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# Water quality and toxicity investigations of two pit lakes at the former Steep Rock iron mines, near Atikokan, Ontario / by Andrea R. Goold.

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# Water quality and toxicity investigations

# of two pit lakes at the former Steep Rock

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by

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**Abstract**

Caland and Hogarth Pit Lakes formed after cessation of mining and dewatering efforts of open-pit iron mines, near Atikokan, Ontario. They were assessed for water quality changes since monitoring began in 1998. Stable isotopes were used to evaluate trends in water columns and gain information on geological processes influencing water quality. Chronic toxicity investigations were carried out for Hogarth Pit Lake.

Approaching depths of 200 m, both pits have been filling with groundwater and precipitation since termination of mining in 1979. Limestone and carbonate deposits in the area counter production of acids from waste rocks, resulting in near-neutral pH's in both lakes. Although proximal pit lakes, there are major chemistry differences between them. Caland is characterized by alkaline, nutrient rich, while Hogarth has elevated conductivity, total dissolved solids (TDS), and $SO_4^{2-}$ levels. Monitoring trends reveal gradual dilution of both pit lakes since 1998. Hogarth has pronounced seasonal variations, with winter months having elevated levels of the aforementioned parameters. Similar $\delta^{34}S$ profiles in Caland and Hogarth suggest pyritic lenses in the ore body are the major source of sulfates for both lakes. Caland $\delta^{13}C_{DIC}$ values reveal organic inputs are the major sources of carbon, whereas Hogarth's major source of carbon comes from weathering carbonates.

Hogarth Pit Lake has experienced a change in toxicity. In 1999 the lake was acutely toxic, and by 2005, chronic effects were present. Chronic toxicity testing using *Ceriodaphnia dubia* resulted in intermittent toxicity occurring in the

winter months. Toxicity Identification Evaluation (TIE) tests did not successfully isolate the cause of toxicity, which led to exploration of TDS toxicity using mock effluents. Mimicking concentrations of the most abundant ions ($Ca^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$), mock effluent test results on both *C. dubia* and *Lemna minor* suggest TDS were responsible for the majority of toxicity in Hogarth. Bioaccumulation studies using *Eleocharis smallii* and *Pyganodon grandis* resulted in elevated concentrations of S and Ni in tissues exposed to Hogarth water. Metals contributing to toxicity in Hogarth, especially Ni, could still a possibility and should not be ruled out.

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## GENERAL INTRODUCTION

### General Information

Northwestern Ontario has an abundance of natural resources. Many established northern communities were and have been sustained by mining activities. The mining industry however, experiences "boom and bust" fluctuations, with aggressive exploration and extraction practices followed by mine closures. Results of such behaviours have left widespread ecological footprints in the northern landscape.

Progress towards environmental responsibility within the industry has been made. In recent years regulations, programs, and legislations at both federal and provincial levels have been implemented. Such examples include Environmental Effects Monitoring (EEM), Accelerated Reduction and Elimination of Toxics Program (ARET), Ontario's Municipal/Industrial Strategy for Abatement (MISA), and amendments to the Ontario Mining Act. Amendments to the *Ontario Mining Act*, part VII, requires, as of 2000, specific closure plans for all mining operations.

At the time of discovery in 1930, Steep Rock Iron Range, located just north of Atikokan, Ontario was the richest large deposit of iron ore in North America (Steep Rock Mines, 1943). Developmental and operational complications arose due to the ore body being located beneath Steep Rock Lake. The lake was the shape of the letter "M", comprised of the "West Arm", "Middle Arm", "East Arm", and "South Arm". Authorized under Canada's War Measures Act due to a period of wartime emergency, isolation and access to

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Steep Rock Lake required major changes to the landscape (MNR, 1986). A massive diversion of the Seine River, which flowed through Steep Rock, was executed in 1944. This included the construction of various dams and tunnels to isolate areas of the lake under which the ore was located. Access to the ore body was accomplished by draining $5.7 \times 10^{11}$ L of water from the "Middle", "East Arms", and "Southeast Arms" and removing $2.25 \times 10^8 \, m^3$ of overburden (Steeprock Resources Inc, 1986). Mining of the Steep Rock area continued for 35 years until 1979, yielding 79 Mt of iron ore from Caland Ore Company and Steep Rock Iron Mines (MNR, 1986). On April 1st, 1988, a Surrender Agreement was signed by Steep Rock Mines and the Ministry of Natural Resources (MNR); and as such, the MNR became the owners of the previously mined area, including Caland and Hogarth Pit Lakes.

Pit lake characteristics

Pit lakes form when open-pit mining operations cease, dewatering efforts stop, and the pit fills with water most commonly through inflows of groundwater, runoff, and precipitation. General characteristics of pit lakes are summarized in Table i. Environmental concerns from the operation of large open pits include: regional effects on water tables, rate of pit lake filling, ultimate water quality, limnology, and potential impacts of the lakes on wildlife (Shevenell et al, 1999). Particular concerns in this study were centered on water quality and impacts on aquatic life.

**Table i. Common characteristics of pit lakes**

| Characteristics | Literature |
| --- | --- |
| • often deep relative to natural lakes of a similar size<br>• relative depth (% ratio between maximum depth of lake and mean diameter)<br>is in the range of 10-40%, natural lakes generally are <2% | Stevens and Lawrence,1998<br>Doyle and Runnells, 1997; Hamblin et al, 1999 |
| • high surrounding walls that often generate a unique microclimate and a steep littoral zone (i.e. 45-50 degrees), if at all present | Stevens and Lawrence,1998; Kalin et al, 2001 |
| • typically very thin sediment layers | Stevens and Lawrence,1998 |
| • lack shorelines, therefore inhibiting development of submerged rooted biological communities | Lyons, 1994 |
| • both primary productivity and biological activity are generally low | Lyons, 1994; Doyle and Runnells, 1997 |
| • solutes are released into the lake through weathering of rock walls<br>- rock walls are typically enriched in metal sulfide minerals (i.e. pyrite)<br><br>-this generally leads to water quality problems including low pH, high metal concentrations, and high levels of suspended and dissolved solids | Davis and Ashberg, 1989; Levy et al, 1995; Doyle et al, 1995; Ramstedt et al, 2003<br><br>Castro and Moore, 2000; Stevens and Lawrence, 1998 |
| - can lead to stratification and/or meromictic conditions | Parshley and Bowell, 2003 |

Controls on pit lake chemistry are complex and include, but are not limited to: groundwater chemistry and inflow, precipitation/evaporation, limnology and internal chemical processes, geochemical influences, pit wall-water interactions, and biological processes (Eary, 1999; Castro and Moore, 2000; Bowell, 2003). Acid mine drainage and acidic pit waters are largely influenced by local geology, and are of concern in previously mined areas. Relative abundance of minerals that generate (i.e. pyrite) or neutralize (i.e. calcite) acidity ultimately determine whether water in contact with a deposit will be acidic (Shevenell et al, 1999). Due to their neutralizing effects, contact with calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) result in better water quality. To generalize resulting characteristics of pit lakes, Eary (1999) outlined three main categories of pit lakes. These are based on trends in total dissolved solids (TDS), major solutes, and metals in hard rock pit lakes: (1) acidic-high TDS, (2) alkaline-high TDS, and (3) circumneutral-low TDS. Based on this classification, Caland Pit Lake fits category 3, while Hogarth corresponds with category 2.

Analysis of Water Quality Monitoring Data

Analysis of water quality monitoring data can be difficult due to large data sets, numerous variables, and many spatial and temporal variations. Multivariate statistical techniques can be applied to characterize and evaluate surface water to verify temporal and spatial variations linked to seasonality (Singh et al, 2004).

Applications of different multivariate statistical techniques, including cluster analysis (CA), principal components analysis (PCA), factor analysis (FA)

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and discriminant analysis (DA) can aid in the interpretation of complex data matrices and allow for a better understanding of the water quality and ecological status of studied systems (Shrestha and Kazama, 2007). To determine dimensionality of group differences and to summarize the differences between groups, DA can be used (McCune and Grace, 2005).

Stable Isotope Analysis

Isotopes are atoms of the same element that have different numbers of neutrons, but the same number of protons and electrons. Two possible mechanisms govern isotopic abundance of elements (1) decay of radioactive elements to their stable daughter products and (2) isotopic fractionation during mass-dependent physical, chemical, or biological processes (Allen and Lepitre, 2004). To "fractionate" is to change the relative proportions of various isotopes. As a result of the fractionation process, water and solutes develop unique isotopic compositions (ratios of heavy to light isotopes) that can be indicative of their source and/or the processes involved in their formation (Kendall and Doctor, 2005).

Environmental stable isotopes are the naturally occurring isotopes of elements found in abundance in our environment: H, C, N, O, and S (Clark and Fritz, 1997). These environmental isotopes can serve as tracers of water, carbon, nutrient, and solute cycling in the environment (Allen and Lepitre, 2004). Isotope-based studies are now integral components in water quality and environmental studies. Stable isotopes have been used in pit lake studies to

better understand past and present mechanisms influencing the water chemistry, and more accurately predict future dynamics of the systems (Allen and Lepitre, 2004; Dold and Spangenberg, 2005; Pellicori *et al*, 2005; Gammons *et al*, 2006, Trettin *et al*, 2007).

Toxicity Testing

Many motives exist for toxicity testing; whether they are for exploratory, monitoring, or regulatory purposes. Applications include assessing effects of present toxicants in aquatic or terrestrial ecosystems and attempting to identify cause of toxicity in these systems (Environment Canada, 1999).

Historically, when effluent has been identified as toxic, or suspected as being toxic, a sample is analyzed for "priority pollutants" (i.e. heavy metals, volatiles, organics, etc.). Concentrations of such pollutant(s) present are then compared to literature toxicity data with the goal of determining which pollutant(s) is responsible for toxicity (U.S. EPA, 1991). Of course, the first of many problems is variability of effluents. Since numerous constituents can contribute to toxicity, distinguishing one or multiple toxicants as causative by comparing their concentrations to literature values can be daunting. Furthermore, when a combination of multiple toxicants serve as the cause of toxicity, conventional methods fail to measure such matrix effects (U.S. EPA, 1991). If toxic effects are present, with no known cause, Toxicity Identification Evaluation (TIE) test methods can be performed. TIE methods employ physical/chemical manipulations on the effluent in an attempt to determine whether any

manipulations result in a reduction in toxicity (Norberg-King $et$ $al$, 2005a). If toxicity is not reduced after TIE manipulations and sample conductivity exceeds 2000 μs/cm in freshwater, total dissolved solid (TDS)-related toxicity should be investigated (Waller $et$ $al$, 2005).

TDS consists of a combination of ions ($Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $HCO_3^-$, $Cl^-$, $NO_3^-$, and $SO_4^{2-}$). Elevated levels can cause toxicity through: increases in salinity, changes in ionic composition of the water, as well as toxicity of individual ions (Weber-Scannell and Duffy, 2007). The aforementioned authors state that increased salinity can cause shifts in biotic communities, limit biodiversity, exclude less-tolerant species, and cause acute or chronic effects at specific life stages. To confirm toxicity caused by TDS, employment of mock effluent testing (prepared effluent using ionic salts to match effluent quality) has been successful (Kennedy $et$ $al$, 2005; Norberg-King $et$ $al$, 2005b).


Objectives

This study had two broad objectives: to continue monitoring and assess the water quality of Caland and Hogarth Pit Lakes to gain a more comprehensive understanding of their characteristics and major influences on water chemistry; and secondly, to investigate the toxicity of Hogarth Pit Lake.

# Chapter 1: Water Quality Monitoring of Two Pit Lakes in Northwestern Ontario

## 1.1 Introduction

Following cessation of mining and dewatering efforts in the Steep Rock area, the mined pits began filling through combinations of groundwater, runoff, and precipitation. Abandoned mines were up to 300 m below the original lake level of 70 m (Steep Rock Resources Inc., 1986). This resulted in the formation of the two main pit lakes: Caland and Hogarth. These pit lakes have been the sites of two previous studies (McNaughton, 2001; Vancook, 2005).

Caland Pit Lake supports a diverse aquatic community, including Snow Lake Fish Farm started in 1988, currently not in operation. Hogarth Pit Lake lacks higher forms of aquatic life and has experienced a change in toxicity over the years. In 1999 the pit lake was acutely toxic, but by 2005, chronic effects were present. Both lakes are meromictic, primarily due to elevated levels of dissolved solids in the lower portions (hypolimnion) in combination with such deep waters, yet overall chemistries do significantly differ ever since monitoring began in 1998.

Caland Pit Lake is characterized by having an anoxic layer, with the fish farm once located in the upper, oxygenated freshwater lens, higher levels of nutrients (TOTN and TOTP), pH, dissolved organic carbon (DOC) and alkalinity. Caland is a circumneutral-low TDS pit lake (Eary, 1999). As proximal pit lakes, they are in an area with similar climatic effects, groundwater, and geology, hence the differences in water quality and resulting aquatic life is an interesting phenomenon.

Hogarth Pit Lake has higher levels of total dissolved solids (TDS) comprised mainly of $Ca^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$, and related parameter including hardness and conductivity. Eary's (1999) characterization, classifies it as alkaline-high TDS. Hogarth water chemistry in particular has changed considerably since monitoring began. Detailed chemistries can be reviewed in McNaughton (2001). Observational changes within the lake began with McNaughton describing the lake as milky-olive in colour with noticeable iron floc compared to recent observations of clear water with no floc. Although monitored since 1998 (with the exception of 2001), more insight into the processes responsible for the variations in water quality were needed. This can be done by exploring the data of each lake annually and seasonally using multivariate analyses and introducing the use of stable isotopes in monitoring pit lakes.

Chemical differences with the meromictic pit lakes have been documented (McNaughton, 2001; Vancook, 2005). Focusing on trends over a longer period of time is critical as the water in these two pit lakes will eventually combine to discharge into the Seine River system, producing potential adverse downstream effects. Seasonal variations are also of interest, as Hogarth Pit Lake now exhibits toxicity during winter months. Environmental isotopes were employed to determine processes and factors influencing the water quality of these pit lakes.

Clark and Fritz (1997) state that environmental isotopes (H, C, N, O, and S) of principal elements in hydrological, geological, and biological systems, can serve as tracers of groundwater sources, recharge and subsurface processes, geochemical reactions and rates, and biogeochemical cycles. Within the

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hydrological community, isotope-based methodologies have become well established for water resource assessment, development, and management; and are now becoming an integral part of water quality and environmental studies (Clark and Fritz, 1997; Kendall and Doctor, 2005). Since pit lake water chemistries are greatly influenced by physical, chemical, and biological factors, environmental isotopes can serve as an important tool in both qualifying and quantifying them.

Stable isotopes of oxygen and hydrogen can provide information on sources of groundwater recharge and recognize physical processes, such as evaporation that have affected water isotope composition (Allen and Lepitre, 2004). Stable isotopes can also aid specifically in pit lake studies through identifying sources of water and $SO_4^{2-}$, quantifying evapo-concentration effects, observing presence or absence of mixing/turnover, and placing constraints on mechanisms of pyrite oxidation (Pellicori *et al*, 2005).

This study continues the water quality monitoring of Caland and Hogarth Pit Lakes. The objectives of this chapter are (1) to assess water quality trends over time and seasonally through the use of multivariate statistics and (2) to introduce stable isotope analyses to evaluate trends in the pit lake water columns to gain more insight into possible influences on water quality.

## 1.2 Methods

### 1.2.1 Site Description

The study sites were Caland Pit Lake, located at the former Caland Ore Company and Hogarth Pit Lake, located at the former Steep Rock Mines near Atikokan, Ontario, Canada (48°48'N, 91°39'W). Major construction efforts were required to access the iron ore, which was located under Steep Rock Lake. Activities included diverting the Seine River, draining the Middle, East, and Southeast arms of Steep Rock Lake ($5.7 \times 10^{11}$ L of water), and removing $2.15 \times 10^8$ $m^3$ of overburden (Steep Rock Resources Inc., 1986) (Figure 1.1). As of 2006, both pit lakes were approximately 200 m in depth. Caland and Hogarth pit lakes areas were approximately 120 ha and 100 ha respectively.

This area is located in the southern margin of the granite-greenstone Wabigoon Subprovince of the Superior Province of the Canadian Shield (OMNDM, 1994) and contains Archean metavolcanic, metasedimentary and intrusive rocks which were displaced by a series of faults (Shklanka, 1972). Footwall rocks, east of the ore zone, consist of the Marmion Complex, the Wagita Bay Formation, and Mosher Carbonate. To the west of the ore zone, the hanging wall consists of the Witch Bay formation and Dismal Ashrock (Kusky and Hudleston, 1998). The ore zone itself, the Jolliffe Ore Zone, extends up to 400 m in thickness and is subdivided into three members: Manganiferous Paint Member, Geothite Member, and Pyrite Member (Jolliffe, 1966). Some differences have been noted in geology between the two mine sites, mainly concerning deposits of pyrite. The Steep Rock Mine site mineralogy, located in

the middle zone (now Hogarth Pit Lake), contained the main pyritic unit between

the dolomite and ashrock (Shklanka, 1972).
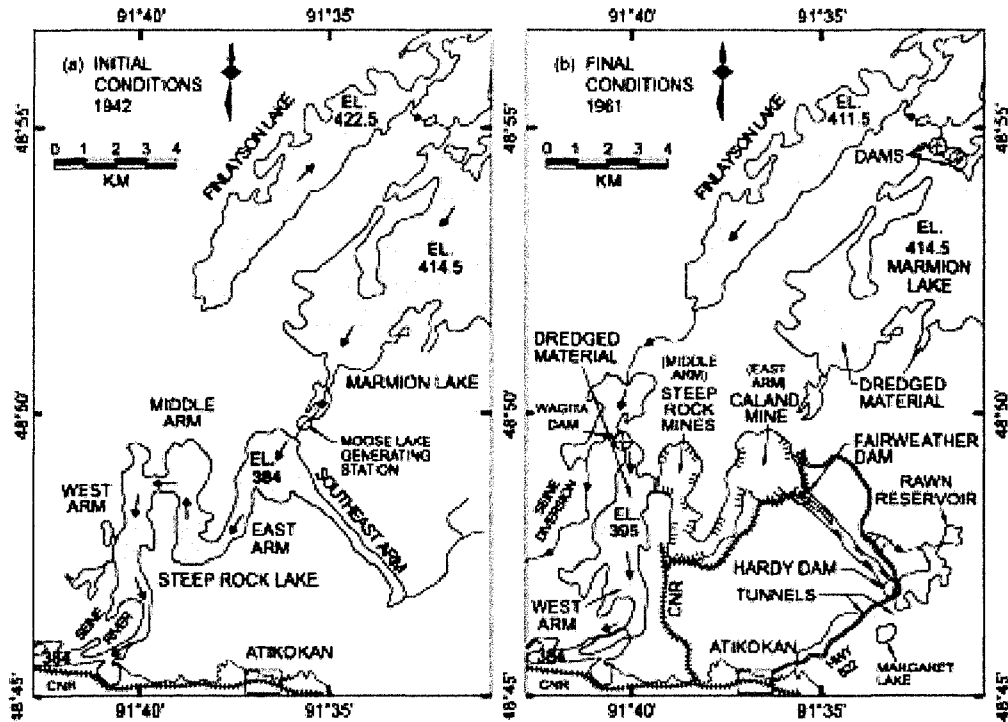


**Figure 1.1. Maps of the Steep Rock Lake area iron mines development: 1a shows initial conditions and 1b shows conditions after development (From Sowa, 2003)**

## 1.2.2 Field Procedures

### 1.2.2.1 Water Quality Monitoring

Two sampling locations were utilized on both Caland and Hogarth Pit

Lakes, corresponding to the previous sites used in McNaughton (2001) and

VanCook (2005), as shown in Figure 1.2. Hogarth Pit Lake sampling locations

were A (48°49'15"N, 91°39'03"W) and B (48°48'23"N, 91°38'36") and Caland

sampling locations were A (48°49'23"N, 91°36'55"W) and B (48°49'01"N, 91°36'21"W).

Water samples were obtained using a 2L Kemmerer on a calibrated rope and transferred into 500mL polyethylene bottles. Depths sampled corresponded with the mixolimnion (2m), chemocline (~18m), monimolimnion (40m), and 1 m off bottom. Duplicate samples were taken at random sample depths, one from each lake, and during each sampling period. Sampling times coincided with each season, when possible. During the course of this study, sampling took place in 2004 (spring, summer, and fall), 2005 and 2006 (winter, spring, and summer).

Dissolved oxygen (DO) and temperature profiles to a depth of 40m were obtained from each lake at both sites A and B with a YSI model 57 DO/temperature probe. In the summer of 2006, a Hydrolab® Datasonde 4 measuring temperature, DO, conductivity, and pH, was used to acquire more detailed depth profiles for each lake. Secchi depths were measured during ice-free months using a secchi disk on a calibrated line.
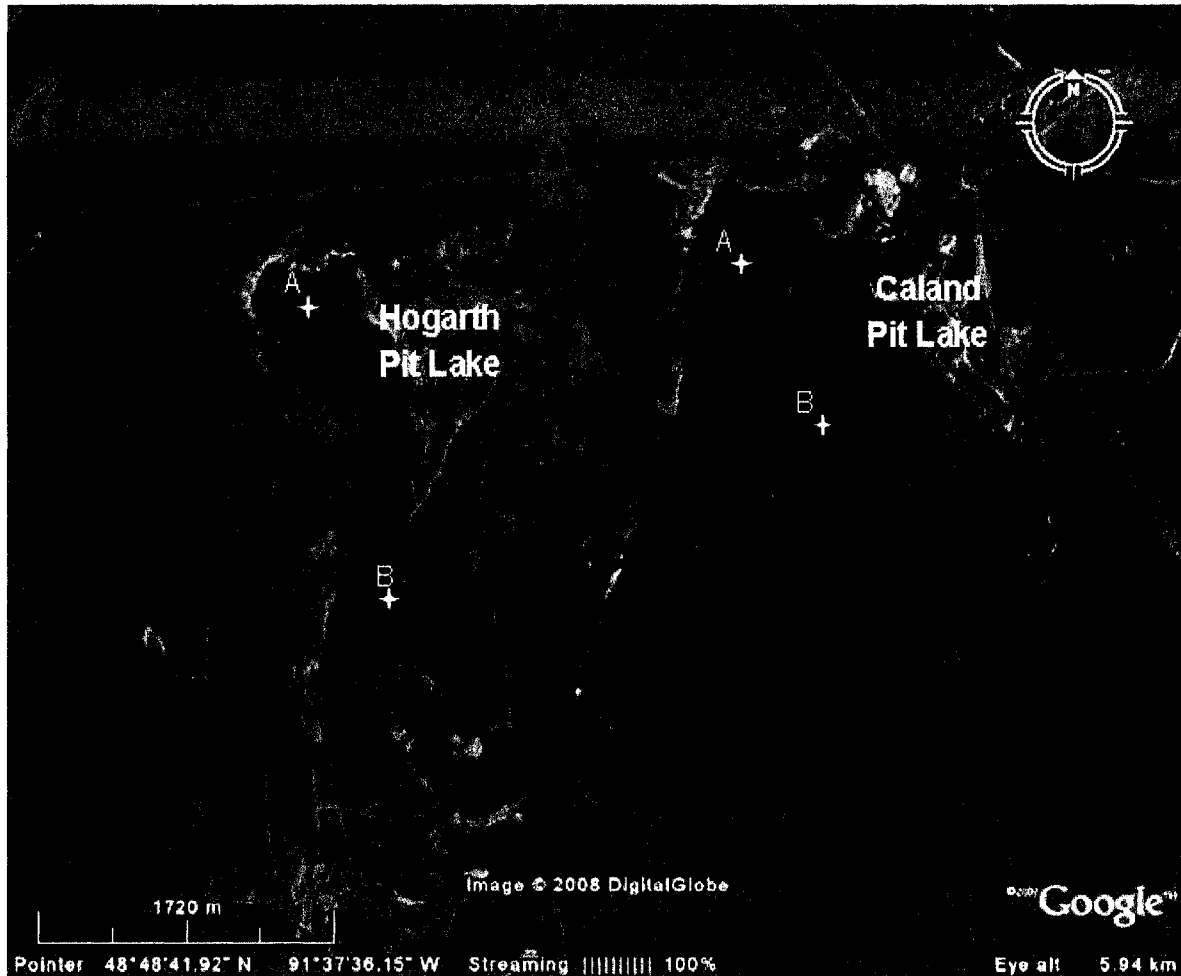
**Figure 1.2. Site location map illustrating sample stations A and B.**

## 1.2.2.2 Stable Isotope Sampling

Locations for stable isotope sampling correspond with sampling stations

"A" in Caland and Hogarth Pit Lakes (Figure 1.2), as these locations were easier

to sample from due to their locations on the lakes (more sheltered). Three

sample periods were included, corresponding with winter, summer, and fall (after

overturn) seasons. Winter samples (full ice cover) were collected on 03/16/06

(Caland) and 03/30/06 (Hogarth), summer samples were collected on 08/16/06

(Caland) and 08/17/06 (Hogarth), and fall sampling occurred on 01/11/06 (both

lakes). A 2L kemmer bottle on a calibrated rope was used for all depths and collected in 250 mL polyethylene sample bottles allowing overflow to ensure no air in the samples. Depths sampled were: 2 m, 10 m, 18 m, 30 m, 40 m, 60 m, 80 m, 100 m, 125 m, and near bottom (x-1)m. A ground water sample was also obtained on 01/11/06 from a drilled well located at the Atikokan Airport, near the pit lakes. Samples were not preserved or filtered and were kept at 4°C until shipment for analysis. Water samples for full chemistry analysis were also taken at these depths.

## 1.2.3 Laboratory/Analytical Procedures

## 1.2.3.1 Water Quality Analyses

All water samples were analyzed at Lakehead University Environmental Laboratory (LUEL) in Thunder Bay, Ontario. LUEL adheres to strict Quality Assurance/Quality Control (QA/QC) guidelines. Their commitment to QA/QC is demonstrated through participation in both the Canadian Association for Environmental and Analytical Laboratory (CAEAL) and the National Water Research Institute (NWRI) proficiency testing programs. Principles followed to ensure reliability of results consist of guidelines, procedures, and practices developed and implemented to produce quality data. Blanks, certified standards, reference materials, and replicates were used to verify effectiveness of QA/QC procedures. Standard operating procedures (SOP) for all tests were modified from Standard Methods for the Examination of Water and Wastewater 18th Edition by Greenberg et al (1992)

Alkalinity, pH, and conductivity were measured within 24 hours of sampling. A 50mL sample aliquot was used to measure conductivity with an Accumet probe using an Accumet XL60 Multimeter System. The same aliquots were analyzed for total alkalinity and pH. Using a Mettler Toledo DL53 Titrator and DL20 Autosampler, pH was measured with a Mettler DG111-SC probe and total alkalinity was measured after being titrated to a pH of 4.5 with 0.02N $H_2SO_4$.

