sp.* was due simply to freezing without adequate insulation in the microcosms, a situation that would not occur naturally. This wetland would serve to extract the maximum amount of S, as well as Al, Cu, Fe, Ni, Sr and Zn. Further studies will have to be performed, however, in order to determine the rate of uptake of Fe, S, SO₄ and other metals in order to determine both the ideal residence time and the exact composition of the treatment wetland for optimal remediation success.

In summary, this thesis successfully isolated and quantified the timing and major effects that can be expected when flood out occurs into the West arm of Steep Rock Lake. It also assessed the feasibility of using wetlands to remediate these effects. However, one major concern remains. It is unknown why Hogarth is devoid of life and as this knowledge is vital to remediation efforts, future studies are needed to discover the exact cause of its toxicity so that efforts may be made to rectify this situation prior to flood out.

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APPENDIX

Appendix 1: Predictive Equations

1.1 Equations to predict water elevation

For the following equations, x represents the year at which the elevation of water is desired while the output (y) is an elevation in m above sea level.

Caland predictive flooding model

- $y = 9192.9527 * (\ln(x)) - 69586.2043 \pm 15.5565$

Hogarth predictive flooding model

- $y = 8307.7437 * (\ln(x)) - 62859.8596 \pm 13.9835$

1.2 Equations to predict concentrations of elements in pit water

The equations created from observations of past trends of chemical concentration changes that were used to estimate the concentrations of elements over time are as follows.

If no significant trend was observed over time for an element, the mean and standard deviation were used as the predictor –it was assumed that as no significant change had occurred in the past, that none would occur in the future.

Predictive Concentration models for Caland (x = year)

- $[Al] = 0.091 \pm 0.199 \text{ mg/L}$
- $\text{Alkalinity} = 166.957 \pm 10.671 \text{ mgCaCO}_3/\text{L}$
- $[Ba] = 0.018 \pm 0.003 \text{ mg/L}$
- $[Ca] = 115.818 \pm 17.610 \text{ mg/L}$
- $[Cl] = 11.081 \pm 3.494 \text{ mg/L}$
- $\text{Conductivity} = 985.721 \pm 78.527 \text{ } \mu\text{S/cm}$
- $[Cr] = 0.006 \text{ mg/L}$
- $[Cu] = \ln(0.0008x - 0.5025) \pm 0.0005 \text{ mg/L}$

- $\text{DOC} = 840.7576 - 0.4190x \pm 0.4935 \text{ mg/L}$
- $[\text{Fe}] = 0.078 \pm 0.227 \text{ mg/L}$
- $[\text{K}] = 4.845 \pm 0.590 \text{ mg/L}$
- $[\text{Mg}] = 57.611 \pm 9.295 \text{ mg/L}$
- $[\text{Mn}] = 0.095 \pm 0.172 \text{ mg/L}$
- $[\text{Na}] = 16.083 \pm 2.936 \text{ mg/L}$
- $[\text{NH}_3] = 0.079 \pm 0.070 \text{ mg/L}$
- $[\text{NH}_4] = 0.093 \pm 0.088 \text{ mg/L}$
- $[\text{Ni}] = 0.009 \pm 0.006 \text{ mg/L}$
- $[\text{NO}_3] = 1191001.3826\ln x + 90747.7091(\ln x)^2 - 14836.7951(\ln x)^3 - 7780196.9144 \pm 0.6057 \text{ mg/L}$
- $\text{pH} = 7.054 \pm .363$
- $[\text{S}] = 112.663 \pm 43.057 \text{ mg/L}$
- $[\text{SO}_4] = 367.656 \pm 47.001 \text{ mg/L}$
- $[\text{Sr}] = 0.1961 + (0.7477/(1 + e^{-(x-1992.8111)/0.3173})) \pm 0.0909 \text{ mg/L}$
- $\text{TDS} = 750.390 \pm 68.913 \text{ mg/L}$
- $[\text{Ti}] = 0.013 \text{ mg/L}$
- $\text{TKN} = 0.198 \pm 0.088 \text{ mg/L}$
- $\text{Total [P]} = 0.012 \pm 0.013 \text{ mg/L}$
- $\text{TSS} = 40.2750x - 80627.0249 \pm 0.5965 \text{ mg/L}$
- $[\text{V}] = 0.271 \pm 0.167 \text{ mg/L}$
- $[\text{Zn}] = 6003.8964/x - 2.9954 \pm 0.0013 \text{ mg/L}$

Predictive Concentration models for Hogarth (x = year)