Sample aliquots for total metals analysis were acidified with 0.4 mL Fisher Trace Metal Grade concentrated $HNO_3$. After an open-vessel CEM Mars5 microwave-assisted digestion, samples were brought to 50 mL with double distilled water (DDW) and analyzed on a Varian Vista Pro Inductively Coupled Argon Plasma Spectrometer (ICP) with Cetac Autosampler.

Anions ($SO_4^{2-}$, $NO_3^-$, and $Cl^-$) were determined using a Dionex DX-120 Ion Chromatograph (IC) with an AS40 Autosampler. Samples passed through an IonPac As14 Analytical Column. Samples with $SO_4^-$ concentrations exceeding 400 mg/L were diluted accordingly. Cations ($Ca^{2+}$, $Mg^{2+}$, $Na^+$, and $K^+$) were determined by ICP. Total hardness was calculated with results from separate ion determinations of calcium and magnesium using the calculation: Hardness ($mgCaCO_3/L$) = 2.497($Ca^{2+}$ mg/L) X 4.118 ($Mg^{2+}$ mg/L) from Greenberg *et al* (1992).

Total suspended solids (TSS) and total dissolved solids (TDS) were gravimetrically determined and reported as weight/volume of sample. For TSS samples, 200 mL of sample was passed through a 0.45 µm glass fiber filter and dried at 103°C overnight. TDS samples were obtained from a 50 mL aliquot of

sample that passed through the glass fiber filter, then poured in a glass beaker and dried at 180°C overnight. Filters and beakers were desiccated to a constant weight and final weights were recorded to five decimal places.

Total UV digestible phosphate (TOTPUV), total UV digestible nitrogen (TOTNUV), dissolved organic carbon (DOC) and $NH_3$ were all analyzed on a Skalar San-System Autoanalyzer. Water chemistry parameters examined for this study and associated minimum detectable limits (MDLs) are listed in Appendix 1.

### 1.2.3.2 Stable Isotope Analyses

Samples collected for isotope analysis were analyzed at the Isotope Science Laboratory in Calgary, Alberta. Isotopic compositions were measured for deuterium/hydrogen ($\delta D$), oxygen ($\delta^{18}O$), sulfur ($\delta^{34}S$), and carbon ($\delta^{13}C_{DIC}$). Techniques for determination were as follows: $\delta D$ by chromium reduction method adapted from Nelson and Dettman (2001), $\delta^{18}O$ by $CO_2$-$H_2O$ equilibration method of Epstein and Mayeda (1953), $\delta^{34}S$ by continuous flow elemental analyzer isotope ratio mass spectrometry (CF-EA-IRMS), and $\delta^{13}C_{DIC}$ by phosphoric acid digestions (McCrae, 1950).

Isotope values were reported in the usual $\delta$ notation in units of ‰ (per mil) relative to the following standards: Vienna Standard Mean Ocean Water (V-SMOW) for $\delta D$, and $\delta^{18}O$, Vienna Canon Diablo Troilite (V-CDT) for $\delta^{34}S$, and Pee Dee Belemnite (PDB) for $\delta^{13}C_{DIC}$. Accuracy and precision for the aforementioned methods are summarized in Appendix 2.

## 1.2.4 Data Analysis

Since this is a continuation of monitoring from previous studies by
McNaughton (2001) and Vancook (2005), Table 1.1 provides a summary of
sampling in the pit lakes since 1998. Separate sample locations on the lakes
(sites A and B) were averaged together, as differences between the sites have
never been detected. Averages were also taken when sampling occurred more
than once per season. Data used for all analyses was categorized by year,
depth, and season. Raw data for both pit lakes used in analyses can be viewed
in Appendix 3. Only preliminary analyses were performed on data sets with both
lakes present. Comparing and contrasting lakes with such difference chemistries
would be redundant; therefore, Caland and Hogarth Pit Lakes were mainly
analyzed separately.

Analyzing water chemistry can be challenging due to the frequency of
"censored values", or concentrations of some elements reported as "non-
detected", "less-than", or "greater than" values which are created by the lower or
upper detection limit of an instrument and/or method used (Güler *et al*, 2002).
Since these censored values are not appropriate for many multivariate statistical
techniques and can complicate all subsequent statistical analyses, these values
must be replaced with "unqualified values" (Farnham *et al*, 2002). Values
commonly used to replace the <MDL values are 0, MDL, or MDL/2. A study by
Farnham *et al* (2002) which developed approaches to determine the best
substitution methods concluded that MDL/2 was the superior substitution.
Caution however, should be used when evaluating either censored data or data

for which substitutions have been made. Changes in precision of methods may have occurred, using various laboratories with different analytical instrumentation, and creating biases in long-term trends (Porter *et al*, 1988; Chambless *et al*, 1992; Farnham *et al*, 2002).

**Table 1.1. Summary of sample information from monitoring of Caland and Hogarth Pit Lakes since 1998.**

| Caland | | | | Hogarth | | | |
|---|---|---|---|---|---|---|---|
| Location | Depths (m) | Seasons | Year | Location | Depths (m) | Seasons | Year |
| A and B | 1, 18, 30, (x-1) | spring | | A and B | 1, 18, 30, (x-1) | spring | |
| A and B | 1, 18, 30, (x-1) | summer(3) | 1998 | A and B | 1, 18, 30, (x-1) | summer(3) | 1998 |
| A and B | 1, 18, 30, (x-1) | fall | | A and B | 1, 18, 30, (x-1) | fall | |
| A and B | 1, 18, 30, (x-1) | winter | | A and B | 1, 18, 30, (x-1) | winter | |
| A and B | 1, 18, 30, (x-1) | spring | 1999 | A and B | 1, 18, 30, (x-1) | spring | 1999 |
| A and B | 1, 18, 30, (x-1) | summer(4) | | A and B | 1, 18, 30, (x-1) | summer(4) | |
| A and B | 1, 18, 30, (x-1) | fall | | A and B | 1, 18, 30, (x-1) | fall | |
| A and B | 1, 18, 30, (x-1) | winter | 2000 | A and B | 1, 18, 30, (x-1) | winter | 2000 |
| A and B | 1, 18 | spring | 2002 | A and B | 1, 18, (x-1) | spring | 2002 |
| A and B | 1, 18, (x-1) | summer(2) | | A and B | 1, 18, (x-1) | summer(2) | |
| A and B | 1, 18, (x-1) | summer(2) | 2003 | A and B | 1, 18, (x-1) | summer(2) | 2003 |
| A and B | 2, 18, 40, (x-1) | spring | | A and B | 2, 18, 40, (x-1) | spring | |
| A and B | 2, 18, 40, (x-1) | summer | 2004 | A and B | 2, 18, 40, (x-1) | summer | 2004 |
| A and B | 2, 18, 40, (x-1) | fall | | A and B | 2, 18, 40, (x-1) | fall | |
| A and B | 2, 18, 40, (x-1) | winter | | A and B | 2, 18, 40, (x-1) | winter | |
| A and B | 2, 18, 40, (x-1) | spring | 2005 | A and B | 2, 18, 40, (x-1) | spring | 2005 |
| A and B | 2, 18, 40, (x-1) | summer | | A and B | 2, 18, 40, (x-1) | summer | |
| A | 2, 18, 40, (x-1) | winter | | A and B | 2, 18, 40, (x-1) | winter | |
| A and B | 2, 18, 40, (x-1) | spring | 2006 | A | 2, 18, 40, (x-1) | spring | 2006 |
| A | 2, 18, 40, (x-1) | summer | | A | 2, 18, 40, (x-1) | summer | |

Resolving the issue of "censored values" or in this case <MDL values was approached in two ways: (1) removing parameters if the majority of data in both lakes were <MDL and (2) replacing <MDL with MDL/2. For data where >90% of the values were <MDL in both lakes, the parameters were removed which included: As, Be, Cd, Co, Cr, Cu, Pb, and V. S was also removed as it was not

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measured prior to 2002 and $SO_4^{2-}$ was measured throughout the entire monitoring period.

Parameters that resulted in >90% of value <MDL in only one lake, or where was a trend in the parameter detectable in more recent years, the <MDL values were replaced with MDL/2. Parameters detected more often in Caland than in Hogarth Pit Lake were TOTN and TOTP whereas, $NH_3$ (in later years), Ni (in later years), and TSS (in earlier years) were detected in Hogarth but not Caland Pit Lake. Other substitutions for <MDL values were used in cases where the parameter was not detected in earlier years of monitoring, either due to different detection limits and/or changes in the actual chemistry. The timing for these changes coincides with a new ICP used in the metal analyses. For both lakes, Al and Ba were not detected until 2002 and 2003 respectively and Ni in Caland was not detected until 2002.

A multivariate approach was taken to evaluate the monitoring data, using discriminant analysis (DA), an eigenanalysis technique. DA was used to describe and summarize differences between a priori groups of samples (i.e. by year and season). Mathematically the same as multivariate analysis of variance (MANOVA), DA emphasizes and summarizes the results differently. Independent variables are used as predictors of group membership in DA as opposed to seeking differences in dependant variables among groups in MANOVA (McCune and Grace, 2002). The end result of DA is maximizing the separation of prior groups. Direct DA was run using SPSS (SPSS, 2006) on raw data.

Due to repetitive nature of the sampling protocols over the years and correlations among variables in limnology (i.e relationships such as TDS, conductivity, and individual ions), the variables cannot be considered truly independent; therefore, forcing assumptions to be violated during analyses. Assumptions of DA include normal distribution, homogeneity of variance, and independent samples, however, these assumptions are almost never met by ecological data (Williams, 1983). Green (1971) stated that variables which are highly intecorrelated with each other will be less effective at separating discriminant categories. Therefore, all data was evaluated for high intercorrelations (positive and negative) and the number of variables were reduced to those that were representative (of the correlations) for use in the discriminant analyses.

## 1.3 Results

### 1.3.1 Water Quality Monitoring

Over eight years of observations (seven years of data), there have been some obvious changes particularly in Hogarth Pit Lake. Summer temperature-oxygen profiles from Caland Pit Lake show the anoxic layer remaining intact at the 25-30 m (Fig 1.3). The years 1998 and 1999 revealed slightly negative heterograde shaped oxygen profiles. Throughout the years this trend moves towards positive heterograde profiles. Hogarth Pit Lake illustrates a shift from a relatively uniform (orthograde) profile (1998 and 1999) to a more distinct change in dissolved oxygen with depth; ultimately resulting in positive heterogrrade

profiles (Figure 1.4). These positive heterograde profiles become increasing pronounced from 2002 to 2006. The major difference between the pit lakes is Hogarth remains oxygenated with depth while Caland is anoxic below 30 m.

Secchi depths for Caland Pit Lake averaged 3.9 m and in Hogarth Pit Lake, 3.3 m. Caland secchi depths remained fairly consistent from 2004 to 2006 while Hogarth secchi depths did increase from 2.7 in 2004 to 3.7 in 2006.

# Caland Pit Lake

## Dissolved Oxygen (mg/L)



Temperature ·—·—· Temperature
———— Dissolved oxygen

## Dissolved Oxygen (mg/L)
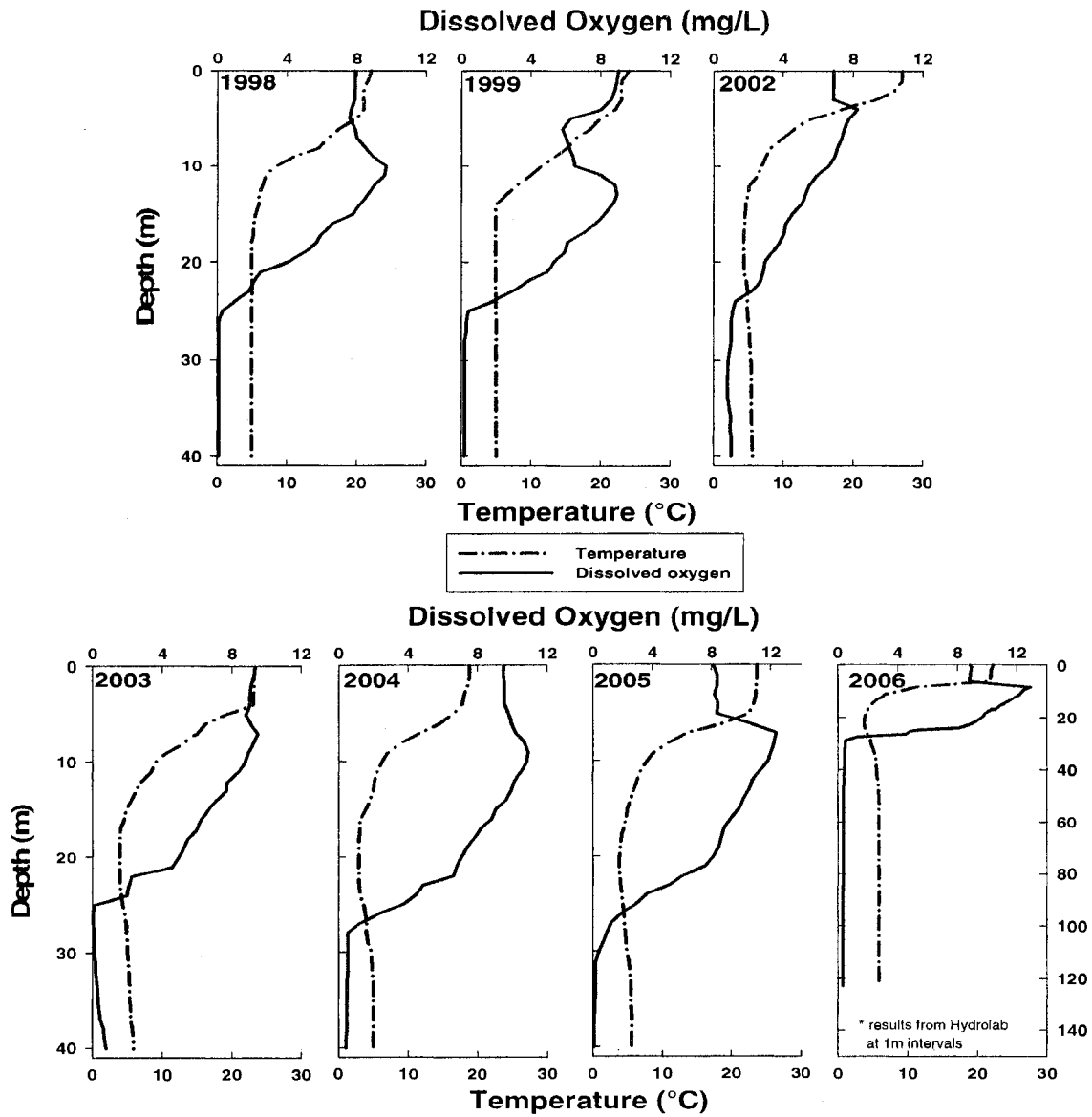


Figure 1.3. Temperature-oxygen profiles of Caland Pit Lake from summers of 1998, 1999, 2002, 2003, 2004, 2005, and 2006 (averaged from the 2 sampling locations).

# Hogarth Pit Lake

**Dissolved Oxygen (mg/L)**
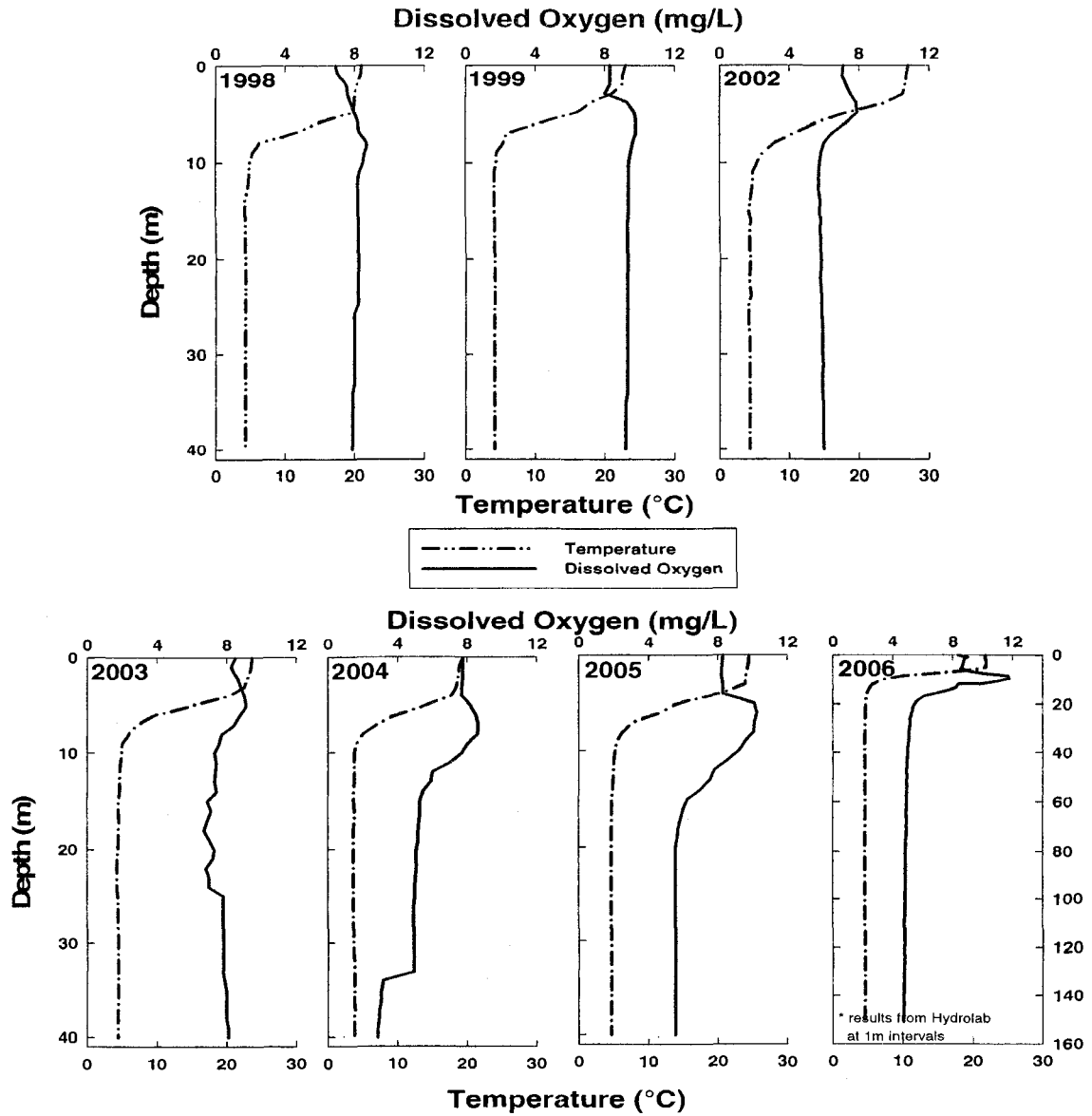


Figure 1.4. Temperature-oxygen profiles of Hogarth Pit Lake from summers of 1998, 1999, 2002, 2003, 2004, 2005, and 2006 (averaged from the 2 sampling locations).

## 1.3.2 Water Chemistry Analyses

### 1.3.2.1 Caland and Hogarth Pit Lake Water Quality

Discriminant analysis of Caland and Hogarth Pit Lakes together (by year) shows distinct separations between the two lakes with Hogarth positioned to the left of Function one and Caland to the right (Figure 1.5). The main objective was to summarize the separation between the two lakes. Classification of data to each lake was achieved with 100% accuracy, while classification of data to each lake and year was done with 72.7% accuracy. Variables used in the analysis were: alkalinity, conductivity, TDS, TOTP, and $SO_4^{2-}$. Of the six functions derived, the first four were significant ($p < 0.05$) (Table 1.2). Table 1.3 summarizes the standardized canonical discriminant coefficients for the four functions. Function one, accounting for almost all (99.0%) of the variation, was characterized by TDS, conductivity, $SO_4^{2-}$, and pH at the negative end (where Hogarth sites are located) and alkalinity and TOTP at the positive end (where Caland sites are located).
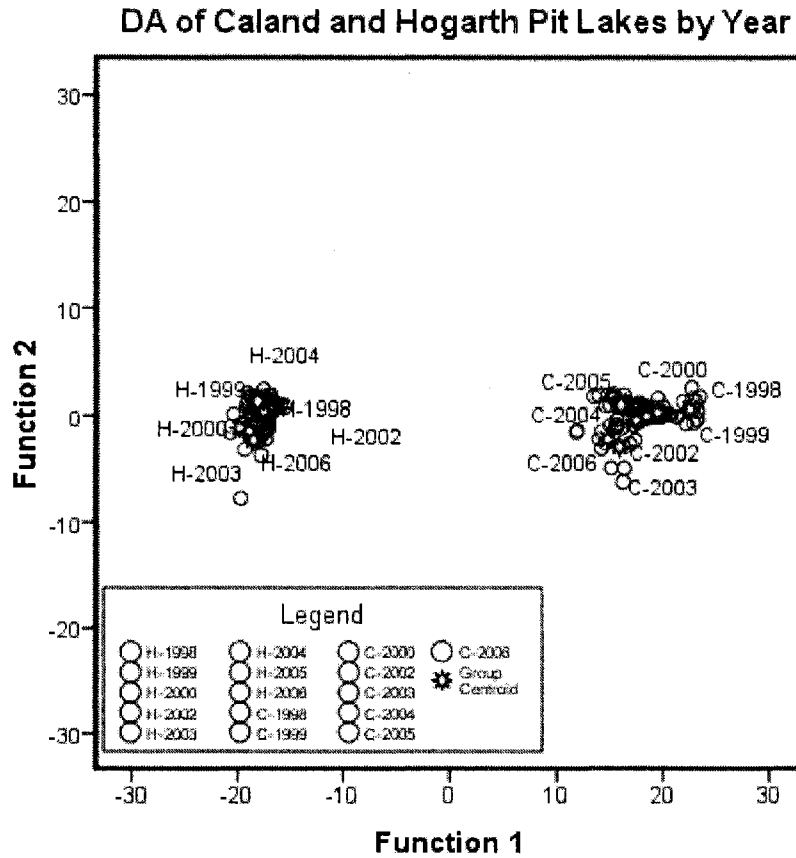
**Figure 1.5. Scatter-plot from DA of Caland and Hogarth Pit Lake water quality data by year.**

**Table 1.2. Summary of statistics from DA of Caland and Hogarth Pit Lake water quality data by year.**

|  | Function | | | |
|---|---|---|---|---|
|  | 1 | 2 | 3 | 4 |
| Eigenvalue | 362.612 | 1.793 | .880 | .666 |
| % of Variance | 99.0 | .5 | .2 | .1 |
| Wilks' Lambda / Significance | .000 / .000 | .091 / .000 | .253 / .000 | .475 / .000 |

**Table 1.3. Summary of standardized canonical discriminant functions of Caland and Hogarth Pit lake water chemistry data by year.**

Standardized Canonical Discriminant Function
Coefficients

| | Function | | | |
|------|--------|--------|--------|--------|
| | 1 | 2 | 3 | 4 |
| ALK | 2.272 | .564 | .672 | -.074 |
| Cond | -.537 | -.194 | .121 | 1.410 |
| SO4 | -.424 | -.027 | .868 | -.971 |
| TDS | -1.810 | .331 | -.674 | -.123 |
| pH | -.117 | .955 | .692 | .323 |
| TOTP | .093 | -1.037 | .222 | -.058 |

## 1.3.2.2 Caland Pit Lake Water Quality

DA successfully separated the data by years with the groupings occurring in time sequence from left (2006) to right (1998) along Function 1 (Figure 1.6). 2004, 2005, and 2006 data forms a tighter grouping to the left, while 1998 and 1999 form a tighter grouping to the right. Data points were classified to each year with 94.8% accuracy. Of the seven canonical discriminant functions used in the analysis, only the first five were significant ($p < 0.05$) (Table 1.4). A summary of the standardized canonical discriminant function coefficients is shown in Table 1.5. The first function accounted for 83.6% of variation and was largely influenced by $NO_3$, Ni, and Ca on the positive end (with previous years) and alkalinity, $SO_4^{2-}$, pH, and conductivity on the negative end (with more recent years). The second function accounted for 9.8% of variation shows separation due to mainly alkalinity and pH.
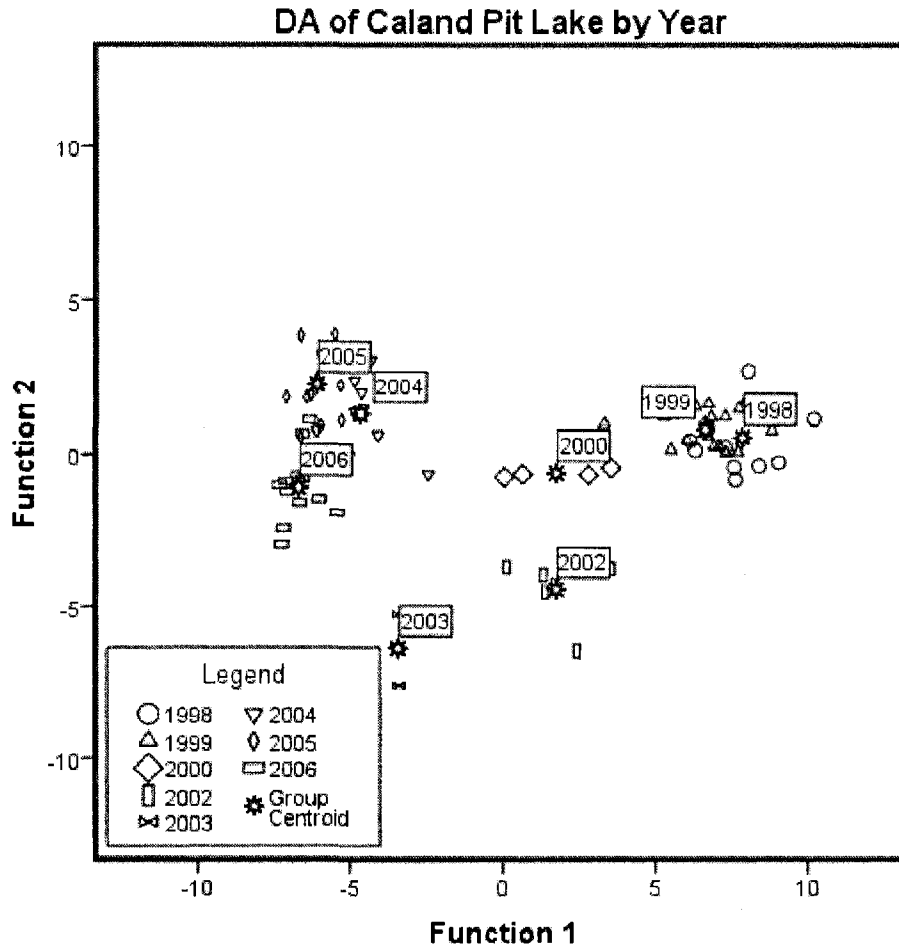
**Figure 1.6. Scatter-plot from DA of Caland Pit Lake water quality data by year.**

**Table 1.4. Summary of statistics from DA of Caland Pit Lake water quality data by year.**

|  | Function | | | | |
| --- | --- | --- | --- | --- | --- |
|  | 1 | 2 | 3 | 4 | 5 |
| Eigenvalue | 33.085 | 3.885 | 1.267 | .687 | .447 |
| % of Variance | 83.6 | 9.8 | 3.2 | 1.7 | 1.1 |
| Wilks' Lambda / Significance | .001 / .000 | .031 / .000 | .149 / .000 | .048 / .000 | .150 / .015 |

**Table 1.5. Summary of standardized canonical discriminant functions of Caland Pit lake water chemistry data, by year.**

Standardized Canonical Discriminant Function Coefficients

|  | Function | | | | |
|---|---|---|---|---|---|
|  | 1 | 2 | 3 | 4 | 5 |
| Ca | .510 | .590 | 3.954 | .077 | -.152 |
| ALK | -7.154 | 2.200 | 2.604 | 1.116 | 3.449 |
| Cond | -.224 | -.614 | -3.521 | .034 | .214 |
| NO3 | 1.140 | -.161 | .045 | .605 | 1.297 |
| Al | -.706 | -1.174 | -.274 | -1.511 | 1.302 |
| Ni | 1.005 | .857 | .207 | 1.901 | -1.451 |
| SO4 | -2.185 | .187 | -.709 | .308 | -1.124 |
| pH | -.174 | 1.727 | .265 | .391 | .046 |
| NH3 | -.071 | -.761 | -.400 | -.579 | -.014 |
| TOTP | .145 | -.789 | .229 | .722 | -.148 |

DA did not separate Caland Pit Lake data by season as well as by year (Figure 1.7). Winter data aggregates to the right of function one, while the other seasons overlap. Only three variables were used in the analysis, pH, Cl⁻, and $NH_3$. Data points were classified to each season with only 44.2% accuracy. Of the three functions, only the first was significant describing 83.6% of the variation among the seasons (Table 1.6) and the standardized canonical discriminant function coefficients are summarized in Table 1.7.
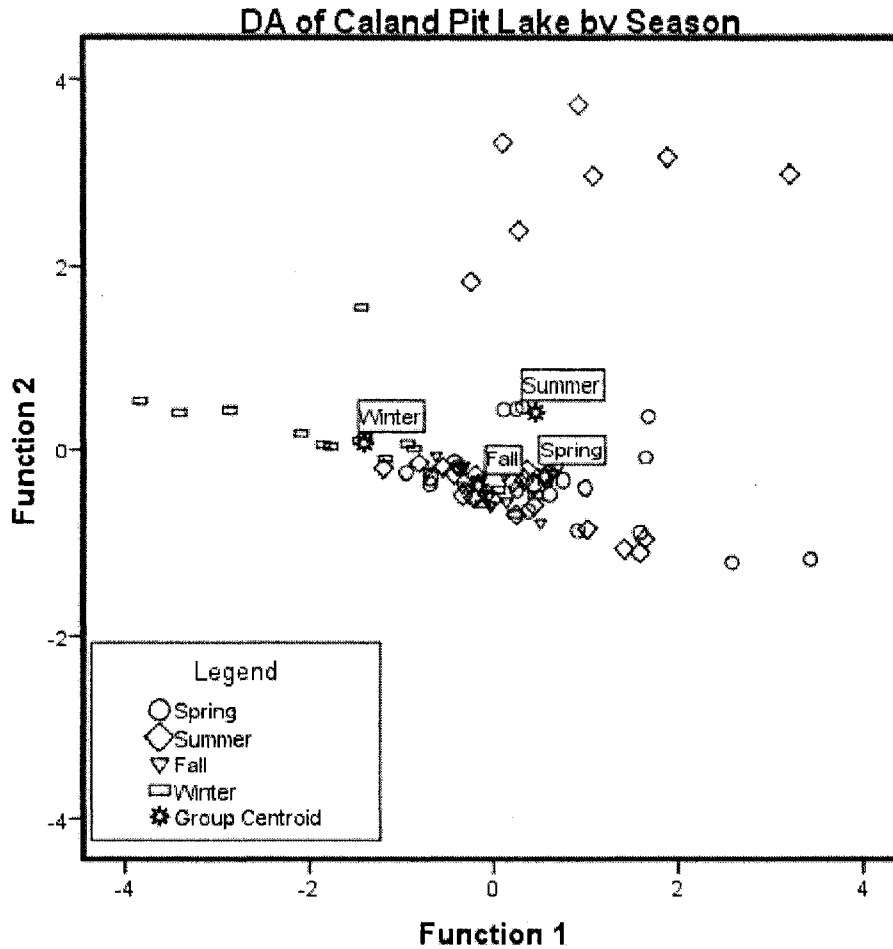
**Figure 1.7. Scatter plot from DA of Caland Pit Lake water quality data by season.**

**Table 1.6. Summary of statistics from DA of Caland Pit Lake water quality data by season.**

|  | Function | | |
|---|---|---|---|
|  | 1 | 2 | 3 |
| Eigenvalue | .605 | .118 | .001 |
| % of Variance | 83.6 | 16.3 | .1 |
| Wilks' Lambda / Significance | .557 / .000 | .894 / .086 | .999 / .800 |

**Table 1.7. Summary of standardized canonical discriminant functions of Caland Pit lake water chemistry data by season.**

| | Standardized Canonical Discriminant Function Coefficients | | |
|---|---|---|---|
| | Function | | |
| | 1 | 2 | 3 |
| Cl | 1.037 | -.156 | .948 |
| NH3 | .392 | .936 | -.019 |
| pH | 1.337 | -.409 | -.069 |

## 1.3.2.3 Hogarth Pit Lake Water Quality

As for Hogarth Pit Lake, DA successfully separated the data by years, with groupings occurring almost in sequential order from left (2006) to right (1998) along function 1 (Figure 1.8). Among the separations are groupings of years along function 1: 2004, 2005 and 2006 to the left, 2003 in the middle, and 1998, 1999, 2000, and 2002 to the right. Data were classified to each year with 87.5% accuracy. Of the seven canonical discriminant functions were used in analysis, only the first three were significant ($p < 0.05$) (Table 1.8). A summary of the standardized canonical discriminant function coefficients used in the analysis is shown in Table 1.9. Function one accounted for 88.2% of the variation and was primarily composed of $Ca^{2+}$, $Na^+$, Ni, pH, and TDS on the positive end (with previous years) and alkalinity, $SO_4^{2-}$, and TSS on the negative end (with recent years). The second function accounting for 5.7% of the variation. This was mainly due to pH and $Ca^{2+}$ at the positive end and $Na^+$ and TSS at the negative end.

**DA of Hogarth Pit Lake by Year**
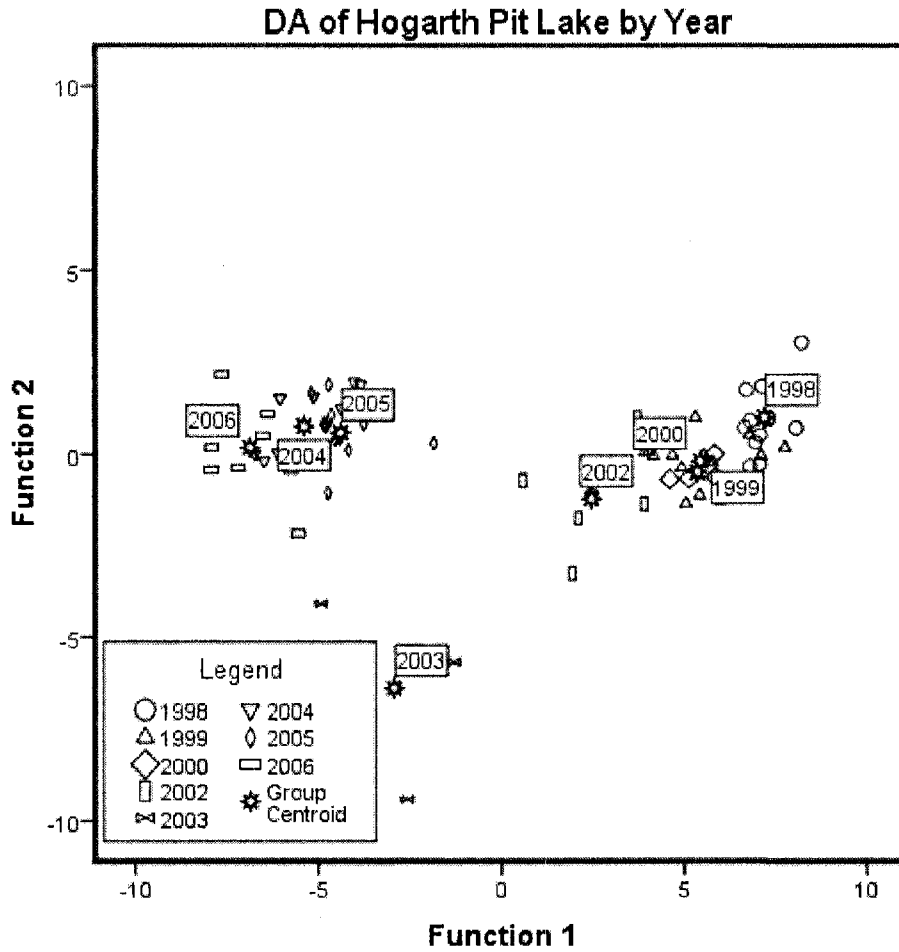
Figure 1.8. Scatter plot from DA of Hogarth Pit Lake by year.

Table 1.8. Summary of statistics from DA of Hogarth Pit Lake water quality data by year.

|  | Function | | |
|---|---|---|---|
|  | 1 | 2 | 3 |
| Eigenvalue | 35.140 | 2.275 | 1.955 |
| % of Variance | 88.2 | 5.7 | 4.9 |
| Wilks' Lambda / Significance | .002 / .000 | .068 / .000 | .223 / .000 |

**Table 1.9. Summary of standardized canonical discriminant functions of Hogarth Pit lake water chemistry data by year.**

| | Standardized Canonical Discriminant Function Coefficients | | |
|---|---|---|---|
| | Function | | |
| | 1 | 2 | 3 |
| Ca | 1.251 | .817 | -.690 |
| Na | 1.562 | -.971 | .700 |
| ALK | -2.032 | .596 | -1.424 |
| Ni | .808 | .286 | -.921 |
| SO4 | -.374 | .051 | 1.395 |
| pH | .404 | .887 | .087 |
| TDS | .179 | .680 | .633 |
| TSS | -.130 | -.793 | .379 |

Hogarth data were also successfully separated by season, with summer/spring data to the left of function one and winter/fall data to the right (Figure 1.9). Data were classified to each season with 84.4% accuracy. Three canonical discriminant function were used in the analysis, all were significant ($p < 0.05$) (Table 1.10). Standardized canonical discriminant functions are summarized in Table 1.11. Variables selected for analysis by season, include most of those selected for year (except Ni and TSS) plus $Mg^{2+}$, $K^+$, conductivity, and $Cl^-$. Function one described 61.3% of the variation and was mainly comprised of $Mg^{2+}$, $Na^+$, $SO_4^{2-}$, and TDS at the positive end (winter/fall data) and $Cl^-$, $K^+$, and conductivity at the negative end (summer/spring data). The second function, accounting for 25.7% of the variation, was shaped by conductivity, TDS, pH, and $Ca^{2+}$ at the positive end (fall data) and $Cl^-$, $K^+$, $SO_4^{2-}$, and alkalinity at the negative end (winter data).
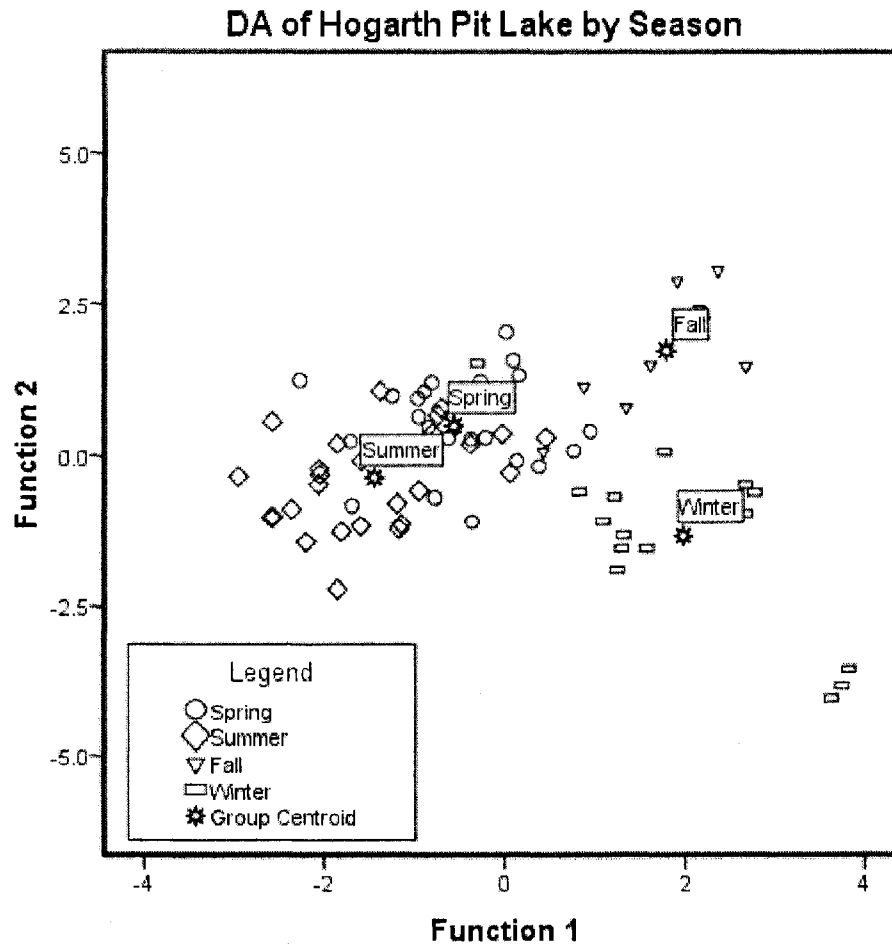
Figure 1.9. Scatter plot from DA of Hogarth Pit Lake by season.

Table 1.10. Summary of statistics from DA of Hogarth Pit Lake water quality data by season.

| | Function | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| Eigenvalue | 2.205 | .960 | .433 |
| % of Variance | 61.3 | 26.7 | 12 |
| Wilks' Lambda / Significance | .111 / .000 | .356 / .000 | .698 / .002 |

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**Table 1.11. Summary of standardized canonical discriminant functions of Hogarth Pit lake water chemistry data by season.**

**Standardized Canonical Discriminant Function Coefficients**

|  | Function | | |
|---|---|---|---|
|  | 1 | 2 | 3 |
| Ca | .054 | -.442 | 1.858 |
| Na | 1.366 | .030 | .183 |
| ALK | .197 | -.310 | .453 |
| SO4 | 1.180 | -.550 | -.204 |
| pH | .026 | .913 | .768 |
| TDS | .346 | -.944 | .084 |
| Cl | -2.212 | .732 | .896 |
| K | -1.730 | .718 | -1.053 |
| Mg | 1.597 | -.400 | -1.362 |
| Cond | -.664 | -1.064 | -.288 |

### 1.3.3 Stable Isotope Analysis of Caland and Hogarth Pit Lakes

Figures 1.10 and 1.11 provide comparisons of temperature, DO, pH, conductivity, $SO_4^{2-}$, and hardness between the pit lakes taken at the same time as sampling for isotopes. Some chemical data is missing for the November sampling period, including temperature and DO readings. pH levels in the lakes are roughly the same; Hogarth Pit Lake does display higher readings near the surface during summer and fall sampling. These trends again confirm differences in chemistry between the lakes; Caland Pit Lake's anoxic layer and Hogarth Pit Lake characterized by higher conductivity, hardness, and $SO_4^{2-}$ levels.
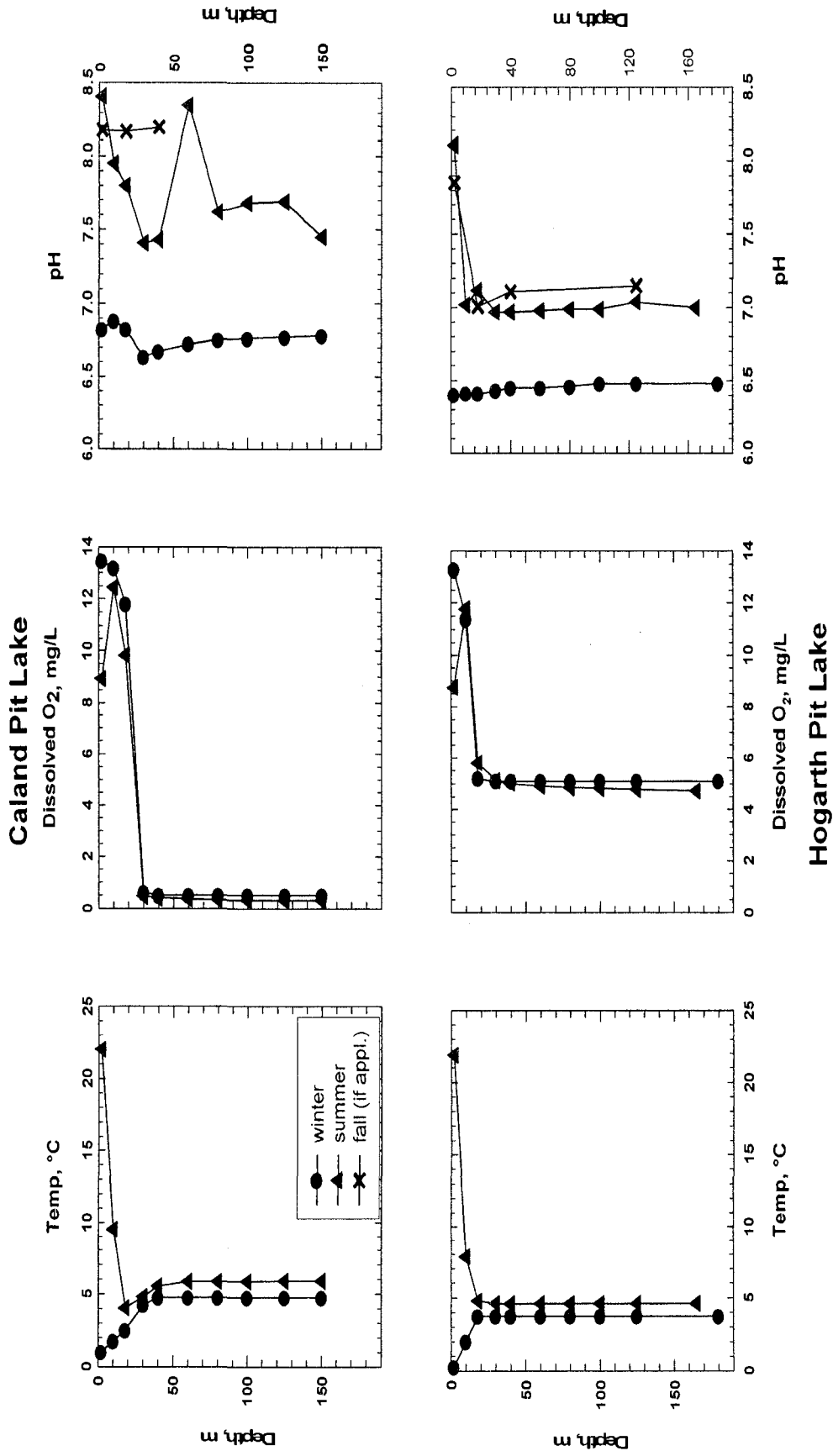
Figure 1.10. Comparisons of temperature, DO, and pH taken at time of isotope sampling on Caland and Hogarth Pit Lakes.
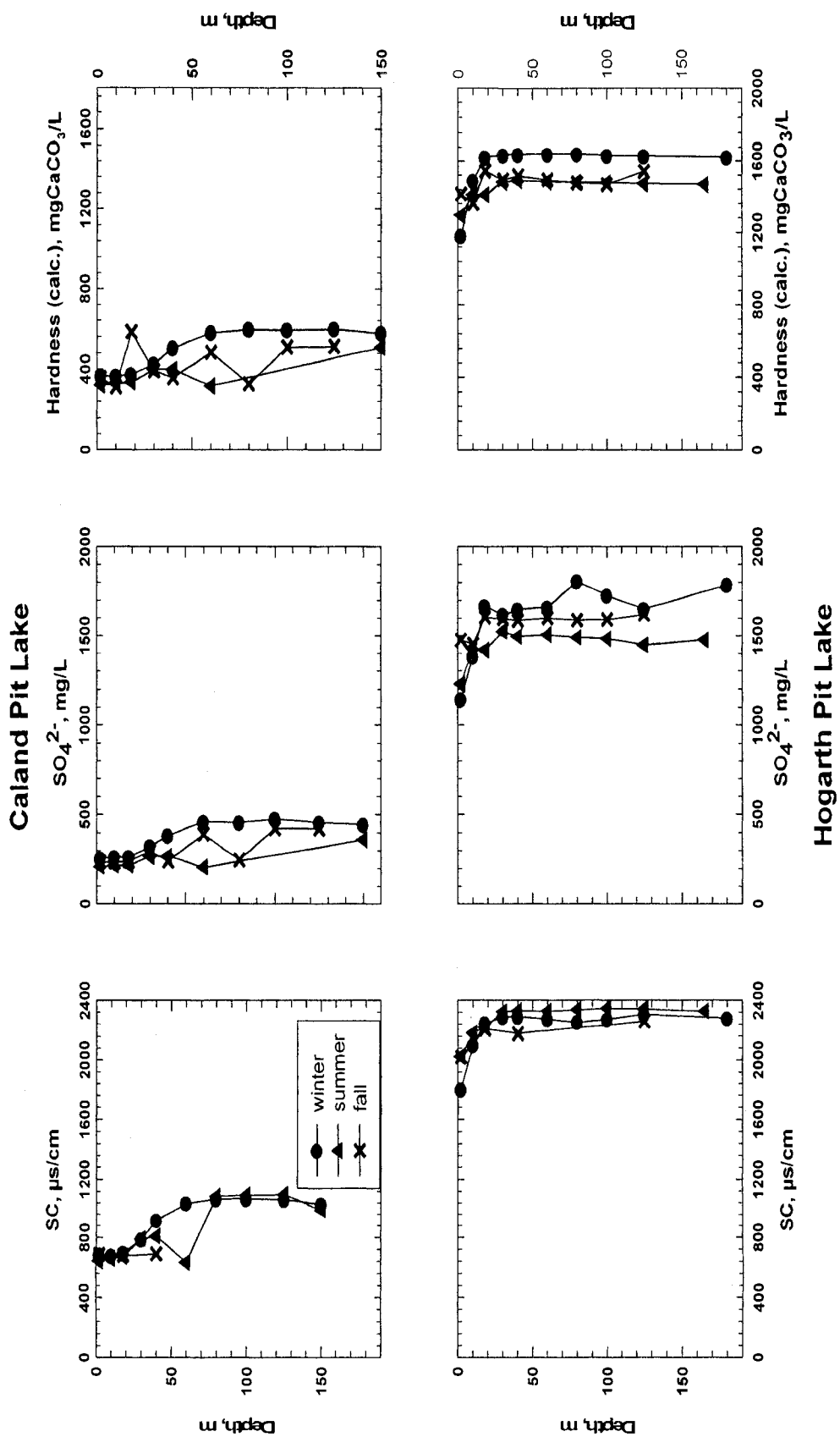
Figure 1.11. Comparisons of temperature, DO, and pH taken at time of isotope sampling on Caland and Hogarth Pit Lakes.

Both lakes have a similar range of $\delta^{18}O$ and $\delta D$ values; however, Hogarth is generally more depleted, as shown in Figure1.12: Caland Pit Lake $\delta^{18}O$ (-8.3 ‰ to -11.1 ‰) and $\delta D$ (-68.1 ‰ to -87.4 ‰) and Hogarth Pit Lake $\delta^{18}O$ (-8.5 ‰ to -11.6‰) and $\delta D$ (-71.1 ‰ to -89.9 ‰). Hogarth Pit Lake profiles are less variable with depth, which may be a result of sampling. However, enrichment of $\delta^{18}O$ and $\delta D$ is evident in both lakes in the upper 20-30 m compared to deeper waters. As expected, a less pronounced trend occurs during the winter, due to ice cover. Groundwater levels of $\delta^{18}O$ and $\delta D$ are -12.9 ‰ and -91.1 ‰ respectively. These values are much lower in comparison to the pit lake surface waters. With depth, the pit lake values do approach the groundwater values.

Profiles of $\delta^{34}S$ do not vary much with depth or between lakes (Figure 1.13). $\delta^{34}S$ values range from -2.9 ‰ to 4.3 ‰ in Caland and -3.2 ‰ to -3.9 ‰ in Hogarth. Groundwater with a $\delta^{34}S$ value of 1.7 ‰ is near the $\delta^{34}S$ values found in the pit lakes.