- $[Al] = 0.112 \pm 0.281 \text{ mg/L}$
- $\text{Alkalinity} = 1.1203 * x^{1.0621} - 3490.9271 \pm 9.3531 \text{ mgCaCO}_3/\text{L}$
- $[Ba] = 0.005 \pm 0.000 \text{ mg/L}$
- $[Ca] = -5.6353 * x + 11596.4024 \pm 9.6525 \text{ mg/L}$
- $[Cl] = .5964 / (1 + e^{-((x-1993.9756) / -0.9494)}) + 13.5485 \pm 1.2492 \text{ mg/L}$
- $\text{Conductivity} = 26.4299 * x - 50530.0597 \pm 67.9201 \text{ }\mu\text{S/cm}$
- $[Cr] = 0.011 \text{ mg/L}$
- $[Cu] = \ln(3.7742 - 0.0014x) \pm 0.0049 \text{ mg/L}$
- $\text{DOC} = -0.4073 * x + 816.3372 \pm 0.2138 \text{ mg/L}$
- $[Fe] = 0.635 \pm 1.593 \text{ mg/L}$
- $[K] = 6.461 \pm 0.627 \text{ mg/L}$
- $[Mg] = 190.623 \pm 17.331 \text{ mg/L}$
- $[Mn] = 0.171 \pm 0.153 \text{ mg/L}$
- $[Na] = 24.282 \pm 1.327 \text{ mg/L}$
- $[\text{NH}_3] = 0.055 \pm 0.026 \text{ mg/L}$
- $[\text{NH}_4] = 0.102 \pm 0.103 \text{ mg/L}$
- $[Ni] = 9.3260 - 0.0046x \pm 0.0113 \text{ mg/L}$
- $[\text{NO}_3] = 1.036 \pm 0.204 \text{ mg/L}$
- $\text{pH} = 297087.6992/x - 141.6898 \pm 0.2515$
- $[S] = 514.687 \pm 40.821 \text{ mg/L}$
- $[\text{SO}_4] = 11.5632x - 21709.417885 \pm 23.11526 \text{ mg/L}$
- $[Sr] = 0.1869 + (1.1533 / (1 + e^{-((x-1993.0705) / 0.4405)})) \pm 0.1813$

- $\text{TDS} = 2305.153 \pm 98.570 \text{ mg/L}$
- $[\text{Ti}] = 0.016 \text{ mg/L}$
- $\text{TKN} = 0.086 \pm 0.066 \text{ mg/L}$
- $\text{Total [P]} = 0.009 \pm 0.002 \text{ mg/L}$
- $\text{TSS} = 28.170 \pm 22.061 \text{ mg/L}$
- $[\text{V}] = 0.631 \pm 0.243 \text{ mg/L}$
- $[\text{Zn}] = 3.1489 - 0.0016x \pm 0.0025 \text{ mg/L}$

Appendix 2: *In Situ* Chronic Toxicity Study

Introduction:

Toxic chemicals can enter a pit lake system in many ways, but this generally occurs through leaching. When mining operations expose rock to the atmosphere, reduced elements and compounds contained on exposed surfaces become oxidized and as post-operations water levels rise, these newly oxidized compounds readily dissolve into the water column (Miller et al 1996). Sulfate, the major contaminant of the Steep Rock pit system, constitutes greater than 99% of the total complement of inorganic sulfur found in aquatic systems (Peterson et al 1991) meaning that there is no other significant form of sulfur present. This may be partially due to the fact that sulfides readily react with dissolved metals (such as Fe) to form insoluble products (i.e. FeS_2) that then precipitate out and are effectively removed from solution (Labrenz et al 2000).

Pit lakes are a concern both for public health and wildlife conservation because they are appealing to both mammals in search of drinking water and migratory birds and because they commonly intersect with ground water supplies –possibly contaminating them (Castro and Moore 2000, Miller et al 1996). It is therefore essential that the effects of these systems on local flora and fauna be understood so that remediation efforts can be carried out with utmost efficiency.

Salmonids are very sensitive to various chemical elements such as aluminum (Axler et al 1996) and as such have been used in the past as indicator species for these elements. In this paper, Rainbow Trout (*Onchorhynchus mykiss*) will be used as indicators in an

attempt to establish the reasons why one of the Steep Rock pit lakes (Hogarth pit lake) is devoid of life while another pit lake (Caland pit lake), less than one kilometer distant is capable of supporting abundant aquatic, and avian, life. This species was chosen as it was known to survive in the Caland pit lake (Rainbow trout is the primary product of the fish farm located in this pit lake) allowing for the use of this pit as a control in the study of the effects on fish health and survivorship of Hogarth pit water –Hogarth being, until spring 2003, a dead lake. Also, Rainbow trout are known to be halotolerant –capable of adapting to and withstanding salt concentrations- this was important to consider as the concentration of dissolved sulfates in Hogarth Pit Lake are 70 times greater than the surrounding natural systems, making it for all intents and purposes a saline lake. By using a halotolerant species, this allowed for its use as an indicator as to whether other chemicals were present at toxic levels, or if it the lake was dead merely because no native organisms were able to adapt to these saline conditions.

Methods:

An *in situ* experiment was carried out in Hogarth and Caland pit lakes between July 22nd and September 24th, 2003. Pens, created by sealing the ends of minnow traps, were suspended at a depth of 9m (Figure 1) at various locations in both Caland and Hogarth. The depth of 9m was chosen as it was at this depth that the trout experienced optimal DO (8ppm) and temperature (12°C). 1.5 g Rainbow trout (*Onchorhynchus mykiss*) were placed in the pens at a density of 5/pen and were given a time-released food source sufficient to last three weeks. These pens were located as shown in the following figure (Figure 2) and table (Table 1) (coordinates gathered using a WAAS-enabled Garmin Etrex Legend GPS unit).

Figure 1: *In situ* experimental setup

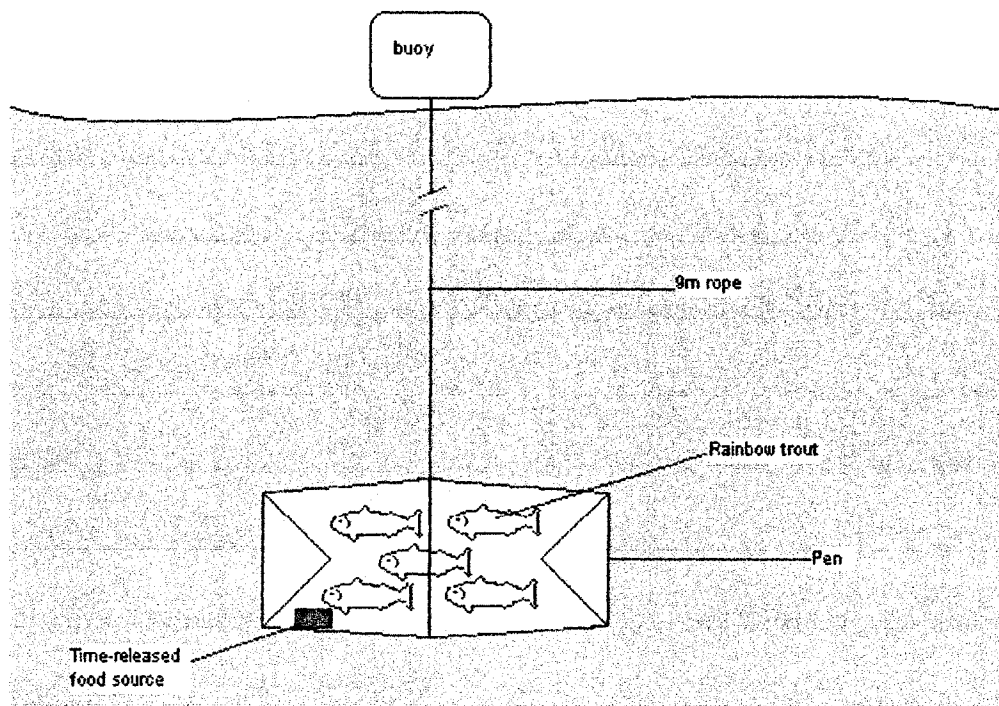


Figure 2: Locations of *In situ* fish pens



Table 1: Location of *In situ* fish pens

Lake	Trap #	North	West
Hogarth	1	48° 47' 977"	091° 38' 843"
Hogarth	2	48° 48' 010"	091° 38' 635"
Hogarth	3	48° 48' 272"	091° 38' 587"
Hogarth	4	48° 48' 431"	091° 38' 598"
Hogarth	5	48° 48' 308"	091° 38' 817"
Caland	1	48° 49' 504"	091° 37' 092"
Caland	2	48° 49' 417"	091° 36' 692"
Caland	3	48° 49' 303"	091° 36' 782"
Caland	4	48° 49' 103"	091° 37' 167"
Caland	5	48° 48' 899"	091° 37' 222"

Feed pellets were replaced twice (August 12th and September 4th) and at each interval, the number of living, dead and missing fish was noted and dead fish were removed. On September 24th, the remaining fish were gathered and the pens were removed.

Results:

The following tables (2-4) show the number of fish alive, dead and missing after each feeding period.