With respect to stable isotope analyses, depth profiles of $\delta^{13}C_{DIC}$ provided the largest difference between the two lakes. Hogarth Pit Lake values ranged from 2 ‰ to -2 ‰; whereas Caland Pit Lake $\delta^{13}C_{DIC}$ values ranged from -4.4 ‰ to -9.2 ‰ (Figure 1.14). Caland Pit Lake $\delta^{13}C_{DIC}$ values came closest to the groundwater value of -12.7‰.
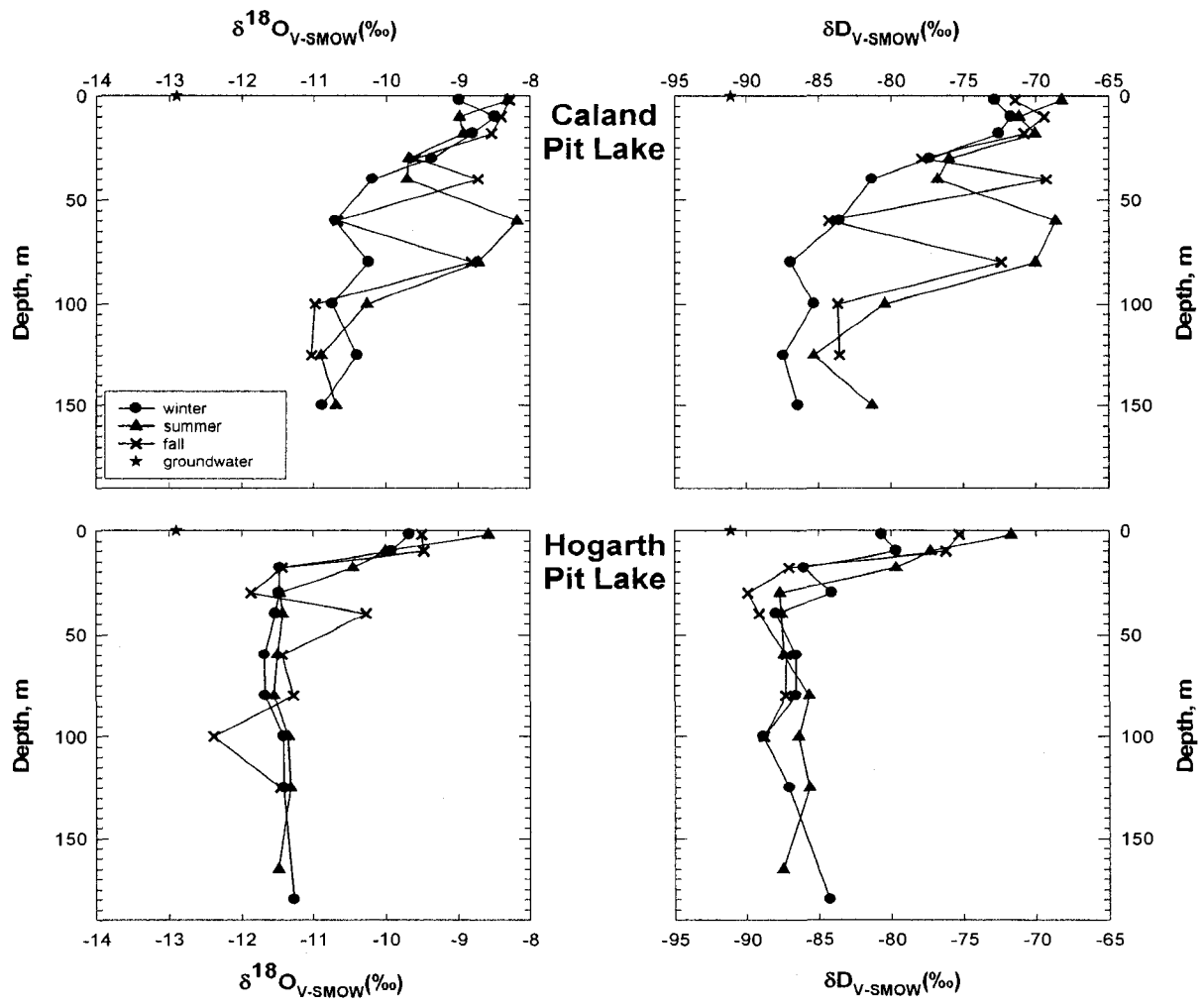
Figure 1.12. Depth profiles of δD and $δ^{18}O$ values in Caland and Hogarth Pit Lakes from seasonal sampling.
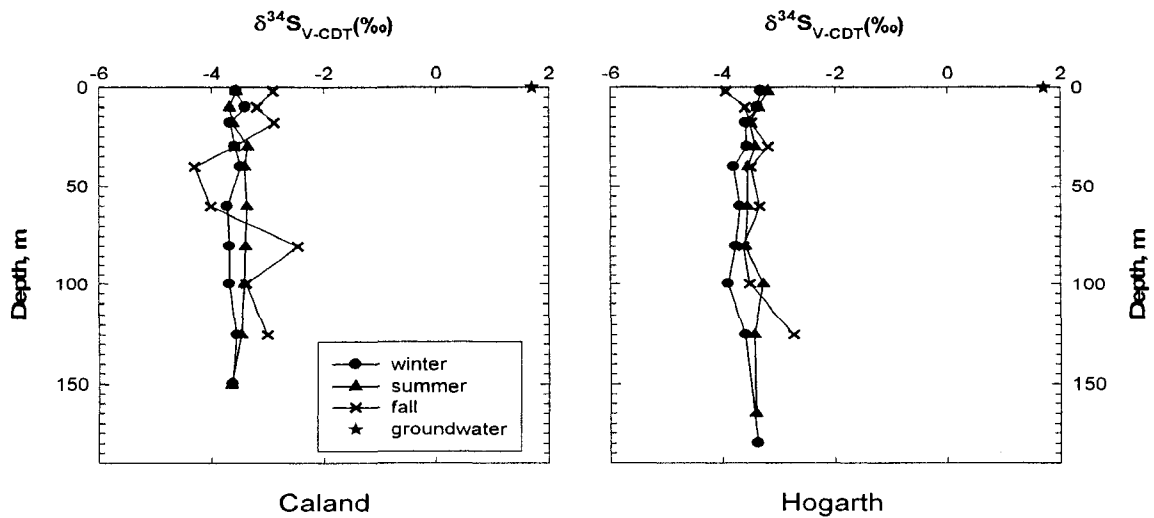
**Figure 1.13. Depth profiles of $\delta^{34}$S values in Caland and Hogarth Pit Lakes from seasonal sampling.**
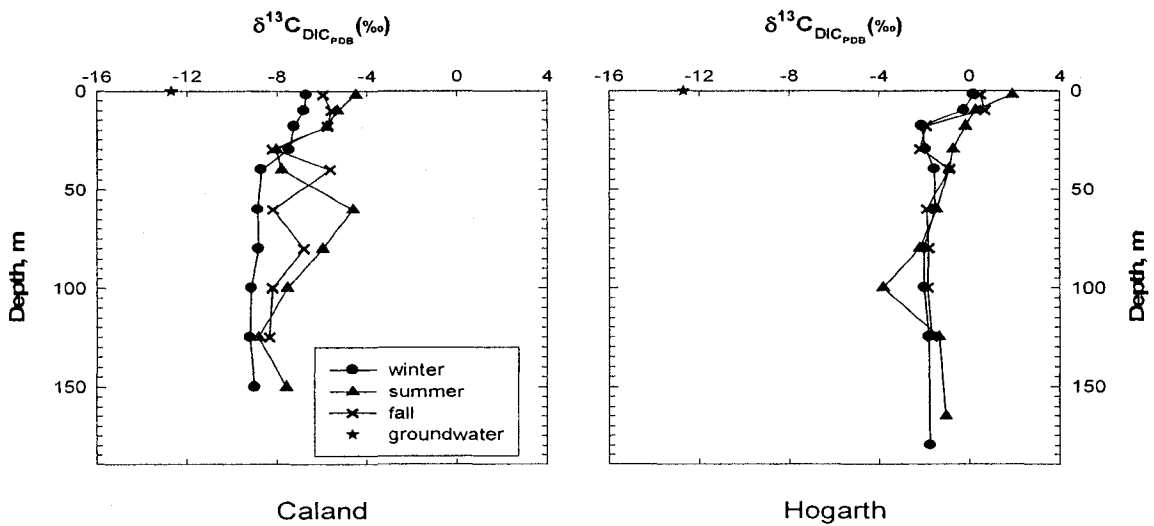


**Figure 1.14. Depth profiles of $\delta^{13}C_{DIC}$ values in Caland and Hogarth Pit Lakes from seasonal sampling.**

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## 1.4 Discussion

### 1.4.1 Water Quality Monitoring

Observed trends in the temperature-oxygen profiles of Caland Pit Lake confirm the presence of a freshwater lens over topping the anoxic layer with the relatively consistent depth of 25-30 m. The positive heterograde oxygen curves in the upper portion of Caland Pit Lake may be the results of seasonal freshwater inflows and photosynthetic activities; while the anoxic conditions observed in the hypolimnion results from the loading of organic matter, thus consuming the oxygen (Wetzel, 2001). Presenting orthograde profiles in earlier years of monitoring (1998 to 2003), characteristic of oligotrophic lakes, Hogarth Pit Lake gradually developed a positive heterograde curve. Orthograde curves are regulated mainly by physical processes during summer stratification, with oxygen levels in the epilimnion decreasing as temperature increase. The formation of the positive heterograde profile in Hogarth may indicate the presence of oxygen production by algae in excess of oxidative consumption in the metalimnion (Wetzel, 2001). Unlike Caland, Hogarth does not become anoxic at any depth.

Other observations noted over the years in Hogarth Pit Lake include improved water clarity and presence of aquatic life. Secchi depths have increased from 1.5 m (1998 to 2000) to 2.8-3.3 m. McNaughton (2001) described the water of Hogarth Pit Lake as a milky-olive colour with noticeable iron floc. During the course of this study, the water was clear, with no noticeable particulate matter in the water column. This change in clarity roughly coincides with water in the pit lake the joining to the water contained in a smaller adjacent

pit, "Robert's Pit" in 2003. Perhaps the mixing of these separate waters caused some precipitation of floc in the water column. Dilution with groundwater over the years may have also influenced the improved clarity of Hogarth water.

Presence of aquatic life in Hogarth Pit Lake was first discovered in the summer of 2004 when grab samples taken at 1-2 m contained green algae including: *Oocystis*, *Botryococus*, *Monoraphridium*, *Diatoma*, *Synedra*, and *Nitzschia*. There have also been observations of gastropods (snails and other small shelled organisms) and evidence of dragonflies near the shoreline areas. In 2006 numerous larval casings of dragonflies were found on the shores at the northern end of Hogarth. Most recently, in the summer of 2007, researchers in the area observed schools of small minnows in pockets near the shores. Attempts to trap and identify them were not successful.

## 1.4.2 Water Chemistry Analyses

Comparisons of water quality data from the pit lakes denote some differences (Figure 1.5). A Wilk's lambda of 0.00 for function one indicates perfect separation of these groups (McCune and Grace, 2005). Function one, accounting for most (99.0%) of the variation separates the two lakes by grouping Hogarth sites to the left side corresponding to higher levels of TDS, conductivity, and $SO_4^{2-}$ levels; and Caland sites to the right side corresponding to the more alkaline, nutrient rich water (TOTP).

### 1.4.2.1 Caland Pit Lake

Caland Pit Lake did show separation throughout the years. More recent years (2004, 2005, and 2006) were separated from 1998, 1999 and 2000 data, with 2002 and 2003 in the middle (Figure 1.6). The general trend shown is a decrease in alkalinity, conductivity, and $SO_4^{2-}$ with time; as they are negatively correlated to the left side of function one. It appears that Caland water is becoming diluted over the years. Ni was positively correlated with function one, corresponding to higher Ni levels in earlier years. TOTP and $NO_3$ are also positively correlated with the right side of function one, coinciding with more productive times. Fish farm operations have slowed over the years to nil production, resulting in a decrease of nutrient inputs over time.

Caland water chemistry data did not show strong seasonal separations. DA classified only 44.2% of data to the correct season. Although function one accounted for 83.6% of the variation, the data were not well separated, as indicated by the Wilk's lambda value of 0.55. pH provided the highest correlation coefficient for function one, corresponding to marginally higher pH values during spring and summer.

### 1.4.2.2 Hogarth Pit Lake

Hogarth Pit Lake water chemistry data demonstrated strong separation over time, with a similar pattern to Caland (Figure 1.7). 2004, 2005, and 2006 data aggregated to the left of function one, 2003 remained near the middle, and 1998, 1999, 2000, and 2002 data to the right. Function one accounted for 88.2%

of the variation and strongly separated the data (Wilk's lambda = 0.02). To the left of function one, data were separated due to lower alkalinity, $SO_4^{2-}$, and TSS values and to the right, data were separated by higher $Ca^{2+}$, Ni, and TDS values (Table 1.9). As with Caland, with the exception of higher nutrient level in previous years, Hogarth Pit Lake is becoming diluted with time.

Data separation by season was more successful for Hogarth Pit than Caland Pit Lake, resulting in 84.4% accuracy for classification. The first function accounts for 61.3% of the data; summer and spring data are positioned to the left of function one, while winter and fall data are to the right. Function one coefficients corresponding to the right include $SO_4^{2-}$, TDS, cations ($Mg^{2+}$, $K^+$, and $Na^+$), indicating these variables are elevated in fall and winter months. Function two accounted for 26.7% of the variation, which was the highest value for a function two throughout all analyses. This shows further separation of fall and winter months: fall sites fall to the top of function two and winter sites to the bottom. Coefficients corresponding to the negative (bottom) end of function two include conductivity, TDS, $SO_4^{2-}$, and cations ($Ca^{2+}$ and $Mg^{2+}$), signifying higher levels of these parameters during winter months. These elevated levels may result from a combination of ice cover limiting mixing of surface waters and reduced dilution effects from precipitation and groundwater seepage.

### 1.4.3. Stable Isotopes of Caland and Hogarth Pit Lakes

Enrichment of $\delta^{18}O$ and $\delta D$ in the surface waters of both pit lakes signifies evaporation as a main process. Although the entire water column of each pit

lake signifies an evaporative signature, evaporation is more pronounced in the surface waters. These waters become enriched with heavier isotopes of oxygen and hydrogen in contrast to less evaporated bottom waters (Gammons *et al*, 2006). These trends were similar to results found by Pellicori *et al* (2005) where strong evaporative effects were observed to depths of 30 m, after which the pit lake was more or less isotopically homogenous. These gradients also confirm that these pit lakes do not thoroughly mix below 30 m, further supporting their meromictic classifications.

The lower $\delta^{18}O$ and $\delta D$ values of groundwater (-12.9 ‰ and -91.1 ‰ respectively) compared to the surface pit lake waters (see Figure 1.11) are expected as groundwater is not under the influence of evaporation. Therefore, with depth, pit lake waters approach the $\delta^{18}O$ and $\delta D$ values of groundwater. This is suggests the groundwater is a major source of water to these pit lakes. It has been estimated that 85% of recharge water in these pit lakes is groundwater (Bernatchez, pers. comm., 2003)

Similar $\delta^{34}S$ profiles in both pit lakes were found, falling within a similar range showing little fluctuation with depth (Figure 1.12). Both lakes range from 2.9 ‰ to 4.3 ‰, which is similar to groundwater $\delta^{34}S$ values of 1.7 ‰. Such results can identify possible sources of aqueous sulfate. Hogarth, known for much higher aqueous $SO_4^{2-}$ levels than Caland, was thought to have more/different sources. However, based on the isotope results, Hogarth appears to have the same sulfate sources. Perhaps they are just more abundant thus allowing for more rock-water interactions. No regional groundwater stable

isotope data exist, but based on the relative consistency of $\delta^{34}S$ in the study area, the likely contributor of sulfur to the pit waters is the ore zone (goethite and pyritic members) itself. Groundwater could very well have come into contact with exposed and unexposed extensions of the ore zone and/or undiscovered pyrite bodies (MacDonald, 2005). Uniformity of the $\delta^{34}S$ profiles also rules out previous theories of the presence of sulfate reducing bacteria (SRB), common in anoxic environments (i.e. Caland Pit Lake). If SRB were present there would be enrichment in $\delta^{34}S$, as bacterial reactions favour the lighter isotope ($^{32}S$) (Hsu and Maynard, 1999).

The largest difference in isotope values between the pit lakes were for $\delta^{13}C_{DIC}$ (Figure 1.13). Carbonate rocks typically have $\delta^{13}C$ values of 0 ± 5 ‰ (Kendall and Doctor, 2005). Hogarth Pit Lake $\delta^{13}C$ values ranged from -2.0 ‰ to 2.0 ‰. This suggests the influence of carbonate walls surrounding the lake since reactions that produce DIC are the weathering of carbonate and silicate minerals (Kendall and Doctor, 2005). Caland Pit Lake $\delta^{13}C_{DIC}$ values ranged from -4.4 ‰ to -9.2 ‰ and $\delta^{13}C$ values for C3 and C4 plants average -25 ‰ and -12 ‰ respectively (Deines, 1980). As there are more organic inputs into Caland Pit Lake (through fish farm operations and submerged vegetation along the shores), Caland is expected to have more $\delta^{13}C_{DIC}$ depleted waters than Hogarth Pit Lake. The DIC depletion in Caland occurs through DIC-DOC isotopic exchanges (Conly et al, in press a).

## 1.5 Conclusions and Future Work

Due to the near-neutral pH of the water in both lakes (4.5-8.5), elevated metal concentrations from oxidation of Fe sulfide minerals, are not a concern as they are regulated by solubility and adsorption controls (Eary, 1998; Eary, 1999). The water quality of Caland and Hogarth Pit Lakes has been changing over the years. Decreasing alkalinity, conductivity, and $SO_4^{2-}$ levels in both lakes are due to. Seasonal differences remain more pronounced in Hogarth Pit Lake. Winter months in Hogarth are characterized with higher levels of conductivity, TDS, and $SO_4^{2-}$. These elevated levels may occur during winter months because the lake is more isolated, hence, surface water can not mix as well as during ice-free periods, nor is it diluted with precipitation and/or runoff during ice cover.

Preliminary table isotope work reveals interactions with the surrounding geology. Hogarth and Caland Pit Lake sulfate sources appear to be the ore body. The $\delta^{34}S$ values of the pit lakes are also close to that of the groundwater suggesting groundwater interactions with the ore. Despite higher sulfate levels in the water and the potential for acidic conditions, Hogarth Pit Lake maintains a neutral pH, due to carbonate buffering. $\delta^{13}C_{DIC}$ results in particular reveal the influence of weathering carbonates. These carbonates are rich in calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), akerite ($Ca_2MgFe(CO_3)_4$), and pyrite ($FeS_2$), which are also a major source of dissolved solids, characteristic of Hogarth water.

Future work should include a more detailed geological approach. This would identify the differences between the two pit lakes, perhaps by quantifying

rock types. Experiments using rock samples and lake water could give insight into which rock formations more than others are influencing the water chemistry. Such information would help predict future rock-water interactions with exposed rocks, waste piles, and tailings piles not yet submerged by the water. Such preliminary work has been completed by Cockerton (2007) and Conly *et al* (in press b).

More information on rock-water interactions would also aid in predicting future water chemistry of the pit lakes. Using geochemical modeling tools, such as PREEQC and MINETEQ which utilize geological information in addition to previous water quality monitoring data can more accurately predict future water chemistry than pit filling models alone.

## Chapter 2: Investigations into Cause of Toxicity in Hogarth Pit Lake

### 2.1 Introduction

Hogarth Pit Lake has evolved from an acutely toxic state, showing no obvious signs of life, to a chronically toxic state showing signs of natural succession. Acute toxicity of Hogarth was discovered in 1999 by McNaughton (2001) and subsequent studies in 2002 and 2003 by VanCook (2005) confirmed the lake to be devoid of life. At present, the lake is chronically toxic, showing signs of life in the water column. To account for such changes, this study focused on chronic test methods and bioaccumulation studies to determine the cause of paucity of life in Hogarth Pit Lake.

Considerations for acute toxic results suggested by McNaughton (2001) included; As, Ni, sulfate salinity, iron floc, and osmotic stress. Metal toxicity does not seem obvious, as the metal levels generally do not approach levels to cause concern (CCME, 2007). Acute toxicity due to sulfate levels was later ruled out by Baker (2004). Chronic effects however, were not examined.

Since Hogarth water did not exhibit acute toxicity, yet showed no obvious signs of life in spring 2004, chronic toxicity was investigated. Chronic *Ceriodaphnia dubia* test methods (EC, 2002) were used to confirm toxicity, and monitor toxicity over the 2 year study period. Using more than one species (preferably trophic levels) for toxicity testing is recommended to determine if effects are limited to only one test species, or whether the toxicant has impacts on other organisms EC, 2005). *Lemna minor* tests (EC, 1999b) were also used to test chronic effects of Hogarth water and mock effluent.

Identifying the cause of toxicity was attempted through the use of chronic toxicity identification evaluation (TIE) methods (USEPA, 2001). Toxicity Identification Evaluation (TIE) methods were developed by United States Environmental Protection Agency (USEPA) to characterize effluent toxicity. The general procedure is to carry out various physical/chemical manipulations on the effluent and determine whether the manipulation changed the toxicity (Norberg-King et al, 2005a).

As suggested by Waller et al (2005), when Phase I TIE manipulations do not substantially reduce toxicity and sample conductivity exceeds 2000 µs/cm for freshwater, TDS-related should be investigated. Major cations and anions adversely affect aquatic organisms either directly or through influencing toxicity of other contaminants (Mount et al, 1997; Tietge et al, 1997; Waller et al, 2005). Possible TDS-related toxicity in Hogarth is a result of elevated ion levels typical of pit lakes. Further investigations into possible ion or TDS-related toxicity may include the use of synthetic effluents that mimic the major ions in the effluent under evaluation (SETAC, 2004)

Synthetic effluents have proven useful for assessment of TDS-related toxicity associated with whole effluent testing (WET) (Goodfellow, 2000; Norberg-King et al, 2005b). Since cations or anions are not present as individual constituents, but are in combination with other ions, individual toxicity of a cation or anion may be masked or inseparably affected by the associated anion or cation. Therefore effects in effluents or waters must result from combinations of ions (Goodfellow, 2000). If synthetic/mock effluents produce similar responses

as the effluent, one can conclude that the major components of the synthetic effluent are the cause of toxicity.

Bioaccumulation studies, controlled in situ studies, can also be used to test for potential toxicants. Bioaccumulation is often a good integrative indicator of chemical exposures of organisms in polluted ecosystems (Phillips and Rainbow, 1994). Aquatic plants take up metals required for growth, such as $Ca^{2+}$, $Cu^{2+}$, $Fe^{3+}$, $K^+$, and $Mg^{2+}$; but will also accumulate other substances in the water column, including those that may be toxic (Raskin, 1996). Test organisms used for *in situ* studies are set out in field sites thus being exposed to any contamination that ordinarily occurs under field conditions (Schulz, 1999). Simplified settings of toxicity tests are incapable of simulating exposures in natural systems. Chappie (1997) maintains that *in situ* testing using caged organisms allows one to assess aquatic contamination and bioaccumulation since the physical, chemical, and biological conditions integrated in the natural environment cannot be accurately reproduced in a laboratory.

This study investigates of the factors/reasons for the lack of aquatic life in Hogarth Pit Lake (McNaughton, 2001; VanCook, 2005). This chapter has two objectives using standard chronic methods, TIE procedures, and bioaccumulation studies: (1) to identify the likely cause of chronic toxicity in Hogarth and (2) utilize bioaccumulation studies to determine other potential toxicants, namely metals.

## 2.2 Methods

### 2.2.1 Study Site

The location of Hogarth Pit Lake, used in toxicity investigations, is shown

by Figure 2.1. A description of the area, including Hogarth and Caland Pit Lakes,

is summarized in Chapter one, section 1.2.1. The West Arm (originally the west

arm of Steep Rock Lake) was not actively mined during operations; however it

was partially filled with overburden, decreasing its average depth from

approximately 30 m to 3 m (Jackson, pers. comm., 2005). Sites in the West Arm,

Caland Pit Lake, and Hogarth Pit Lake were selected for the *in situ* study and are

illustrated in Figure 2.1.
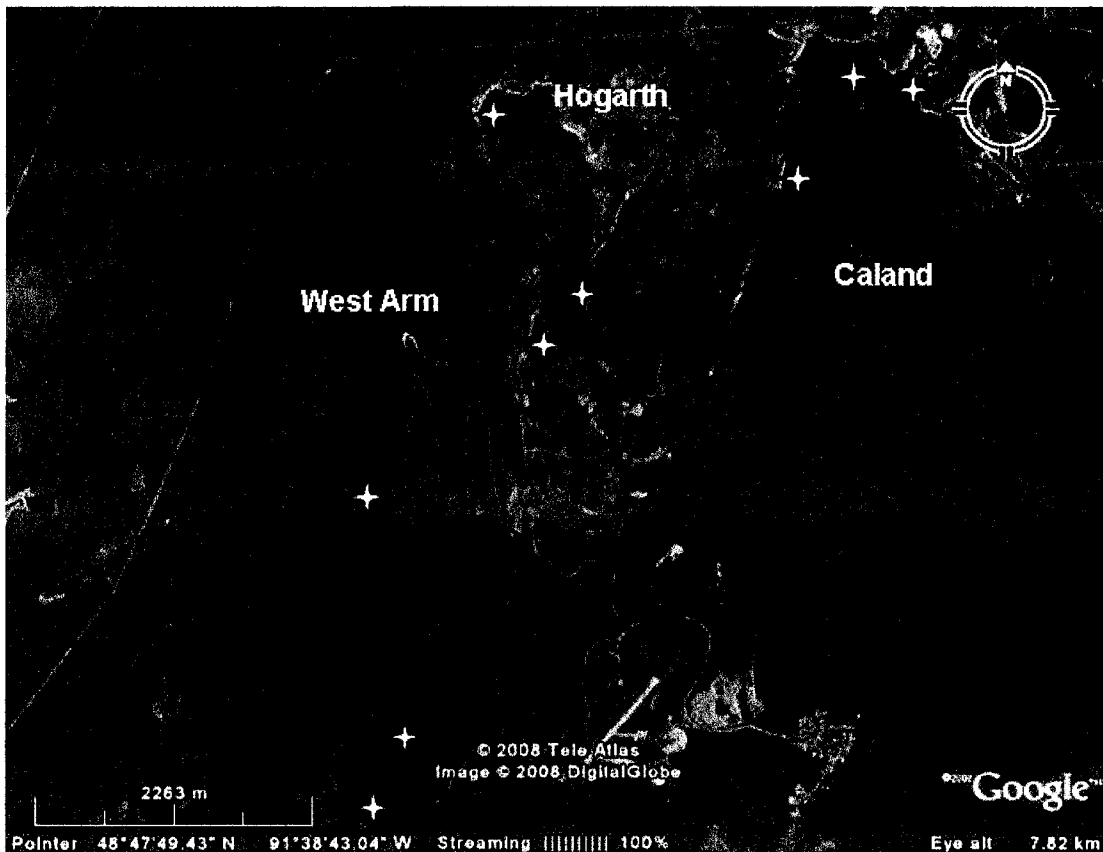


**Figure 2.1. Site location map showing sites used for bioaccumulation studies.**

## 2.2.2 Field Procedures

### 2.2.2.1 Toxicity Sampling

Water samples for toxicity testing were obtained at a depth of 2m using a 2L Kemmerer from sampling station "B" (Figure 1.2) located in the Northeast part of the lake (N 48° 49' 23", W 091° 38' 36") Samples were collected in polyethylene 1L bottles. When larger volumes were required for TIE testing, a peristaltic pump and hose was used to obtain samples from the desired depth and collected in clean 10L or 25L polyethylene containers. Samples collected for toxicity testing were not filtered or preserved and were kept at 4°C until time of testing.

### 2.2.2.2 Bioaccumulation Studies

In late spring of 2006, *Eleocharis smallii* clumps were obtained from a wetland located near Mission Island Marsh in Thunder Bay, Ontario (48°20'07"N, 89°12'40"W) to conduct a greenhouse experiment. For the *in situ* test on bivalves, floater mussels, *Pyganadon grandis,* were collected by Dr. Joe Carney, from LaSalle River, in Manitoba. This test species was selected after repeated failed attempts to locate bivalves near the study sites in populations dense enough to facilitate such a test. At test initiation and test termination temperature, dissolved oxygen (DO), pH, and conductivity were obtained using a Hydrolab DataSonde®4.

## 2.2.3 Laboratory Analysis

Analyses of test waters followed methods outlined by Lakehead University Environmental Laboratory (LUEL), which were adapted from Standard Methods for the Examination of Water and Wastewater 18th Edition (Greenberg *et al*, 1992). All methods used here were also subjected to the same QA/QC procedures elaborated on in Chapter 1 section 1.2.2.2.

### 2.2.3.1 Mock Effluent Preparation and Analysis

Test solutions made to mimic Hogarth water were prepared by dissolving individual ion salts in moderately hard reconstituted water (MHRW). Salts used were reagent grade Simga brand $CaSO_4$ ($CaSO_4 \cdot 2H_2O$) and Caledon Laboratories Ltd. $MgSO_4$ ($MgSO_4 \cdot 7H_2O$) in concentrations that would result in similar ratios of Ca:Mg found in Hogarth, and also achieve the appropriate $SO_4^{2-}$ levels. Test water with just $SO_4^{2-}$ was prepared using a 1000 mg/L stock solution of SPEX CertiPrep $SO_4^{2-}$ anion standard. Concentrations of major ions were determined analytically on mock solutions used in testing; $Ca^{2+}$ and $Mg^{2+}$ were determined by ICP and $SO_4^{2-}$ was determined by IC, the Dionex Dx-120, as previously described in Chapter 1, section 1.2.2.2.

### 2.2.3.2 Plant Tissue Analysis

Plant samples were dried for three days in an oven at 30°C. After ground to a fine powder, 0.5 g of each sample was place into 50 ml XP1500 Teflon® microwave vessels and a ratio of 3 $HNO_3$:1 HCl Fisher Trace Metal Grade

concentrated acids added to each. The closed vessels were placed in a CEM Mars5 for a microwave-assisted high pressure, high temperature digestion, ramped to a temperature of 175°C and held for 25 minutes. When cooled, samples were brought to 50 ml with double distilled water (DDW) and analyzed for metals on a Varian Vista Pro Inductively Coupled Argon Plasma spectrometer with Cetac Autosampler. Parameters included in analysis were: Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Si, Sr, and Zn. Minimum detectable limits (MDLs) for this method can be viewed in Appendix 1.

### 2.2.3.3 Bivalve Tissue Analysis

Whole tissue analysis was carried out on the bivalves after removing the tissue from the shell and rinsing with DDW (Foster and Bates, 1978; Soto *et al*, 2000; Markich *et al*, 2001). Bivalve tissues were thoroughly mixed with a tissue homogenizer. A 5.0g aliquot, wet weight of each sample was placed in a glass test tube and a ratio of 3 HCl :1 $HNO_3$ Fisher Trace Metal Grade concentrated acids was added to each. Samples were allowed to pre-digest overnight then underwent an open digestion at 95°C for 4 hours on a block heater. When cooled, samples were brought to 25 ml with DDW and analyzed for metals on a Varian Vista Pro Inductively Coupled Argon Plasma spectrometer with Cetac Autosampler. Parameters included in analysis were: Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, S, Se, Si, and Zn. Minimum detectable limits (MDLs) for this method are provided in Appendix 1.

## 2.2.4 Toxicity Testing

### 2.2.4.1 Acute Toxicity Test Methods

In June and July 2004, rainbow trout and *Daphnia magna* acute lethality tests were conducted by the Lakehead University Aquatic Toxicology Research Centre (ATRC) according to EPS 1/RM/13 and EPS 1/RM/14 respectively (EC, 2000a; EC, 2000b).

### 2.2.4.2 Chronic Toxicity Test Methods

#### 2.2.4.2.1 *Ceriodaphnia dubia* Chronic Test Methods

Chronic toxicity investigations began with *Ceriodaphnia dubia,* tests of reproduction and survival, based on the Environment Canada Biological Test Method (1992). *C. dubia* were cultured at Lakehead University in moderately hard reconstituted water (MHRW). This water was also used for dilution water. Water characteristics for MHRW were as follows: pH (7.55-7.90), conductivity (100-110 μs/cm), DO (85-95% saturation), and hardness (160-180 mgCaCO$_3$/L)

Prior to each test, confirmation was needed that all culturing health criteria were met to ensure accurate and reliable test results. This was achieved through reference toxicant tests performed by the Lakehead University TIE Laboratory. Test trays held plastic cups in which 10 mL of test water were placed. Tests were conducted using full dilution series: 12.5%, 25%, 50%, and 100% strength, five replicates for each. At least one control was run with each test, also with five replicates. Neonates (<24-h-old daphnia) were transferred to

each test cup and fed with 0.67μL each of yeast, Cerophyll™, and trout chow (YCT) and algae.

Daphnids were fed and checked daily with any progeny or other observations recorded. Chronic *C. dubia* tests are termed static-renewal toxicity tests; solutions are renewed (replaced) periodically during the test. Test solutions for this study were renewed at intervals of ≤ 48 h throughout the tests with the first-generation daphnid transferred to the new solution. Water quality variables including temperature, conductivity, pH, and dissolved oxygen were measured at the beginning/end and at the renewal/post exposure of each toxicity test, depending on the nature of the test, i.e. static or static-renewal tests. Conductivity, pH, and temperature were measured using a Fisher Scientific Accumet® multimeter system with Accumet probes. DO was measured on a Hach sensION378 with a Hach DO Probe.

Tests were carried out in Sanyo Versatile Environmental Test Chambers maintained at 25 ± 1°C and a photoperiod of 16 h light: 8 h darkness. Duration of tests was 8 days or fewer. Criterions for test acceptability were a mean survival of ≥80% and a mean reproduction of 15 young/surviving females. Endpoints for these tests were two-fold; first being mortality of the first-generation daphnids (i.e. original neonates) and second, the number of live neonates produced by each first-generation daphnid during the test period.

## 2.2.4.2.2 *Ceriodaphnia dubia* Chronic Toxicity Identification Evaluation Test (TIE) Methods

Chronic Toxicity Identification Evaluation (TIE) Phase I tests followed the general guidance of the U.S. Environmental Protection Agency (USEPA, 1992). For both the chronic and TIE Phase I toxicity tests, similar test methods were followed (see section 2.2.5.1.). Manipulation tests performed for TIE Phase I included: filtration, aeration, post $C^{18}$ solid phase extraction column test (post SPE), graduated pH adjust, methanol eluate, sodium thiosulfate ($Na_2S_2O_3$) additions (10 mg/L and 25 mg/L), and ethylenediaminetetraacetic acid (EDTA) additions (3 mg/L and 8 mg/L).

## 2.2.4.2.3 Mock Effluent Chronic Toxicity Test Methods

Standard chronic toxicity tests based on the EC (1992) and EC (1999b) test methods were conducted on mock effluents. Water characteristics for mock effluent were as follows: pH (7.30-7.70), conductivity (2260-2400 µs/cm), DO (80-95% saturation), and hardness (1420-1500 mgCaCO$_3$/L). The dilution series (12.5%, 25%, 50%, and 100%) of mock effluent water were tested and the results were then compared previous Hogarth toxicity results.

Attempts to test effects of only $SO_4^{2-}$ addition failed. It was not possible to adjust the low pH without compromising concentrations of other ions as a result of the base that was used to adjust pH. Artifactual toxicity was introduced as a result.

### 2.2.4.2.4 *Lemna minor* Toxicity Test Methods

Growth inhibition tests on *Lemna minor* were carried out following the Environment Canada Biological Test Method (1999b). Plants were cultured in Hoagland's E+ medium (1999b). Controls and dilutions were prepared with modified APHA (American Public Health Association) growth medium.

Trays held plastic cups in which 100 mL of test water was placed. Tests were conducted using the dilution series: control, 25%, 50%, and 100% strength, four replicates for each. Two three-frond plants were transferred to each cup. All cups were covered, placed in Versatile Environmental Test Chambers maintained at 25 ± 1°C and continuous full-spectrum lighting. *Lemna minor* tests were static, non-renewal, therefore after 7 days the final counts of fronds were recorded. Criteria for test acceptability were controls with a >8-fold increase in fronds.

### 2.2.5 Bioaccumulation Studies

A greenhouse study using *Eleocharis smallii* was carried out since exposing them in pit lakes is not possible due to lack of a littoral zone with sediment/substrate. Small clumps (rhizomes and shoots) of *E. smallii* were transplanted into tubs and allowed to acclimate in the Lakehead University greenhouse, using greenhouse water. Soil media consisted of black earth and an aquatic clay-type soil to anchor the plants. All media was autoclaved at 120°C for 40 minutes prior to the experiment for sterilization.

Water from the West Arm Lake, Caland Pit Lake, and Hogarth Pit Lake was collected from the surface and transported to the greenhouse using 25L plastic containers. In total, 4 treatments, including the control, with 4 replicates per treatment were maintained from June 19th to October 10th, 2006 (see Figure 2.2) for over four months of exposure. At the end of the exposure period, plants were dried and prepared for analysis.



**Figure 2.2. Photos illustrating *Eleocharis smallii* greenhouse experiment (left) and watering system (right).**

For the *in situ* study, the bivalve *Pyganodon grandis* was used. Following a 3-day acclimation period after transport from Manitoba, test organisms were ready for exposure. Each mussel was individually marked, weighed, and measured with calipers across the longest plane, widest plane, and thickest plane (Fig 2.3). Custom made cages (see Figure 2.3), by SureCraft Plastics Ltd. were constructed of co-polyester plastic and all hardware was made of a plastic

material, ensuring no metallic compounds were near the bivalves. Dimensions were 17.5 cm wide, 24.5 cm long, and 17 cm high. A window, 5 cm by 20.5 cm screened in with a 2mm by 2 mm mesh to allow for water flow-through. Within each cage, a fixed amount of black earth, aquatic soil (clay-like), and coarser sand were layered to provide a substrate to anchor in. All media was autoclaved at 120°C for 40 minutes prior to the experiment for sterilization.

Bivalves were transported in coolers, aerated, and placed in a water bath of lake water for acclimation until submersion. Exposure sites were situated near shores/land to allow for easy access and tie-off spots to monitor them regularly. Each cage was securely anchored and submerged to a depth of 1.5 to 2 meters. Three replicate cages, each containing five mussels were deployed in the West Arm Lake, Caland Pit Lake, and Hogarth Pit Lake (n=15). Locations for the sites are shown in Figure 2.1 and the corresponding coordinates in Table 2.1. Water chemistry measurements of each site within the three study lakes are summarized in Table 2.2.

Duration of exposure was from July 26th to September 14th, 2006 for a total of seven weeks exposure. Bivalves not used in the exposure treatments were frozen to serve as a reference. At the end of the test period, the bivalves were collected, measured, and weighed for a final time and frozen whole in the shell until analysis.
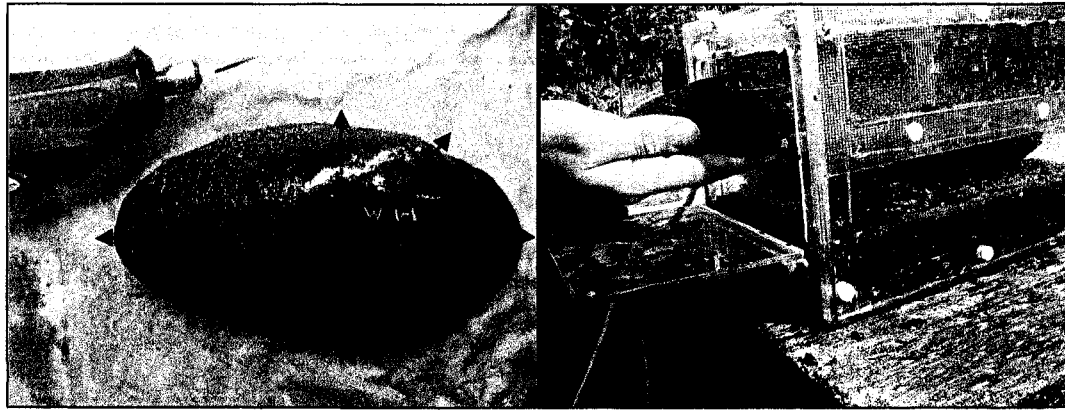
**Figure 2.3. Photos illustrating *Pyganodon grandis* with the planes taken for measurement (left) and cages used during exposure (right).**

**Table 2.1. Locations of bivalve cages in study lakes.**

| West Arm | Caland | Hogarth |
|---|---|---|
| Site 1 | Site 1 | Site 1 |
| 48°46'01.85"N | 48°49'21.13"N | 48°48'23.44"N |
| 91°39'41.03"W | 91°36'16.48"W | 91°38'50.01"W |
| Site 2 | Site 2 | Site 2 |
| 48°46'36.76"N | 48°49'23.03"N | 48°48'25.30"N |
| 91°39'40.88""W | 91°36'40.06"W | 91°38'32.36"W |
| Site 3 | Site 3 | Site 3 |
| 48°47'34.04"N | 48°48'57.47"N | 48°49'18.69"N |
| 91°40'05.33"W | 91°37'12.91"W | 91°39'13.78"W |

**Table 2.2. Water chemistry measurements at exposure locations for bivalves.**

| | West Arm | | | Caland Pit Lake | | | Hogarth Pit Lake | | |
|---|---|---|---|---|---|---|---|---|---|
| | Site 1* | Site 2 | Site 3 | Site 1 | Site 2 | Site 3 | Site 1 | Site 2 | Site 3 |
| DO | 8.6 | 8.4±0.8 | 8.7±0.5 | 8.9±0.2 | 8.8±0.2 | 8.6±0.4 | 8.7±0.1 | 8.8±0.3 | 8.5±0.3 |
| Temp.(°C) | 22.3 | 19.9±2.1 | 19.6±1.3 | 20.0±1.3 | 20.3±1.1 | 19.6±0.7 | 19.8±1.2 | 20.5±0.9 | 20.3±0.7 |
| pH | 6.9 | 7.0±0.3 | 6.9±0.4 | 8.9±0.5 | 8.41±0.2 | 8.3±0.3 | 8.2±0.3 | 8.2±0.2 | 8.4±0.2 |
| Cond.[a] | 85.3 | 85.4±1.9 | 80.2±1.5 | 663±6.4 | 643±5.0 | 642±7.2 | 2095±9.2 | 2077±12.4 | 2102±18.0 |

Values are means ± SD for intial and final readings (n = 2)

* only one reading was taken, complete mortality after 2 weeks

[a] As μs/cm

Both the greenhouse and *in situ* studies examined bioaccumulation in the three lakes, including Hogarth Pit Lake to determine whether bioaccumulation would be similar in more than one organism.

## 2.2.6 Data Analysis

### 2.2.6.1 Toxicity Testing

The *C. daphnia* 7-day chronic test is a dual-effect test, assessing both mortality and number of progeny. Mortality is considered a quantal effect, for which each test organism either shows the effect or does not. Number of progeny is a quantitative effect, in which the measured effect can take any whole or fractional value on a numerical scale. Results of dual-effect tests should be analyzed separately (EC, 2005). *L. minor* growth inhibition tests are quantitative sublethal tests.

Toxicity data was assessed by statistical comparison with data from the controls using ToxCalc™ version 5.0 (2000). Most common endpoints for quantal tests are median lethal concentration (LC50) or median effective concentration (EC50) (EC, 1999a). The preferred standard method is probit or logit regression by maximum likelihood regression; however, for tests that produce only one partial effect (i.e. an effect at only one concentration), the Trimmed Spearman-Kärber method is recommended (EC, 2005). 7-day EC50 values, using mortality as the endpoint, were determined using the Auto-Trimmed Spearman-Kärber method as the majority of tests resulted in mortality solely at 100% strength. For quantitative tests, the preferred endpoint is the Inhibiting Concentration for a (specified) Percent Effect (ICp) calculated by regression

techniques, such as linear interpolation (EC, 1999a; EC 2005). Both *C. daphnia* (using number of neonates) and *L. minor* (using number of fronds) tests were evaluated using the Linear Interpolation method. All toxicity data is reported with 95% confidence limits. Due to limited mortality, reproduction was the more informative endpoint for the *C. daphnia* chronic tests. IC50s were used for evaluating TIE results, as they are more useful for Phase I TIEs when trying to correlate the characterization test results to effluent toxicity (Goodfellow *et al*, 2005).

### 2.2.6.2 Bioaccumulation Studies

In cases where the vast majority (>95%) of the data, for all treatments, were below minimal detectable limits, the parameters were removed and in cases where some samples had metal values which were below detection limits, one-half of the detection limits were used in analyses (Gauthier et al, 2006).

Based on these criteria, for plant tissue data, As, Be, Cd, Co, and Pb parameters were removed and for bivalve data, As, Cd, and Pb were removed as all samples resulted in less than detectable limits. Bivalve reference data set was removed for comparative analyses due higher metal levels and low replication, which skewed the overall data sets and violated assumptions of subsequent statistical analyses. There was also a lack of water quality data to help account for metal levels. Reference data was solely used to account for any prior contamination of the bivalves.

Accumulation data was analyzed using SPSS 16.0 (SPSS 2007). Means and standard deviations were used to summarize the data. Analysis of Variance (ANOVA) determined whether significant (p<0.05) differences were detectable between the treatments (lakes/control). Kolomogorv-Smirnoff and Levene's tests were used to test the assumptions of normality and equal variance respectively. Where significant differences (SD) were detected, Tukey's Least Significance Difference (LSD) Post Hoc test was used to determine where they differed among the treatments. For data sets with equal sample sizes, Tukey's LSD test was used; however this was not suitable for unequal sample sizes (Miller, 1977). Due to unequal sample sizes in the bivalve data, Gabriel's Post Hoc was used.

## 2.3 Results

## 2.3.1 Toxicity Testing

## 2.3.1.1 Acute Toxicity

In the spring and summer of 2004, no mortality resulted from either the Rainbow Trout or *Daphnia magna* acute lethality tests.

## 2.3.1.2 Chronic Toxicity and Chronic Toxicity Identification Evaluation

In November 2004, the result of a 7-day chronic test on Hogarth Pit Lake water was an IC25 of 75% and IC50 >100%. Subsequent toxicity tests throughout the years were intermittent (Table 2.3). Results of chemical analysis from previous monitoring show elevated levels of conductivity, TDS, hardness, and $SO_4^{2-}$ in winter months (Table 2.4).

**Table 2.3. Summary of Hogarth toxicity tests over time (in percent).**

|  | Nov 2004 | Jan 2005* | May 2005 | June 2005 | Nov 2005 | Jan 2006* | June 2006 | July 2006 |
|---|---|---|---|---|---|---|---|---|
| **IC25** | 75 (n/a) | 23.1 (7-80) | >100 | >100 | >100 | 32.1 (11-68) | >100 | >100 |
| **IC50** | >100 | 62.0 (28-79) | >100 | >100 | >100 | 66.9 (21-94) | >100 | >100 |
| **7-day EC50** | >100 | 61.1 (48-79) | >100 | >100 | >100 | 99 (71-217) | >100 | >100 |

*from #1 and #2 TIE baselines

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**Table 2.4. Seasonal water chemistry of Hogarth Pit Lake (2m).**

| | 2004 | | 2005 | | | 2006 | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Fall | Winter | Spring | Summer | Fall | Winter | Spring | Summer | Fall |
| pH | 7.77 | 7.74 | 7.54 | 7.84 | n/a | 6.59 | 8.09 | 8.10 | 7.85 |
| pH* | 7.63 | 7.81 | 7.57 | 7.90 | 7.82 | 7.10 | 8.01 | 8.10 | 7.64 |
| Conductivity | 2290 | **2319** | 2058 | 2071 | n/a | **2120** | 2009 | 2024 | 2020 |
| Conductivity* | 2180 | **2347** | 2070 | 1965 | 2090 | **2330** | 2027 | 2036 | 2085 |
| TDS | 2104.80 | **2166.20** | 1970.40 | 1796.90 | n/a | **2104.20** | 2028.70 | 1806.60 | 2123.00 |
| Hardness | 1426.50 | **1498.30** | 1362.86 | 1327.13 | n/a | **1422.38** | 1284.97 | 1295.49 | 1413.00 |
| Cl⁻ | 12.00 | 10.04 | 10.08 | 11.42 | n/a | 10.51 | 8.91 | 8.91 | 11.89 |
| SO₄⁻ | 1321.60 | **1435.50** | 1323.78 | 1448.25 | n/a | **1465.97** | 1258.57 | 1227.37 | 1476.91 |
| NO₃⁻ | 0.47 | 0.58 | 0.51 | 0.46 | n/a | 0.56 | 0.46 | 0.47 | 0.57 |
| Ca²⁺ | 284.00 | 296.80 | 275.60 | 268.00 | n/a | 283.00 | 253.80 | 261.20 | 294.00 |
| K⁺ | 5.81 | 6.23 | 5.49 | 5.36 | n/a | 5.72 | 5.33 | 5.72 | 5.80 |
| Mg²⁺ | 170.80 | 180.80 | 161.10 | 157.10 | n/a | 170.90 | 155.50 | 153.60 | 162.10 |
| Na⁺ | 19.97 | 22.41 | 18.37 | 18.44 | n/a | 20.88 | 18.43 | 18.02 | 18.59 |
| Al | 0.0394 | 0.0393 | 0.0654 | 0.0700 | n/a | 0.0450 | 0.0410 | 0.0370 | 0.0100 |
| As | <MDL | <MDL | <MDL | 0.0170 | n/a | <MDL | <MDL | 0.0080 | 0.0070 |
| Ba | 0.0065 | 0.0073 | 0.0051 | 0.0120 | n/a | 0.0090 | 0.0070 | 0.0100 | 0.0030 |
| Be | <MDL | <MDL | <MDL | <MDL | n/a | <MDL | <MDL | <MDL | <MDL |
| Cd | <MDL | <MDL | <MDL | <MDL | n/a | <MDL | <MDL | <MDL | <MDL |
| Co | 0.0225 | 0.0240 | <MDL | <MDL | n/a | <MDL | <MDL | <MDL | <MDL |
| Cr | <MDL | <MDL | <MDL | <MDL | n/a | <MDL | <MDL | <MDL | <MDL |
| Cu | <MDL | <MDL | <MDL | <MDL | n/a | <MDL | <MDL | <MDL | 0.0130 |
| Fe | 0.1362 | 0.2127 | 0.2127 | 0.0420 | n/a | 0.1770 | 0.0910 | 0.0350 | 0.0270 |
| Mn | 0.2098 | 0.2300 | 0.4060 | 0.5292 | n/a | 0.3289 | 0.3427 | 0.2264 | 0.0683 |
| Ni | 0.0254 | 0.0282 | 0.0366 | 0.0530 | n/a | 0.0340 | 0.0350 | 0.0250 | 0.0130 |
| Pb | 0.0749 | 0.0885 | <MDL | 0.0100 | n/a | <MDL | <MDL | <MDL | <MDL |
| S | 419.80 | 444.67 | 391.43 | 477.00 | n/a | 447.94 | 460.00 | 467.56 | 184.40 |
| V | <MDL | <MDL | <MDL | <MDL | n/a | <MDL | <MDL | <MDL | <MDL |
| Zn | <MDL | 0.0014 | 0.0016 | 0.0020 | n/a | 0.0030 | <MDL | <MDL | 0.2000 |
| Total metal ions with S | 420.315 | 445.301 | 392.157 | 477.735 | n/a | 448.537 | 460.517 | 467.901 | 184.741 |
| Total metal ions w/o S | 0.515 | 0.631 | 0.727 | 0.735 | n/a | 0.597 | 0.517 | 0.341 | 0.341 |

all values expressed as mg/L, except conductivity (µS/cm)

* taken at test initiations (average value if more than one toxicity test was run)

** calculated using: $2.497(Ca^{2+})+4.188(Mg^{2+})$, expressed as $mg(CaCO_3)/L$
bolded values indicate highest values of all seasons, corresponding to toxic responses

January 2005 was the initiation of TIE Phase I. The baseline (a full

dilution series of Hogarth Pit Lake water with no manipulations) had an IC25 of

23% and an IC50 of 62%. Results from all the manipulation tests are

summarized in Table 2.5. A visual comparison of baseline results to all

manipulations is illustrated in Figure 2.4. The only manipulation of the first TIE

Phase I that showed a reduction in toxicity (i.e. a higher IC50 value) was the

EDTA 8 mg/L addition test. In comparison to the baseline, it reduced toxicity

from an IC50 of 62% to >100%.