Table 2: 1st Feeding (August 12, 2003)

Lake	Trap #	alive	dead	missing	notes
Hogarth	1	2	0	3	
Hogarth	2	1	4	0	
Hogarth	3	0	5	0	
Hogarth	4	5	0	0	
Hogarth	5	5	0	0	
Caland	1	4	1	0	dead fish was eaten (skeleton)
Caland	2	4	1	0	
Caland	3	5	0	0	
Caland	4	4	1	0	
Caland	5	5	0	0	

Table 3: 2nd Feeding (September 4, 2003)

Lake	Trap #	alive	dead	missing	notes
Hogarth	1	2	0	0	1 dying
Hogarth	2	1	0	0	
Hogarth	3	0	0	0	
Hogarth	4	2	3	0	
Hogarth	5	3	0	2	1 skeletal
Caland	1	2	0	2	
Caland	2	1	0	3	
Caland	3	3	1	1	
Caland	4	4	0	0	
Caland	5	2	0	3	

Table 4: Final tally of fish pens (September 24, 2003)

Lake	Trap #	alive	dead	missing	notes
Hogarth	1	1	0	1	
Hogarth	2	1	0	0	
Hogarth	3	0	0	0	
Hogarth	4	1	1	3	
Hogarth	5	1	1	1	
Caland	1	1	0	1	
Caland	2	1	0	0	
Caland	3	0	0	3	
Caland	4	1	0	3	
Caland	5	0	0	0	trap was missing

Prior to analysis, it is obvious that there are differences in the survival rates of the fish in the two pit lakes after three weeks, with the mortality rate in Hogarth being three times that in Caland (9/25 in Hogarth, 3/25 in Caland).

Discussion and Recommendation:

Unfortunately, fish began to go missing immediately, with 3 gone after three weeks, 14 after 6 weeks and a total of 26 fish missing from both pit lakes after 9 weeks. As only 50 trout were used between the two pit lakes, this means that greater than 50% of all the trout disappeared during the course of this study. It is impossible to know whether these missing fish escaped, were consumed by other fish in the pens, died and decomposed to the point that they fell apart and out of the enclosures, or whether a combination of these things occurred. While this experiment did not yield valid results due to the uncertainty of the fate of so many of the fish, it did show promise as a means to study the chronic effects of the waters in Hogarth pit lake. It is my recommendation that this experiment be repeated with the following modifications to the procedure:

1. Pen size should be enlarged so as to be able to accommodate a greater number of rainbow trout fingerlings (10 or more per pen). This may also necessitate the use of additional feed pellet(s).
2. Smaller mesh size. Standard minnow traps were modified to form the enclosure in the original experiment. It is possible that the mesh size was too large and as the fish became stressed and lost body mass, they were able to slip out of the enclosure. In order to assure that escape was not the means of disappearance of the fish in the original experiment, larger fish or smaller sized mesh should be used (e.g. large weave window screening).

3. Time between checks of pens should be reduced by at least half (one to 1 ½ weeks as opposed to three week periods) in order to get more accurate times of death of the fish.
4. More enclosures per lake should be used. The original experiment called for 10 pens per lake, but due to time constraints this number was reduced to 5. It is recommended that at least 10 pens be dispersed evenly in each lake.

These changes to the original experimental procedures should reduce the margin for error and allow for the retrieval of valid chronic toxicity results.

Appendix 3: Predicted Water Quality Comparison

The predicted concentrations for the entire pit at flood out were compared to the Canadian Water Quality Guidelines (TFWQCCREM 1987). The results of the comparison are shown in Table 1.3. It was found that, in terms of aquatic life the following elements exceeded the legal limits: Cr, and Cu while predicted Fe concentrations were slightly less than the limits.

Table 1.3: Predicted concentrations (mg/L) compared with the Canadian Water Quality Guidelines

Parameter	Aquatic life	Drinking water	Predicted concentrations
Al	0.1		0.091
As	0.05	0.05	
Ba		1	0.022
Cd	0.0018	0.005	
Cr α	0.002	0.05	0.016
Cu α	0.004	1	0.005
Fe $\alpha\beta$	0.3	0.3	0.311
Pb	0.007	0.05	
Mn β		0.05	0.31
NH3			0.139
Ni	0.15		0.058
pH	6.5 to 9.0	6.5 to 8.5	7.145
SO4 β		500	1537.161
S β		0.05	531.225
Sr		10 Bq/L	1.745
TDS β		500	2560.091
Zn	0.03	5	0.008

Results shown in table 1.4 are given in mg/L except for alkalinity

(mgCaCO₃/L), conductivity (μ S/cm), and pH

When comparing the predicted values to the limits set drinking water, it was found that Mn, S, SO₄ and TDS all exceeded the legal limit. It is likely, however, that the predicted concentration of S would include precipitated S²⁻ that would settle out from the water

column, thus reducing the amount of available S. While predicted Al and Fe concentrations were found to be slightly lower than the limit set for the preservation of aquatic life.