**Table 2.5. Summary of results from the first Phase I Characterization Tests (in percent).**

| | Characterization Tests | | | | | |
|---|---|---|---|---|---|---|
| Endpoint | Baseline | Filtration | Aeration | pH 6 Buffered | pH 7 Buffered | Post SPE |
| IC25 | 23.1 (7-80) | 27.0 (1-44) | 28.8 (8-47) | 28.7 (12-68) | 29.5 (7-82) | 10.65 (4-73) |
| IC50 | 62 (28-79) | 52.1 (28.79) | 59.2 (32-67) | 61.3 (25-72) | 64.2 (31-78) | 49.2 (0-80) |
| 7-day EC50 | 61.6 (48-79) | 35.3 (n/a) | 61.6 (n/a) | 77.1 (64-94) | 77.1 (64-94) | 53.6 (n/a) |

| | Characterization Tests | | | | |
|---|---|---|---|---|---|
| Endpoint | $Na_2S_3O_3$ addition (10mg/L) | $Na_2S_3O_3$ addition (25mg/L) | EDTA addition (3.0 mg/L) | EDTA addition (8.0 mg/L) | Methanol Eluate |
| IC25 | 9.0 (4-71) | 42.5 (28.72) | 10.3 (3-78) | 84 (n/a) | < 12.5%* |
| IC50 | 60.6 (0-83) | 61.1 (30-82) | 58.8 (33-74) | >100 | < 12.5%* |
| 7-day EC50 | 70.2 (65-93) | 46.6 (32-69) | 89.1 (58-135) | >100 | >100 |
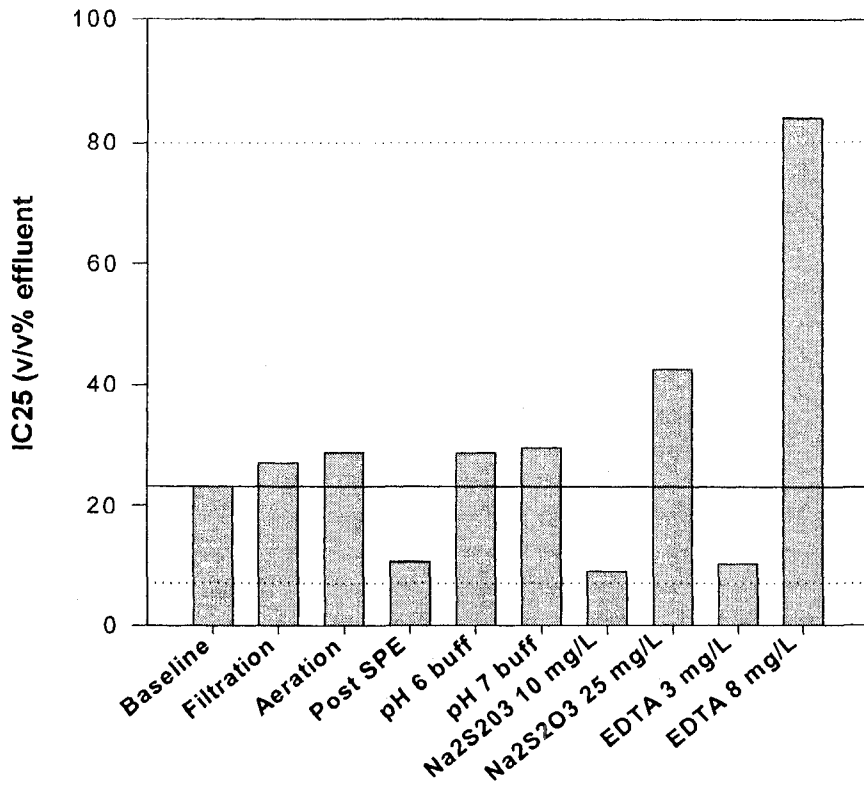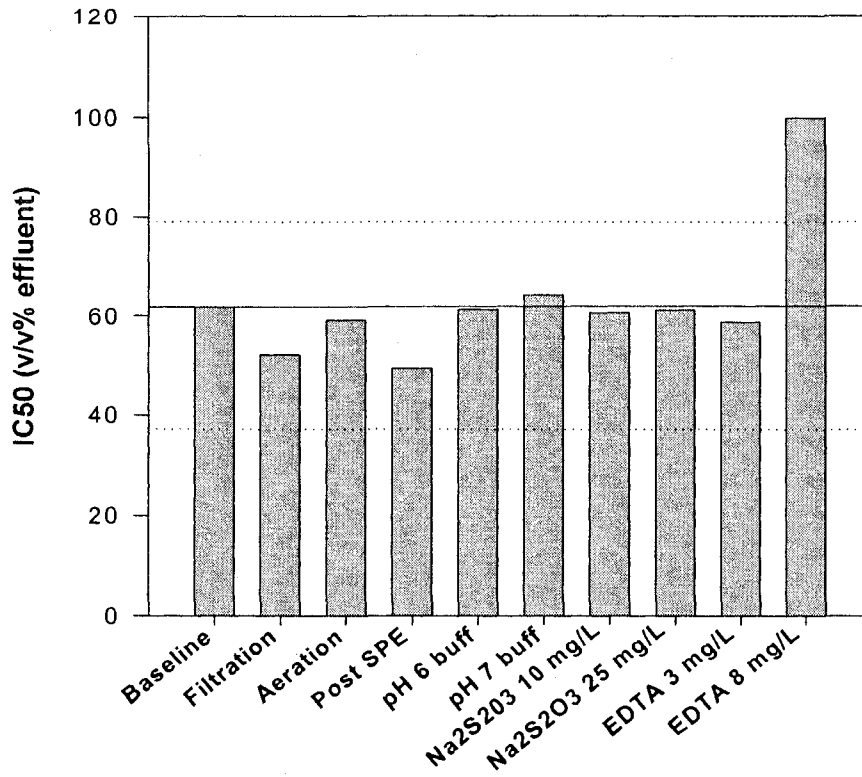
* indicates IC estimate less than the lowest concentration

Figure 2.4. Effects of toxicity identification evaluation (TIE#1) Phase I manipulations on *Ceriodaphnia dubia* 7-day IC25 values (top graph) and IC50 values (bottom graph). Dotted lines mark the levels of upper and lower limits (95% confidence limits) for the baseline toxicity test.

The second TIE Phase I in January 2006 resulted in the baseline having an IC25 of 32.1% and an IC50 of 66.9%. Results of these manipulation tests are summarized in Table 2.6 and a visual comparison of the baseline to the manipulations is illustrated in Figure 2.5. No manipulations resulted in a marked decrease in toxicity.

**Table 2.6. Summary of results from the second Phase I Characterization Tests (in percent).**

| | | | Characterization Tests | | | |
|---|---|---|---|---|---|---|
| Endpoint | Baseline | Filtration | Aeration | pH 6 Buffered | pH 7 Buffered | Post SPE |
| IC25 | 32.1 (11-68) | 32.3 (8-59) | 35.6 (13-52) | 44.6 (19-63) | 39.5 (14-88) | 30.7 (8-74) |
| IC50 | 66.9 (21-94) | 62.4 (33.76) | 60.1 (28-97) | 65.5 (42-88) | 66.2 (42-87) | 49.0 (0-83) |
| 7-day EC50 | >100 | 98 (n/a) | 87 (53-142) | >100 | >100 | 54 (38-76) |

| | | | Characterization Tests | | |
|---|---|---|---|---|---|
| Endpoint | $Na_2S_3O_3$ addition (10mg/L) | $Na_2S_3O_3$ addition (25mg/L) | EDTA addition (3.0 mg/L) | EDTA addition (8.0 mg/L) | Methanol Eluate |
| IC25 | 30.4 (22-76) | 29.0 (6-42) | 29.0 (6-42) | 33.7 (10-74) | < 12.5%* |
| IC50 | 60.6 (30-90) | 69.3 (36-84) | 48.8 (8-72) | 70 (n/a) | < 12.5%* |
| 7-day EC50 | 99 (71-217) | 99 (71-217) | >100 | >100 | >100 |
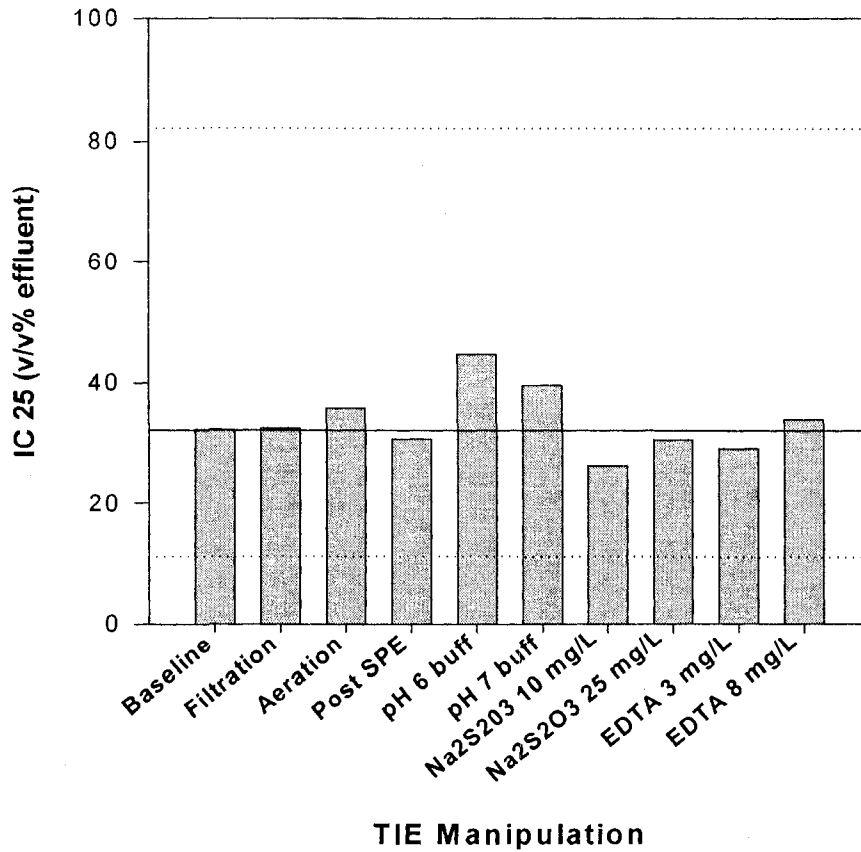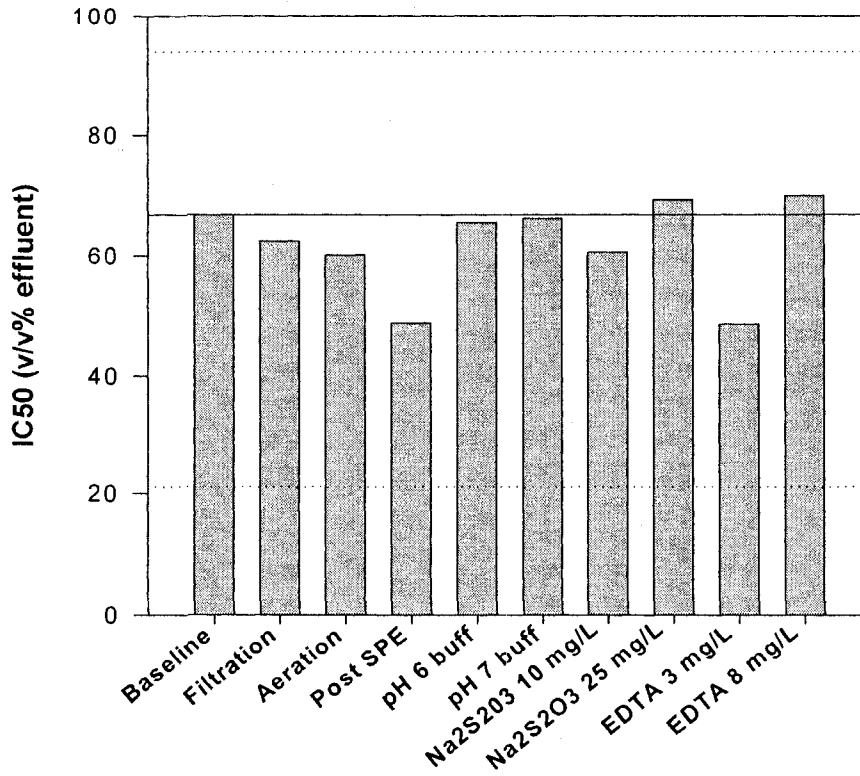
* indicates IC estimate less than the lowest concentration

Figure 2.5. Effects of toxicity identification evaluation (TIE#2) Phase I manipulations on *Ceriodaphnia dubia* 7-day IC25 values (top graph) and IC50 values (bottom graph). Dotted lines mark the levels of upper and lower limits (95% confidence limits) for the baseline toxicity test.

## 2.3.1.3 Mock Effluent Chronic Toxicity

Ionic composition of the prepared mock effluents in comparison to Hogarth Pit Lake water is summarized in Table 2.7. The major ions in Hogarth ($Ca^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$) constitute the majority of TDS as represented by the mock effluent. Results of mock effluent toxicity testing results compared to previous Hogarth Pit Lake toxicity results are shown in Table 2.8.

### Table 2.7. Ionic composition of Hogarth water and mock effluent.

| Sample | $Ca^{2+}$ | $K^+$ | $Mg^{2+}$ | $Na^+$ | $HCO_3^{-*}$ | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ | TDS** |
|---|---|---|---|---|---|---|---|---|---|
| Hogarth | 296 | 6 | 181 | 22 | 101 | 10 | 1 | 1436 | 2053 |
| Mock Eff. | 298 | n/a | 179 | n/a | n/a | n/a | n/a | 1443 | 1920 |

all values reported as mg/L, except * from total alkalinity ($mgCaCO_3/L$)
**as sum of all major anions and cations

### Table 2.8. Summary of *C. dubia* mock effluent tests compared to Hogarth tests (in percent).

| | Mock Test #1 | Mock Test #2 | Jan 2005 | Jan 2006 |
|---|---|---|---|---|
| IC25 | 33.9 (9-81) | 38.2 (14-85) | 23.1 (7-80) | 32.1 (11-68) |
| IC50 | 80.3 (n/a) | 66.5 (50-81) | 62.0 (28-79) | 66.9 (21-94) |
| 7-day EC50 | 98 (n/a) | >100 | 61.1 (48-79) | >100 |

## 2.3.1.4 *Lemna minor* Toxicity

*Lemna minor* testing showed the effluents (both Hogarth Pit Lake and mock effluent) to be less toxic to this species as indicated by higher IC25 values summarized in Table 2.9. No data for IC50s is available because a 50% reduction in the number of fronds did not occur at the concentrations tested. It

should be noted that the appearance of the plants in the higher dilution series (50% and 100%) of both effluents showed signs of stress including smaller unhealthy looking fronds that were chorotic and had shorter roots.

**Table 2.9. Summary of *Lemna minor* mock effluent tests compared to Hogarth tests (in percent).**

|       | Mock Test #1   | Mock Test #2   | Aug 2006 | Sept 2006      | Oct 2006       |
|-------|----------------|----------------|----------|----------------|----------------|
| IC25  | 90.74 (n/a)    | 88.7 (n/a)     | >100     | 93.4 (n/a)     | 85.1 (n/a)     |
| IC50  | n/a            | n/a            | n/a      | n/a            | n/a            |

## 2.3.2 Bioaccumulation Studies

Mean tissue concentrations (+/- standard deviations [SD]) for *E. smallii* and *P. grandis* are summarized in Table 2.10. The thirteen variables depicted in Figures 2.6, 2.7, and 2.8 are the only variables that showed significant differences ($p < 0.05$) between the lakes. Trends of most interest are those that resulted in the highest concentrations in Hogarth Pit Lake water. For *E. smallii*, Ba, Ca, Cr, Fe, Mg, Mn, Na, Ni, S, Sr, and Zn showed significant differences, with Ni and S levels highest in Hogarth water. *E. smallii* Ca, Na, and Mg concentrations were also significantly higher in Hogarth water, but not only Hogarth water. *P. grandis*, Al, Cr, Cu, Fe, Ni, and S concentrations revealed significant differences, with Al, Cu, Fe, Ni, and S highest in Hogarth water.

Ni and S levels were the only two variables that resulted in the highest levels in Hogarth water for both tissues.

## Table 2.10. Mean tissue concentrations in (μg/g) for *Eleocharis smallii* and *Pyganodon grandis*.

| | | *Eleocharis smallii* | | | | *Pyganodon grandis* | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Ctrl/Ref | West Arm | Caland | Hogarth | Ctrl/Ref | West Arm | Caland | Hogarth |
| Al[a] | Mean | 109.71 | 105.00 | 122.64 | 98.95 | 4.45 | 2.15 | 3.18 | 4.87 |
| | SD | 21.92 | 12.22 | 18.32 | 11.06 | 0.92 | 0.63 | 0.83 | 0.24 |
| As | Mean | <MDL* | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL |
| | SD | -- | -- | -- | -- | -- | -- | -- | -- |
| Ba[A] | Mean | 63.44 | 36.27 | 59.97 | 48.42 | 36.00 | 38.35 | 33.09 | 29.21 |
| | SD | 5.15 | 5.67 | 9.78 | 6.15 | 0.44 | 17.25 | 9.67 | 0.53 |
| Be | Mean | <MDL | <MDL | <MDL | <MDL | n/a** | n/a | n/a | n/a |
| | SD | -- | -- | -- | -- | n/a | n/a | n/a | n/a |
| Ca[A] | Mean | 5996.98 | 3824.25 | 6257.75 | 5332.55 | n/a | n/a | n/a | n/a |
| | SD | 457.96 | 549.13 | 648.18 | 408.12 | n/a | n/a | n/a | n/a |
| Cd | Mean | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL |
| | SD | -- | -- | -- | -- | -- | -- | -- | -- |
| Co | Mean | <MDL | <MDL | <MDL | <MDL | 0.05 | 0.08 | 0.07 | 0.08 |
| | SD | -- | -- | -- | -- | 0.00 | 0.03 | 0.02 | 0.01 |
| Cr[Aa] | Mean | 0.47 | 0.26 | 0.08 | 0.05 | 0.14 | 0.11 | 0.05 | 0.05 |
| | SD | 0.03 | 0.14 | 0.05 | 0.00 | 0.00 | 0.06 | 0.00 | 0.00 |
| Cu[a] | Mean | 2.81 | 2.52 | 2.92 | 2.60 | 1.71 | 0.55 | 0.55 | 0.68 |
| | SD | 0.49 | 0.20 | 0.62 | 0.28 | 0.02 | 0.16 | 0.11 | 0.01 |
| Fe[Aa] | Mean | 209.15 | 140.15 | 151.15 | 171.93 | 146.17 | 127.78 | 118.22 | 147.82 |
| | SD | 51.54 | 30.58 | 30.49 | 34.35 | 1.97 | 45.75 | 17.55 | 1.70 |
| K | Mean | 31392.40 | 31185.70 | 32949.85 | 30184.88 | n/a | n/a | n/a | n/a |
| | SD | 1805.48 | 2264.78 | 2729.79 | 4132.81 | n/a | n/a | n/a | n/a |
| Mg[A] | Mean | 3326.68 | 2037.43 | 2931.10 | 3017.49 | n/a | n/a | n/a | n/a |
| | SD | 82.77 | 224.42 | 325.65 | 325.93 | n/a | n/a | n/a | n/a |
| Mn[A] | Mean | 536.63 | 377.27 | 520.93 | 594.86 | 439.37 | 549.32 | 436.11 | 434.43 |
| | SD | 37.41 | 117.68 | 177.77 | 81.95 | 7.53 | 228.18 | 123.85 | 7.42 |
| Na[A] | Mean | 518.51 | 358.02 | 793.59 | 687.38 | n/a | n/a | n/a | n/a |
| | SD | 55.95 | 48.90 | 89.48 | 134.70 | n/a | n/a | n/a | n/a |
| Ni[Aa] | Mean | 0.05 | 0.07 | 0.09 | 0.38 | 0.12 | 0.12 | 0.12 | 0.30 |
| | SD | 0.00 | 0.04 | 0.04 | 0.14 | 0.00 | 0.00 | 0.00 | 0.01 |
| P | Mean | 6673.13 | 7031.45 | 6230.20 | 5109.87 | n/a | n/a | n/a | n/a |
| | SD | 589.30 | 1201.83 | 730.73 | 1294.01 | n/a | n/a | n/a | n/a |
| Pb | Mean | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL |
| | SD | -- | -- | -- | -- | -- | -- | -- | -- |
| S[Aa] | Mean | 2191.41 | 1264.67 | 3300.77 | 4771.98 | 585.81 | 584.37 | 628.23 | 736.57 |
| | SD | 232.05 | 181.44 | 255.36 | 200.81 | 68.23 | 37.21 | 54.54 | 11.85 |
| Si | Mean | 447.65 | 499.11 | 498.33 | 500.27 | 0.29 | 0.36 | 0.35 | 0.40 |
| | SD | 34.79 | 32.67 | 29.70 | 27.57 | 0.02 | 0.09 | 0.06 | 0.03 |
| Sr[A] | Mean | 34.16 | 20.64 | 40.42 | 35.52 | n/a | n/a | n/a | n/a |
| | SD | 1.99 | 1.91 | 4.77 | 2.68 | n/a | n/a | n/a | n/a |
| Zn[A] | Mean | 30.99 | 32.87 | 43.11 | 36.58 | 23.41 | 23.56 | 19.40 | 17.51 |
| | SD | 8.40 | 2.60 | 2.64 | 4.01 | 0.38 | 9.92 | 4.38 | 0.28 |

* <MDL, below detectable limits, see Appendix 1 for MDLs ** n/a, parameter not included in tissue analysis [A/a] denotes significant difference (p<0.05) in *Eleocharis smallii* and *Pyganodon grandis* respectively
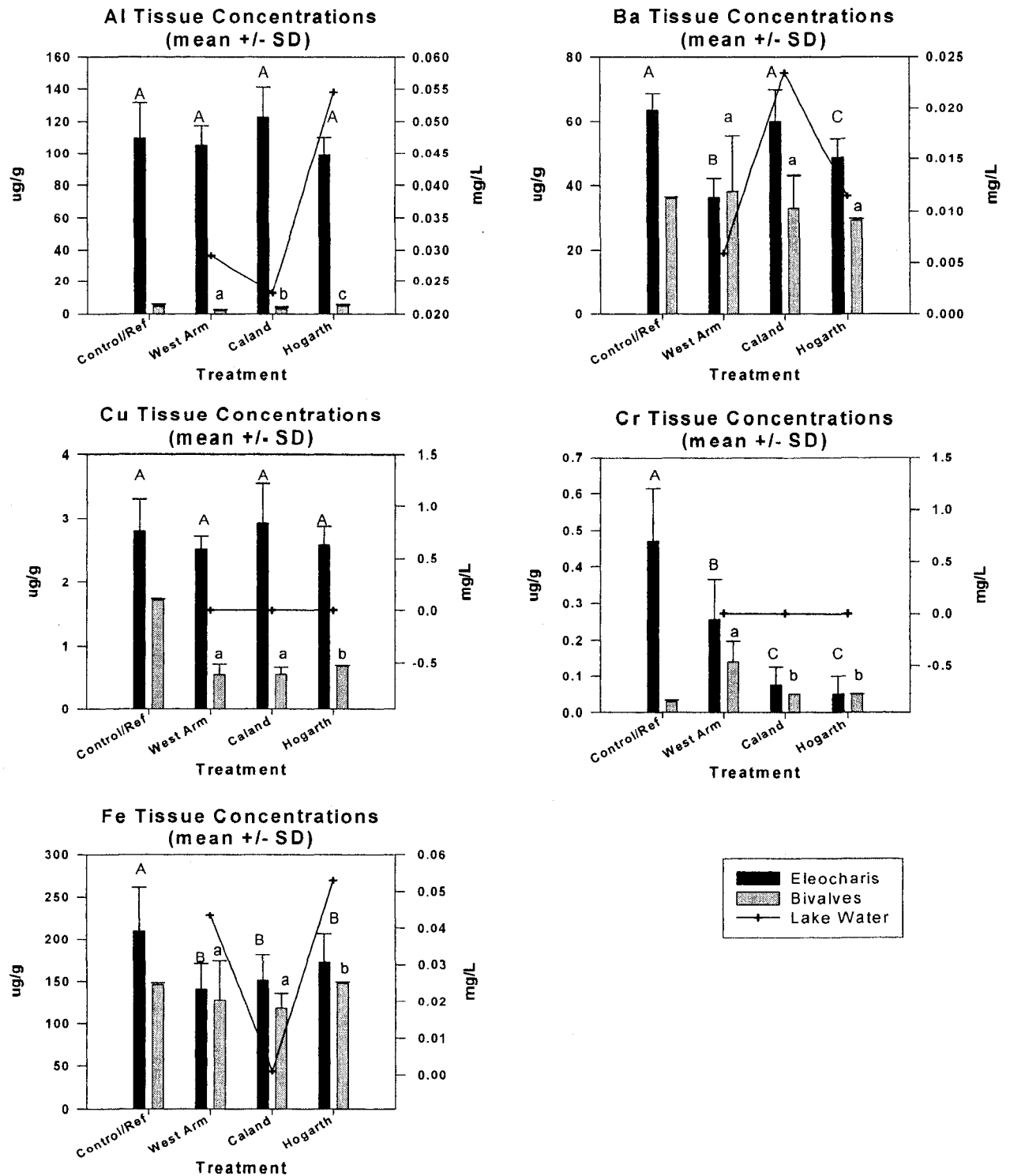
**Figure 2.6.** Mean tissue concentrations (Al, Ba, Cr, Cu, and Fe) for Control/Reference, West Arm, Caland, and Hogarth Treatments. Scale on right side of graphs corresponds to lake water concentrations. Capital letters indicate significant differences (p<0.05) for *Eleocharis* (Tukey's LSD post hoc) and lower case letters indicate significant differences for *Pyganodon* (Gabriel post hoc).

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## Mn Tissue Concentrations (mean +/- SD)

## Ni Tissue Concentrations (mean +/- SD)

## S Tissue Concentrations (mean +/- SD)

## Zn Tissue Concentrations (mean +/- SD)

Eleocharis
Bivalves
Lake Water
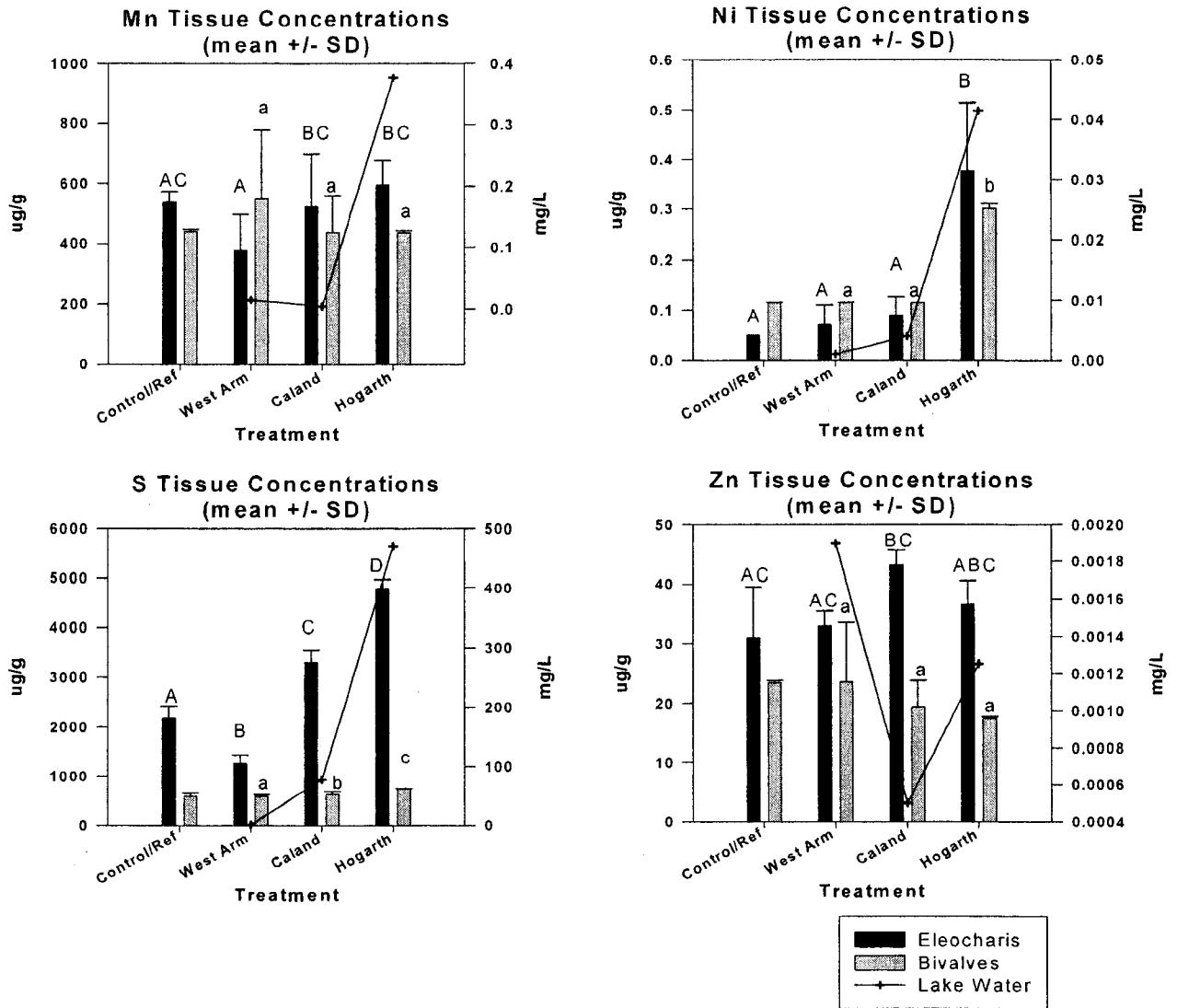
Figure 2.7. Mean tissue concentrations (Mn, Ni, S, and Zn) for Control/Reference, West Arm, Caland, and Hogarth Treatments. Scale on right side of graphs corresponds to lake water concentrations. Capital letters indicate significant differences (p<0.05) for *Eleocharis* (Tukey's LSD post hoc) and lower case letters indicate significant differences for *Pyganodon* (Gabriel post hoc).
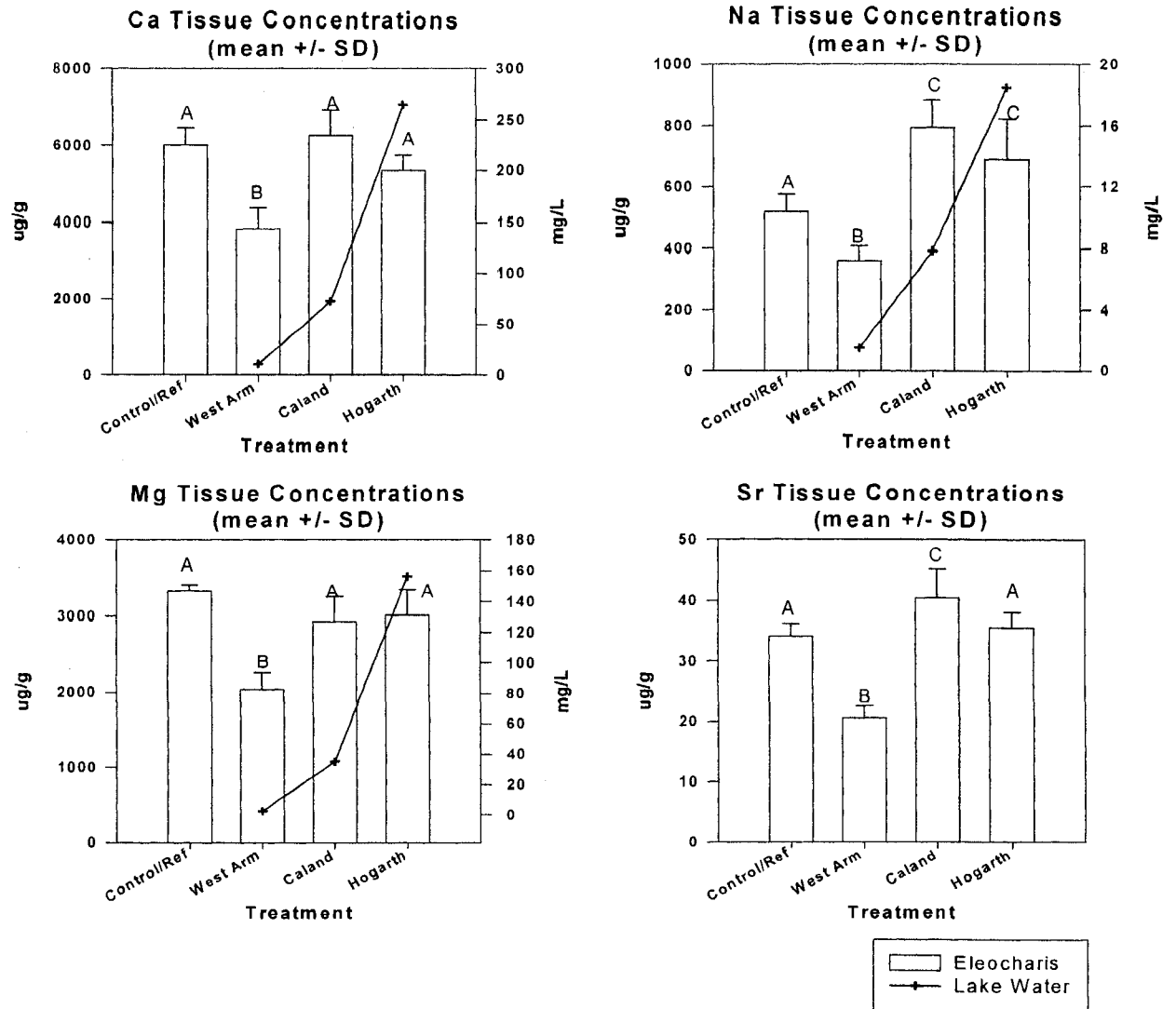
Figure 2.8. Mean tissue concentrations (Ca, Na, Mg, and Sr) for
Control/Reference, West Arm, Caland, and Hogarth Treatments. Scale on
right side of graphs corresponds to lake water concentrations.
Capital letters indicate significant differences (p<0.05) for *Eleocharis*
(Tukey's LSD post hoc) and lower case letters indicate significant
differences for *Pyganodon* (Gabriel post hoc).

One bivalve replicate (Site 1) in the West Arm suffered 100% mortality 2 weeks into the study. No other cages experienced such high rates of mortality; the following sites had one bivalve die during the course of the exposure period: West Arm #3, Caland #2 and #3, and Hogarth #1, #2, and #3. Bivalve weights, initial and final, along with differences between the sites and lakes are summarized in Table 2.11. Hogarth Pit Lake sites were the only bivalves to lose weight, while Caland sites gained the most on average, but not significantly higher than West Arm sites.

**Table 2.11. Bivalve mean weights and differences within sites and lakes.**

| | West Arm | | | Caland Pit Lake | | |
|---|---|---|---|---|---|---|
| | Site 1 | Site 2(n=5) | Site 3(n=5) | Site 1(n=5) | Site 2(n=5) | Site 3(n=5) |
| Weight$_i$ | n/a | 151.59±34.60* | 152.96±12.53 | 163.69±20.57 | 145.92±30.02 | 175.93±35.28 |
| Weight$_f$ | n/a | 153.85±12.53 | 154.15±12.48 | 166.40±30.89 | 148.09±30.89 | 178.18±34.88 |
| Difference | n/a | 2.26±2.07 | 1.19±0.54 | 2.17±1.02 | 2.17±1.02 | 2.25±1.33 |
| Lake mean difference | 1.78±1.76 (n=9) [a]** | | | 2.40±0.94 (n=13) [a] | | |
| | **Hogarth Pit Lake** | | | | | |
| | Site 1(n=5) | Site 2(n=5) | Site 3(n=5) | | | |
| Weight$_i$ | 153.31±44.28 | 131.96±19.58 | 130.01±19.54 | | | |
| Weight$_f$ | 151.28±44.86 | 128.86±19.17 | 127.44±18.56 | | | |
| Difference | -2.03±3.23 | -2.41±1.10 | -2.57±1.77 | | | |
| Lake mean difference | -2.34±2.02 (n=13) [b] | | | | | |

* values are means with SD

**Different letter indicate significant difference (p<0.05), as determined by ANOVA Gabriel Post Hoc Test

## 2.4 Discussion

### 2.4.1 Toxicity Testing

#### 2.4.1.1 Acute Toxicity

Lack of toxicity to *Daphnia magna* was a change compared to McNaughton's (2001) results in May 1999, which resulted in 100% mortality using full strength effluent (Hogarth water). This may be the result of changes in lake water quality since that time. In 1999, $SO_4^{2-}$ and TDS levels approached 1792 mg/L and 2477 mg/L respectively, while in 2006 they were 1513 mg/L and 2352 mg/L respectively (both years as annual averages). Nickel levels from 1999 were also higher at 0.058 mg/L and in 2006, averaged 0.030 mg/L.

#### 2.4.1.2 Chronic Toxicity and Chronic TIE Toxicity

Chronic test results were inconsistent throughout the 2 years, with toxicity occurring during the winter months. It was noted that conductivity, $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$, and TDS were slightly higher during those months (Table 2.4). These parameters are discussed further in section 2.4.1.3.

The first TIE Phase I test resulted in a reduction in toxicity (i.e. a higher IC50 value) with the EDTA 8 mg/L addition manipulation test (Table 2.5 and Figure 2.4). Reductions in toxicity are also evident when looking at the IC25 values of the sodium thiosulfate 25 mg/L and 8 mg/L addition tests; however, as suggested by Goodfellow *et al* (2005), IC50s may be more useful for Phase I TIEs when trying to correlate the characterization test results to effluent toxicity. The use of a consistent endpoint effect level is important for subsequent TIE

work (USEPA, 1992), therefore, it was also the endpoint observed in the second TIE Phase I tests.

Reductions in toxicity following EDTA additions are indicative of cationic metal toxicity. Cationic metals strongly chelated by EDTA include, $Al^{3+}$, $Cd^{2+}$, $Cu^{2+}$, $Fe^{3+}$, $Pb^{2+}$, $Mn^{2+}$, $Ni^{2+}$, and $Zn^{2+}$ (Stumm and Morgan, 1981); however, EDTA can remove non-metal ions such $Ca^{2+}$ and $Mg^{2+}$ (Flaschka and Barnard, 1967; Sovari and Sillanpaa, 1996 ). Also corresponding to this reduction or toxicity in the winter of 2005, was a relatively isolated high level of Pb in the water (Table 2.4). At 0.0885 mg/L, this exceeds the CWQG of 0.007 mg/L at hardnesses > 180 $mgCaCO_3$/L (CCME, 2007). Ni levels at this time were 0.0282 mg/L, well within the CWQG limit of 0.150 mg/L at hardnesses >180 $mgCaCO_3$/L. Based on these results, cationic metal toxicity should not be ruled out as a possibility.

Continuing with TIE work, such as Phase II to further isolate the cause of toxicity, could not happen in the spring of 2005, as there was no toxic response from Hogarth water. Summer and fall testing also showed no toxic response. January 2006 tests resulted in a toxic response; therefore, a subsequent TIE was carried out to determine whether the results were reproducible.

None of the Phase I manipulations in the second TIE greatly reduced toxicity (Table 2.6 and Figure 2.5). Pb levels at this time fell below the detection limit of 0.005 mg/L while Ni remained fairly consistent at 0.034 mg/L (Table 2.4). Given that toxicity was still present, and occurring in the winter months when TDS levels and corresponding parameters including conductivity and hardness

were elevated, further investigations into TDS-related toxicity were continued. Since TDS behave as a mixture of toxicants, only general relationships exist between toxicity and TDS (USEPA, 1992). Due to this variation, TDS does not sort out clearly in Phase I. Waller *et al* (2005) suggest if Phase I TIE manipulation fail to substantially reduce toxicity and sample conductivity is >2000 µs/cm, TDS toxicity should be investigated. Effluents may be toxic due to elevated ions, while other effluents may be toxic due to ratios of ions or types of ions that are not supportive of test organisms (Norberg-King *et al*, 2005a). Hogarth effluent does have conductivity values >2000 µs/cm and elevated TDS (and associated ions) concentrations (Table 2.4). The possibility of TDS toxicity in Hogarth Pit Lake was explored through testing mock effluents.

### 2.4.1.3 Mock Effluent Chronic Toxicity

Numerous authors concede that the use of mock effluents can effectively evaluate toxicity due to high TDS or unusual ionic balances (Mount *et al*, 1997; Tietge *et al*, 1997; Goodfellow *et al*, 2000; SETAC, 2004). A review of Hogarth water (effluent) data shows that 93% of effluent TDS could be accounted for by the sum of $Ca^{2+}$, $Mg^{2+}$, and $SO_4^{2-}$. Therefore, it is likely the mock effluent was representative of TDS in Hogarth water (Table 2.7). Toxicity test results demonstrated that mock effluent produced similar responses to Hogarth water. The mock effluent was slightly less toxic than Hogarth water generating IC25s of 33.9% and 38.2% compared to 23.1% and 32.1% and IC50s of 80.3% and 66.5% compared to 62.0% and 66.9% (Table 2.8). This may suggest that

although the mock effluent, while simulating TDS levels in Hogarth water does account for the majority of toxicity, other toxicants may be acting in addition to TDS.

A study by Norberg-King *et al* (2005b) using mock effluent to determine TDS toxicity concluded that although their results from mock effluents did prove to be a major contributor to effluent toxicity, it could not rule out the possibility of additional non-TDS toxicants being present. In this case, the additional non-TDS toxicants were assumed to be metals (due to small reductions in toxicity seen with EDTA additions); however, unless the TDS ions are reduced, it is difficult to identify any other toxicants.

### 2.4.1.4 *Lemna minor* Toxicity

To introduce an additional species to toxicity testing, *L. minor* tests were used in the fall of 2006. Responses of *L. minor* to Hogarth water and mock effluent were not as evident in comparison to *C. daphnia* (i.e. producing only an IC25 and no IC50); however, there were similar responses to both effluents (Table 2.9). It is also important to note that the plants did show signs of stress including smaller fronds, shorter roots, and chlorosis (discolouration of the plant due to lack of chlorophyll).

Toxicity to this species as a result of metals, specifically Pb and Ni, is unlikely. Pb levels during the time of testing were below detection limits. Wang (1987) reported IC50s for Ni to *Lemna minor* of 0.36 and 0.21 mg/L for water with hardness ranging from 37 to 78 mgCaCO$_3$/L respectively. He also estimated that

at a concentration of 1 mg/L, Ni can cause a 30% inhibition (IC30) of duckweed growth in almost all surface waters, and a 70% inhibition (IC70) in extremely soft waters. With Ni levels in Hogarth of 0.013 – 0.025 mg/L during the time of *L. minor* testing, the toxicity is unlikely due to Ni. This is not even taking into account the ameliorating effects of hardness levels on metal toxicity which is later discussed. Hence, Ni levels toxic to *L. minor* would have to exceed 1.0 mg/L, a level substantially higher than found in Hogarth Pit Lake.

The toxic response of *L. minor* to Hogarth water and mock effluent then is due to TDS levels, with $SO_4^{2-}$ as the major contributing ion. A few studies have documented the effects of elevated TDS on aquatic plants. (Sorenson *et al*, 1977) reported declines in productivity in algae (species not given) at TDS concentrations >1400 mg/L. *Selanastrum capricornutum*, green algae, resulted in an EC20 value of 551.3 mg/L TDS, as $CaSO_4$ (LeBlond and Duffy, 2001) and effects to higher order plants including the near elimination of coontail (*Ceratophyllus demersum*) and cattails (*Typha* sp.) in water with 1170 mg/L TDS (Hallock and Hallock)

Based on these studies, most likely the toxicity of *L. minor* to both Hogarth water and mock effluent is the result of TDS levels at approximately 2000 mg/L.


## 2.4.2 Bioaccumulation Studies

Ecological effects and risks from metal contamination are challenging to document due to variable responses among species, differing threats among metals, and complex environmental influences (Luoma and Rainbow, 2005).

Metal bioavailability, subsequent bioaccumulation, and risks presented by metals is a complex issue, which still must be better understood and quantified to a greater degree (McGeer et al, 2004). Issues confounding the science on bioaccumulation of metals in aquatic biota include: uptake mechanisms, accumulation strategy, trophic transfer, adaptation and acclimation (tolerance), intra/intercellular speciation, and metabolism/detoxification (McGeer et al, 2004; Chapman et al, 2003). Even choice of test species can influence variability in results. Within the same species of bivalves there can be major differences in bioaccumulation attributed to biological factors such as age, size, sex, genotype, phenotype, feeding activity, and reproductive state (Boening, 1999).

It was not the intent of this bioaccumulation study to attempt to explain such complex issues; rather, act as an aid in determining whether there exists the potential for metals in Hogarth Pit Lake to accumulate in aquatic biota. Essentially, it acted as a magnifying glass to account for toxic responses not fully explained by TDS toxicity. Trends of particular interest were metals that accumulated in both plant and animal tissue, while corresponding to increased levels of total metals in the water. In both E. smallii and P. grandis elevated concentrations of Ni and S were found when exposed to Hogarth Pit Lake water (Table 2.10 and Figure 2.7). Such an obvious trend, given the complexities associated with bioaccumulation, should not be overlooked. Having already reckoned toxic effects of S (as $SO_4^{2-}$) in TDS-related toxicity, Ni remains the metal of interest.

Some metal levels were higher in the control/reference tissues compared to the lake treatments (Figures 2.6 and 2.7). Cr and Fe in *E. smallii* were higher in the controls, and may be result of levels in the greenhouse water supply, which was not analyzed for metals at the time. Higher levels of metals in reference *P. grandis* tissues were not compared to the other treatments for reasons discussed in section 2.2.6.2.

Aside from bioaccumulation results, the bivalves also served as an *in situ* toxicity test by assessing how well (if at all) an organism could survive in Hogarth Pit Lake given its historical absence of life. No significant differences in mortality occurred in the study lakes, with the exception of West Arm Site 1. This can be attributed to low water levels during a dry period in the summer. Due to its location, near shoreline, the cage was more susceptible to changes in water level, resulting higher temperatures. No increased mortality in Hogarth Pit Lake indicates it was a suitable environment to live in. Hogarth bivalves did however experience net average weight loss, while the other two study lakes had average net weight gain. The lack of suspended food in Hogarth's water column may be the cause of weight loss. No differences in bivalve size were observed. The duration of exposure time (7 weeks) may have been insufficient to produce any detectable differences.

Variability between individuals inhibits demonstrations of statistically different changes of metal concentration in tissues (Markich et al, 2001). By investigating tissue concentrations using biotic predictors, such as sex and age, this could be improved.

## 2.5 Conclusions and Future Work

Based on TIE Phase I and mock effluent results on *C. dubia*, most of the toxicity in Hogarth Pit Lake can be attributed to the presence of the major ions $SO_4^{2-}$, $Ca^{2+}$, and $Mg^{2+}$. However, the reduction of toxicity shown in the first TIE with EDTA suggests metals may possibly contribute to toxicity. Pb levels at the time (January 2005) were high, and in later sampling, fell below detection limits; which may explain those isolated results.

Further evidence that may contribute to toxicity is suggested by the bioaccumulation results. Ni stands out as it was the only metal, other than S to bioaccumulate most in Hogarth water in both *Eleocharis smallii* and *Pyganodon grandis* tissues. *C. daphnia* appears to be the most sensitive species tested with nickel in both acute and chronic exposures. Keithly *et al* (2004) showed chronic effects (EC20s) at concentrations of < 3.8, 4.7, 4.0, and 6.9 µg/L at hardnesses of 50, 113, 161, and 253 $mgCaCO_3$/L respectively. Levels of nickel in Hogarth Pit Lake range from 13 to 53 µg/L, or 0.0130 to 0.0530 mg/L (Table 2.4). With hardness values in Hogarth water far exceeding levels tested at for chronic nickel toxicity (Keithly *el al*, 2004), it can be assumed the Ni concentrations would have to be much greater to cause an effect in Hogarth water. CWQG allowable Ni concentration ranges from 0.025-0.150 mg/L, with 0.150 mg/L being the limit for water with hardness >180$mgCaCO_3$/L (CCME, 2007).

Reductions and modifications of metal toxicity in freshwater organisms due to effects of hardness (Stubblefield *et al*, 1997; Welsh *et al*, 2000; Gensemer *et al*, 2002; Pyle *et al*, 2002; Heijerick, 2003; Keithly *et al*, 2004), and

calcium/magnesium ratios (Naddy *et al*, 2002) have been well documented. $Ca^{2+}$ and $Mg^{2+}$ are known to compete with metal ions for binding sites on organic matter or test species.

Toxicity testing should be continued, as there have been considerable changes over the years, even seasonally. Future work could include the removal of ions from Hogarth water to take a closer look at the possibility of Pb and Ni toxicity without implications of water hardness; however, removing hardness as a factor is not ecologically relevant since it is a part of the local limnology. The complex interactions of metal toxicity with biotic and abiotic factors presents a challenge. Mock effluent testing mimicking TDS with spiked additions of metals may be way of observing both effects.

In the case of *L. minor* testing, quantifying the health of the organisms would help to interpret results, rather than just counting the number of fronds. Perhaps incorporating an endpoint such as colour of the plants would be possible through photographic techniques. *L. minor* could also provide more insight into the possibility of metal effects. This could be achieved through analyzing the exposed test tissues for metals. Several studies have shown that *L. minor* can accumulate high concentrations of various heavy metals (Kara *et al*, 2003) including Ni and Pb (Jain *et al*, 1988; Axtell *et al*, 2003).

Further bioaccumulation investigations should be considered, utilizing indigenous species may allow for less variation in data as they would be geographically closer, exposed to more similar environments. Based on the preliminary findings, influences on Ni bioavailability and bioaccumulation should

be elaborated on to assess its potential environmental risks in Hogarth Pit Lake water. Studies solely on metal availability and uptake mechanisms of aquatic organisms would also prove useful due to the complex nature of metal bioaccumulation in aquatic environments

## GENERAL CONCLUSIONS

Caland and Hogarth Pit Lakes have demonstrated dilution trends from 1998 through 2006. This is more pronounced in Hogarth, as observed through toxicity changes (acute to chronic). Major differences in chemistry still exist: Caland is more alkaline with higher nutrient levels while Hogarth displays higher TDS values (and related parameters including conductivity, $SO_4^{2-}$ and cations). Caland Pit Lake contains a freshwater lens covering anoxic waters while Hogarth Pit Lake now contains aquatic organisms in the water column. This results in the development of a positive heterograde oxygen profile. Throughout the study period, observations of aquatic life forms in Hogarth Pit Lake were documented. This significant change differs from 2003 when at that time the lake was devoid of life (VanCook, 2005). More pronounced seasonal changes have also occurred in Hogarth. Winter months are characterized with higher levels of conductivity, TDS, and $SO_4^{2-}$, which also corresponds with the presence of toxicity in winter months.

Stable isotope analyses were employed to identify trends and influences on the pit lake water quality. Strong evaporative effects to depths of approximately 30 m are apparent in both lakes. This isolates bottom waters, creating permanent meromixes conditions. The ore body is the main source of sulfate for both lakes as $\delta^{34}S$ values show little variation in either pit lake and groundwater. Carbon inputs into the lakes differ. Hogarth Pit Lake is influenced by surrounding carbonate formations, while Caland Pit Lake is more influenced

by organic sources. Groundwater is still considered to be the major source of water in the pit lakes.

Toxicity in Hogarth Pit Lake during winter months correspond to observed seasonal variations. TDS, mainly comprised of $SO_4^{2-}$, $Ca^{2+}$, and $Mg^{2+}$ appears to be the main cause of toxicity in Hogarth Pit Lake. Metals contributing to toxicity, especially Ni, could still be a possibility and should not be ruled out. With the continuing trend of dilution and presence of aquatic life in Hogarth Pit Lake, forecasts of natural succession may continue over time. Thus far, failure for successful establishment of lower organisms such as invertebrates and plants (i.e. *Daphnia* and *Lemna minor*) severely inhibits the succession of higher organisms, and hence the productivity of the lake itself. Steep sides and continuously rising water levels are also not advantageous for organism establishment, specifically those shoreline plants and aquatic organisms requiring macrophytes for habitat (such as aquatic insects and fish).

This unique study area provides a very interesting opportunity for numerous and diverse research studies. It is a prime example of the resiliency of ecosystems and "how nature takes its course"; yet still reminds us of our ecological footprints and their resulting consequences.

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**APPENDIX**

# Appendix 1

## Minimum Detectable Limits for Analytical Methods

## Water Chemisty Minimun Detectable Limits

| Parameter | MDL | Units | Parameter | MDL | Units |
|---|---|---|---|---|---|
| Conductivity | 0.2 | µS/cm | Chromium | 0.002 | mg/L |
| Hardness (cacl.) | n/a | mgCaCO₃/L | Copper | 0.002 | mg/L |
| pH | n/a | n/a | Iron | 0.002 | mg/L |
| Calcium | 0.01 | mg/L | Manganese | 0.0002 | mg/L |
| Potassium | 0.10 | mg/L | Nickel | 0.002 | mg/L |
| Magnesium | 0.005 | mg/L | Lead | 0.005 | mg/L |
| Sodium | 0.01 | mg/L | Sulphur | 0.05 | mg/L |
| Chloride | 0.05 | mg/L | Vanadium | 0.01 | mg/L |
| Sulphate | 0.05 | mg/L | Zinc | 0.001 | mg/L |
| Aluminum | 0.005 | mg/L | Ammonium ($NH_3$-N) | 0.05 | mg/L |
| Arsenic | 0.01 | mg/L | Total Dissolved Solids | 10.0 | mg/L |
| Barium | 0.003 | mg/L | Total Suspended Solids | 2.0 | mg/L |
| Beryllium | 0.002 | mg/L | Total K. Nitrogen | 0.015 | mg/L |
| Cadmium | 0.001 | mg/L | Total Phosphorus | 0.005 | mg/L |
| Cobalt | 0.01 | mg/L | Nitrate | 0.009 | mg/L |
| Dissolved Organic Carbon | 0.50 | mg/L | Total Alkalinity measured as CaCO₃ | 1.0 | mgCaCO₃/L |

## Plant Tissue Chemistry Minimun Detectable Limits

| Parameter | MDL | Units | Parameter | MDL | Units |
|---|---|---|---|---|---|
| Aluminum | 5.00 | µg/g | Magnesium | 0.10 | µg/g |
| Arsenic | 2.50 | µg/g | Manganese | 0.01 | µg/g |
| Barium | 0.05 | µg/g | Sodium | 0.10 | µg/g |
| Beryllium | 0.02 | µg/g | Nickel | 0.10 | µg/g |
| Calcium | 0.10 | µg/g | Phosphorus | 0.80 | µg/g |
| Cadmium | 0.40 | µg/g | Lead | 0.50 | µg/g |
| Cobalt | 0.10 | µg/g | Sulphur | 3.00 | µg/g |
| Chromium | 0.10 | µg/g | Silicon | 0.50 | µg/g |
| Copper | 0.02 | µg/g | Strontium | 0.10 | µg/g |
| Iron | 0.10 | µg/g | Zinc | 0.10 | µg/g |
| Potassium | 5.00 | µg/g | | | |

## Clam Tissue Chemistry Minimun Detectable Limits

| Parameter | MDL | Units | Parameter | MDL | Units |
|---|---|---|---|---|---|
| Aluminum | 0.70 | ug/g | Manganese | 0.03 | ug/g |
| Arsenic | 1.25 | ug/g | Nickel | 0.23 | ug/g |
| Barium | 0.25 | ug/g | Lead | 0.13 | ug/g |
| Cadmium | 0.04 | ug/g | Sulphur | 1.25 | ug/g |
| Cobalt | 0.10 | ug/g | Selenium | 0.25 | ug/g |
| Chromium | 0.10 | ug/g | Silicon | 0.25 | ug/g |
| Copper | 0.10 | ug/g | Zinc | 0.02 | ug/g |
| Iron | 0.25 | ug/g | | | |

# Appendix 2

## Stable Isotope Analysis Reported Precision and Accuracy

## Stable Isotope Precision and Accuracy

| Parameter and Method | Reference | Precision/Accuracy |
|---|---|---|
| $\delta D$, chromium reduction | V-SMOW | +/- 2.0 ‰ (one standard deviation based on n=10 lab standards |
| $\delta^{18}O$, $CO_2$-$H_2O$ equilibration | V-SMOW | +/- 0.2 ‰ (one standard deviation based on n=10 lab standards |
| $\delta^{34}S$, CF-EA-IRMS | V-CDT | +/- 0.7 ‰ (one standard deviation based on n=10 lab standards |
| $\delta^{13}C_{DIC}$, phosphoric acid digestion | PDB | +/- 0.2 ‰ (one standard deviation based on n=10 lab standards |

# Appendix 3

**Raw data for Caland and Hogarth Pit Lakes (averages taken when sampling occurred more than once per season)**

| Location | Season | year | Ca | K | Mg | Na | ALK | Cond | Hardness | DOC | Cl | NO3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Caland 1m | spring | 1998 | 83.90 | 4.60 | 36.54 | 11.83 | 123.80 | 714.00 | 362.51 | 5.1800 | 8.3800 | 2.8800 |
| Caland 1m | summer | 1998 | 82.32 | 4.40 | 36.53 | 11.78 | 122.61 | 721.14 | 358.56 | 3.7986 | 7.6457 | 2.5851 |
| Caland 1m | fall | 1998 | 83.81 | 4.15 | 35.90 | 12.01 | 125.45 | 694.00 | 359.61 | 2.7100 | 6.5340 | 1.9660 |
| Caland 1m | winter | 1999 | 90.55 | 4.65 | 38.07 | 12.66 | 132.35 | 635.00 | 385.52 | 2.7750 | 7.3500 | 2.1530 |
| Caland 1m | spring | 1999 | 78.69 | 3.85 | 33.11 | 10.79 | 120.48 | 588.00 | 335.14 | 4.7475 | 6.1250 | 1.8618 |
| Caland 1m | summer | 1999 | 75.47 | 4.00 | 32.98 | 11.22 | 115.27 | 594.43 | 326.57 | 3.6314 | 6.1286 | 1.8750 |
| Caland 1m | fall | 1999 | 81.10 | 4.15 | 35.68 | 11.36 | 124.35 | 639.00 | 351.93 | 2.9350 | 6.6500 | 2.0640 |
| Caland 1m | winter | 2000 | 82.92 | 3.70 | 36.53 | 11.43 | 148.00 | 649.00 | 360.04 | 2.0500 | 6.8000 | 2.1310 |
| Caland 2m | spring | 2002 | 73.90 | 3.50 | 38.57 | 10.52 | 122.33 | 640.67 | 346.04 | 2.1467 | 13.8867 | 1.4883 |
| Caland 2m | summer | 2002 | 68.91 | 3.34 | 35.25 | 8.27 | 112.55 | 648.83 | 319.67 | 2.4100 | 4.6083 | 0.9095 |
| Caland 2m | summer | 2003 | 85.11 | 3.95 | 38.19 | 10.56 | 137.58 | 714.00 | 372.44 | 2.4770 | 6.8825 | 1.1913 |
| Caland 2m | spring | 2004 | 74.47 | 3.54 | 36.55 | 8.84 | 126.00 | 681.67 | 339.05 | 2.5413 | 5.2300 | 1.0653 |
| Caland 2m | summer | 2004 | 69.13 | 3.48 | 35.64 | 8.61 | 125.70 | 670.33 | 321.89 | 2.8857 | 4.6867 | 0.7943 |
| Caland 2m | fall | 2004 | 77.90 | 3.64 | 38.76 | 8.90 | 127.50 | 701.00 | 356.82 | 3.8430 | 4.5000 | 0.6780 |
| Caland 2m | winter | 2005 | 78.51 | 3.63 | 38.79 | 9.20 | 134.45 | 675.50 | 358.46 | 3.4310 | 4.6300 | 0.8900 |
| Caland 2m | spring | 2005 | 74.85 | 3.39 | 36.11 | 8.08 | 121.75 | 733.50 | 338.10 | 3.6500 | 4.5300 | 0.7370 |
| Caland 2m | summer | 2005 | 73.17 | 3.27 | 35.80 | 7.88 | 121.15 | 643.00 | 332.64 | 7.2105 | 4.4200 | 0.5620 |
| Caland 2m | winter | 2006 | 76.17 | 3.41 | 36.84 | 8.81 | 134.10 | 663.90 | 344.48 | 2.8000 | 4.4300 | 0.6280 |
| Caland 2m | spring | 2006 | 68.43 | 3.23 | 33.81 | 7.83 | 123.85 | <MDL | 312.43 | 2.6000 | 3.8350 | 0.5470 |
| Caland 2m | summer | 2006 | 71.20 | 3.44 | 34.35 | 7.65 | 124.10 | 643.30 | 321.64 | 3.1000 | 3.9000 | 0.4940 |
| Caland 18m | spring | 1998 | 86.42 | 4.65 | 37.63 | 12.17 | 127.40 | 737.00 | 373.37 | 5.4900 | 8.6900 | 3.0350 |
| Caland 18m | summer | 1998 | 84.89 | 4.23 | 36.76 | 11.84 | 128.15 | 737.17 | 365.90 | 3.6733 | 7.6333 | 2.6378 |
| Caland 18m | fall | 1998 | 86.19 | 4.15 | 36.63 | 12.34 | 127.70 | 712.50 | 368.62 | 2.5800 | 6.6680 | 2.0625 |
| Caland 18m | winter | 1999 | 95.95 | 4.50 | 39.78 | 13.21 | 135.87 | 664.50 | 406.16 | 2.5200 | 7.7500 | 2.4435 |
| Caland 18m | spring | 1999 | 82.40 | 4.15 | 34.69 | 11.34 | 124.98 | 616.50 | 351.02 | 4.7350 | 6.3250 | 1.9775 |
| Caland 18m | summer | 1999 | 77.64 | 3.85 | 33.33 | 11.35 | 118.04 | 609.14 | 333.47 | 3.4950 | 6.1843 | 1.9055 |
| Caland 18m | fall | 1999 | 80.80 | 3.45 | 35.52 | 11.28 | 124.50 | 634.50 | 350.50 | 2.7950 | 6.6500 | 2.0425 |
| Caland 18m | winter | 2000 | 83.47 | 4.35 | 36.84 | 11.56 | 148.25 | 643.50 | 362.69 | 2.3200 | 6.8500 | 2.1385 |
| Caland 18m | spring | 2002 | 72.53 | 3.51 | 38.09 | 10.36 | 128.40 | 675.00 | 340.63 | 2.1150 | 5.7950 | 1.6400 |
| Caland 18m | summer | 2002 | 71.55 | 3.48 | 36.34 | 8.88 | 115.65 | 657.00 | 330.85 | 2.1750 | 5.2800 | 1.0863 |
| Caland 18m | summer | 2003 | 83.86 | 3.98 | 38.07 | 10.23 | 138.88 | 707.25 | 368.84 | 2.2963 | 12.3150 | 1.4843 |
| Caland 18m | spring | 2004 | 80.16 | 3.77 | 39.91 | 9.56 | 134.77 | 731.33 | 367.29 | 2.4930 | 5.6467 | 1.2377 |

| Location | Season | year | Ca | K | Mg | Na | ALK | Cond | Hardness | DOC | Cl | NO3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Caland 18m | summer | 2004 | 72.29 | 3.63 | 37.36 | 9.13 | 132.00 | 703.67 | 336.97 | 2.6560 | 5.0967 | 1.0300 |
| Caland 18m | fall | 2004 | 79.60 | 3.68 | 39.53 | 9.14 | 129.83 | 713.67 | 364.30 | 3.1987 | 4.7700 | 0.8517 |
| Caland 18m | winter | 2005 | 79.35 | 3.66 | 39.77 | 9.36 | 133.50 | 677.50 | 364.68 | 3.0980 | 4.6600 | 0.9365 |
| Caland 18m | spring | 2005 | 80.07 | 3.61 | 39.01 | 8.75 | 130.75 | 781.00 | 363.29 | 4.6245 | 5.0300 | 0.8760 |
| Caland 18m | summer | 2005 | 79.61 | 3.51 | 38.90 | 8.98 | 133.45 | 703.00 | 361.68 | 2.4495 | 5.2200 | 0.9515 |
| Caland 18m | winter | 2006 | 76.21 | 3.42 | 37.47 | 8.89 | 133.40 | 672.60 | 347.22 | 2.6000 | 4.4300 | 0.6560 |
| Caland 18m | spring | 2006 | 73.50 | 3.44 | 36.84 | 8.58 | 131.70 | <MDL | 336.50 | 2.4500 | 4.2600 | 0.6755 |
| Caland 18m | summer | 2006 | 74.39 | 3.52 | 35.81 | 8.15 | 130.50 | 672.80 | 335.72 | 2.7000 | 4.1800 | 0.7830 |
| Caland 30m | spring | 1998 | 135.07 | 5.05 | 69.33 | 18.84 | 170.55 | 1156.00 | 627.61 | 5.5850 | 14.1150 | 5.2900 |
| Caland 30m | summer | 1998 | 131.17 | 5.57 | 64.62 | 18.00 | 167.70 | 1098.50 | 598.15 | 3.2167 | 13.8333 | 4.3935 |
| Caland 30m | fall | 1998 | 130.79 | 5.00 | 65.42 | 18.35 | 168.85 | 1048.50 | 600.53 | 2.3050 | 11.1635 | 3.6080 |
| Caland 30m | winter | 1999 | 130.91 | 5.10 | 63.63 | 18.10 | 167.50 | 895.00 | 593.34 | 2.6250 | 10.9500 | 3.6050 |
| Caland 30m | spring | 1999 | 117.56 | 4.80 | 55.43 | 16.15 | 157.63 | 847.25 | 525.69 | 4.8400 | 10.2000 | 3.1133 |
| Caland 30m | summer | 1999 | 121.71 | 4.88 | 60.25 | 17.02 | 163.80 | 915.75 | 556.24 | 3.1300 | 10.7833 | 3.3394 |
| Caland 30m | fall | 1999 | 120.98 | 4.90 | 59.13 | 16.53 | 167.20 | 905.00 | 549.69 | 2.4700 | 9.7500 | 3.0275 |
| Caland 30m | winter | 2000 | 118.93 | 5.35 | 57.62 | 16.20 | 170.35 | 878.50 | 538.27 | 2.2150 | 9.8500 | 2.9080 |
| Caland 40m | spring | 2004 | 108.60 | 4.46 | 52.32 | 14.47 | 167.75 | 957.50 | 490.27 | 2.3165 | 9.5000 | 1.8025 |
| Caland 40m | summer | 2004 | 106.35 | 4.64 | 54.33 | 15.37 | 175.80 | 1001.00 | 493.07 | 2.4670 | 9.5300 | 1.5925 |
| Caland 40m | fall | 2004 | 102.97 | 4.28 | 50.73 | 13.02 | 157.55 | 911.00 | 469.55 | 2.6195 | 7.2150 | 1.3010 |
| Caland 40m | winter | 2005 | 111.37 | 4.44 | 53.76 | 14.78 | 171.07 | 911.67 | 503.23 | 2.2827 | 8.2800 | 1.3753 |
| Caland 40m | spring | 2005 | 114.17 | 4.69 | 53.57 | 14.40 | 169.53 | 1066.33 | 509.43 | 3.0333 | 9.2800 | 1.4303 |
| Caland 40m | summer | 2005 | 108.15 | 4.30 | 51.46 | 14.10 | 168.60 | 926.00 | 485.57 | 2.1175 | 9.1650 | 1.4130 |
| Caland 40m | winter | 2006 | 103.80 | 4.21 | 49.24 | 14.05 | 170.00 | 882.90 | 465.41 | 2.7000 | 8.0000 | 1.0870 |
| Caland 40m | spring | 2006 | 98.12 | 4.17 | 47.01 | 13.27 | 166.25 | <MDL | 441.88 | 2.3500 | 7.8850 | 1.0765 |
| Caland 40m | summer | 2006 | 89.12 | 4.02 | 41.85 | 10.94 | 153.70 | 807.50 | 397.80 | 2.8000 | 6.5700 | 1.0800 |
| Caland (x-1)m | spring | 1998 | 135.91 | 5.85 | 70.62 | 18.94 | 169.95 | 1155.50 | 635.09 | 5.4700 | 14.0150 | 5.1000 |
| Caland (x-1)m | summer | 1998 | 140.43 | 6.19 | 71.68 | 18.91 | 172.86 | 1180.29 | 650.84 | 3.4943 | 14.5829 | 4.3657 |
| Caland (x-1)m | fall | 1998 | 132.42 | 5.30 | 68.33 | 18.31 | 167.05 | 1063.00 | 616.81 | 2.3450 | 10.7185 | 3.1800 |
| Caland (x-1)m | winter | 1999 | 145.99 | 5.50 | 74.16 | 19.72 | 175.17 | 1007.50 | 675.09 | 3.1550 | 12.2000 | 3.3730 |
| Caland (x-1)m | spring | 1999 | 140.53 | 5.25 | 71.76 | 18.96 | 174.15 | 1012.75 | 651.42 | 4.3250 | 11.2000 | 2.8928 |
| Caland (x-1)m | summer | 1999 | 135.12 | 5.13 | 70.68 | 18.78 | 173.14 | 1017.50 | 633.38 | 3.1086 | 11.7143 | 2.8369 |
| Caland (x-1)m | fall | 1999 | 138.20 | 5.15 | 71.99 | 18.73 | 180.30 | 1050.50 | 646.55 | 2.5000 | 11.6000 | 2.3495 |

| Location | Season | year | Ca | K | Mg | Na | ALK | Cond | Hardness | DOC | Cl | NO3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Caland (x-1)m | winter | 2000 | 133.66 | 5.10 | 68.88 | 18.01 | 177.40 | 988.50 | 622.22 | 2.0700 | 11.5500 | 2.5265 |
| Caland (x-1)m | spring | 2002 | 108.49 | 4.83 | 56.05 | 16.73 | 168.00 | 948.00 | 505.64 | 1.7900 | 9.9800 | 2.5580 |
| Caland (x-1)m | summer | 2002 | 108.60 | 4.49 | 55.26 | 14.95 | 156.50 | 960.50 | 502.60 | 1.4800 | 8.5550 | 1.8745 |
| Caland (x-1)m | summer | 2003 | 121.92 | 4.91 | 57.31 | 16.35 | 173.93 | 988.75 | 544.45 | 1.8585 | 13.5200 | 1.9258 |
| Caland (x-1)m | spring | 2004 | 118.28 | 4.68 | 58.46 | 15.75 | 174.50 | 1041.50 | 540.19 | 2.2370 | 10.6700 | 1.6550 |
| Caland (x-1)m | summer | 2004 | 97.99 | 4.37 | 50.94 | 13.80 | 164.95 | 934.00 | 458.01 | 2.3925 | 8.5550 | 1.4880 |
| Caland (x-1)m | fall | 2004 | 117.80 | 4.65 | 58.06 | 15.36 | 171.95 | 1033.50 | 537.30 | 3.3300 | 8.8200 | 1.2750 |
| Caland (x-1)m | winter | 2005 | 114.20 | 4.76 | 61.69 | 16.73 | 180.50 | 998.00 | 543.49 | 2.1030 | 9.6700 | 1.2495 |
| Caland (x-1)m | spring | 2005 | 127.60 | 4.84 | 62.07 | 16.29 | 179.85 | 1207.50 | 578.55 | 2.9750 | 11.0200 | 1.3195 |
| Caland (x-1)m | summer | 2005 | 125.30 | 4.69 | 62.04 | 16.76 | 182.00 | 1074.00 | 572.70 | 2.1980 | 11.5500 | 1.2140 |
| Caland (x-1)m | winter | 2006 | 116.10 | 4.50 | 57.32 | 16.26 | 179.80 | 1003.00 | 529.96 | 2.3000 | 9.8200 | 1.0280 |
| Caland (x-1)m | spring | 2006 | 79.80 | 3.68 | 39.92 | 9.80 | 140.60 | <MDL | 366.45 | 2.3000 | 5.1700 | 0.9530 |
| Caland (x-1)m | summer | 2006 | 114.20 | 4.63 | 53.45 | 14.55 | 179.20 | 989.90 | 509.01 | 2.3000 | 9.6700 | 0.9980 |

| Location | Season | year | Al | As | Ba | Be | Cd | Co | Cr | Cu | Fe | Mn | Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Caland 1m | spring | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0355 | 0.0085 | <MDL |
| Caland 1m | summer | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0160 | 0.0076 | <MDL |
| Caland 1m | fall | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0260 | 0.0055 | <MDL |
| Caland 1m | winter | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0100 | 0.0020 | <MDL |
| Caland 1m | spring | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0195 | 0.0065 | <MDL |
| Caland 1m | summer | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0149 | 0.0066 | <MDL |
| Caland 1m | fall | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0360 | 0.0090 | <MDL |
| Caland 1m | winter | 2000 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0100 | 0.0030 | <MDL |
| Caland 2m | spring | 2002 | 0.0203 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0010 | 0.0287 | 0.0087 | 0.0040 |
| Caland 2m | summer | 2002 | 0.0345 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0024 | 0.0140 | 0.0035 | 0.0068 |
| Caland 2m | summer | 2003 | 0.0189 | <MDL | 0.0185 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0140 | 0.0233 | 0.0046 |
| Caland 2m | spring | 2004 | 0.0407 | <MDL | 0.0193 | <MDL | <MDL | <MDL | <MDL | 0.0031 | 0.0104 | 0.0331 | 0.0150 |
| Caland 2m | summer | 2004 | 0.0377 | <MDL | 0.0198 | <MDL | 0.0015 | <MDL | <MDL | <MDL | 0.0123 | 0.0072 | 0.0103 |
| Caland 2m | fall | 2004 | 0.0230 | <MDL | 0.0187 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0087 | 0.0029 | 0.0022 |
| Caland 2m | winter | 2005 | 0.0103 | <MDL | 0.0177 | <MDL | <MDL | 0.0103 | <MDL | <MDL | 0.0028 | 0.0022 | 0.0028 |
| Caland 2m | spring | 2005 | 0.0257 | <MDL | 0.0180 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0144 | 0.0090 | 0.0034 |
| Caland 2m | summer | 2005 | 0.0310 | 0.0050 | 0.0230 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0041 | 0.0060 |
| Caland 2m | winter | 2006 | 0.0160 | <MDL | 0.0230 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0030 | 0.0038 | 0.0050 |

| Location | Season | year | Al | As | Ba | Be | Cd | Co | Cr | Cu | Fe | Mn | Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Caland 2m | spring | 2006 | 0.0270 | <MDL | 0.0210 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0175 | 0.0126 | 0.0045 |
| Caland 2m | summer | 2006 | 0.0150 | <MDL | 0.0240 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0033 | 0.0030 |
| Caland 18m | spring | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0235 | 0.0060 | <MDL |
| Caland 18m | summer | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0125 | 0.0042 | <MDL |
| Caland 18m | fall | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0125 | 0.0020 | <MDL |
| Caland 18m | winter | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0100 | 0.0050 | <MDL |
| Caland 18m | spring | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0200 | 0.0060 | <MDL |
| Caland 18m | summer | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0136 | 0.0064 | <MDL |
| Caland 18m | fall | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0310 | 0.0080 | <MDL |
| Caland 18m | winter | 2000 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0100 | 0.0025 | <MDL |
| Caland 18m | spring | 2002 | 0.0105 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0015 | 0.0125 | 0.0045 | 0.0030 |
| Caland 18m | summer | 2002 | 0.0250 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0023 | 0.0155 | 0.0050 | 0.0065 |
| Caland 18m | summer | 2003 | 0.0088 | <MDL | 0.0185 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0050 | 0.0025 | 0.0048 |
| Caland 18m | spring | 2004 | 0.0236 | <MDL | 0.0189 | <MDL | 0.0012 | <MDL | <MDL | <MDL | 0.0065 | 0.0266 | 0.0084 |
| Caland 18m | summer | 2004 | 0.0153 | <MDL | 0.0192 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0045 | 0.0062 | 0.0071 |
| Caland 18m | fall | 2004 | 0.0182 | <MDL | 0.0187 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0095 | 0.0026 | 0.0024 |
| Caland 18m | winter | 2005 | 0.0088 | <MDL | 0.0171 | <MDL | <MDL | 0.0100 | <MDL | <MDL | 0.0026 | 0.0036 | 0.0033 |
| Caland 18m | spring | 2005 | 0.0139 | <MDL | 0.0181 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0055 | 0.0046 | 0.0041 |
| Caland 18m | summer | 2005 | 0.0110 | <MDL | 0.0215 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0047 | 0.0055 |
| Caland 18m | winter | 2006 | 0.0140 | <MDL | 0.0230 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0030 | 0.0027 | 0.0050 |
| Caland 18m | spring | 2006 | 0.0110 | <MDL | 0.0210 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0070 | 0.0039 | 0.0055 |
| Caland 18m | summer | 2006 | 0.0110 | <MDL | 0.0230 | <MDL | <MDL | <MDL | <MDL | 0.0020 | <MDL | 0.0023 | 0.0040 |
| Caland 30m | spring | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0260 | 0.1080 | <MDL |
| Caland 30m | summer | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0123 | 0.0535 | <MDL |
| Caland 30m | fall | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0140 | 0.0630 | <MDL |
| Caland 30m | winter | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0100 | 0.0730 | <MDL |
| Caland 30m | spring | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0193 | 0.0450 | <MDL |
| Caland 30m | summer | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0174 | 0.0635 | <MDL |
| Caland 30m | fall | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0235 | 0.0695 | <MDL |
| Caland 30m | winter | 2000 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0110 | 0.0805 | <MDL |
| Caland 40m | spring | 2004 | 0.0644 | <MDL | 0.0156 | <MDL | 0.0015 | <MDL | 0.0020 | <MDL | 0.0541 | 0.0700 | 0.0104 |
| Caland 40m | summer | 2004 | 0.0075 | <MDL | 0.0172 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0650 | 0.0076 |

| Location | Season | year | Al | As | Ba | Be | Cd | Co | Cr | Cu | Fe | Mn | Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Caland 40m | fall | 2004 | 0.0068 | <MDL | 0.0179 | <MDL | <MDL | 0.0117 | <MDL | <MDL | <MDL | 0.0725 | 0.0037 |
| Caland 40m | winter | 2005 | 0.0082 | <MDL | 0.0156 | <MDL | <MDL | 0.0124 | <MDL | <MDL | 0.0069 | 0.0674 | 0.0050 |
| Caland 40m | spring | 2005 | 0.0071 | <MDL | 0.0156 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0026 | 0.0374 | 0.0044 |
| Caland 40m | summer | 2005 | 0.0085 | 0.0050 | 0.0200 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0136 | 0.0070 |
| Caland 40m | winter | 2006 | 0.0080 | <MDL | 0.0210 | <MDL | <MDL | <MDL | <MDL | 0.0050 | 0.0060 | 0.1145 | 0.0060 |
| Caland 40m | spring | 2006 | 0.0065 | <MDL | 0.0195 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0075 | 0.0435 | 0.0055 |
| Caland 40m | summer | 2006 | <MDL | <MDL | 0.0220 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0232 | 0.0050 |
| Caland (x-1)m | spring | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.1200 | 0.2215 | <MDL |
| Caland (x-1)m | summer | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0240 | 0.1691 | <MDL |
| Caland (x-1)m | fall | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0355 | 0.1605 | <MDL |
| Caland (x-1)m | winter | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0240 | 0.2815 | <MDL |
| Caland (x-1)m | spring | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0585 | 0.2728 | <MDL |
| Caland (x-1)m | summer | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0553 | 0.3274 | <MDL |
| Caland (x-1)m | fall | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0545 | 0.4825 | <MDL |
| Caland (x-1)m | winter | 2000 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0255 | 0.4000 | <MDL |
| Caland (x-1)m | spring | 2002 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0020 | 0.0170 | 0.0720 | 0.0080 |
| Caland (x-1)m | summer | 2002 | 0.0140 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0010 | 0.0180 | 0.0115 | 0.0090 |
| Caland (x-1)m | summer | 2003 | 0.1307 | <MDL | 0.0181 | <MDL | <MDL | <MDL | 0.0059 | 0.0020 | 0.2208 | 0.1895 | 0.0105 |
| Caland (x-1)m | spring | 2004 | 0.0362 | <MDL | 0.0163 | <MDL | 0.0014 | <MDL | <MDL | <MDL | 0.0124 | 0.1420 | 0.0099 |
| Caland (x-1)m | summer | 2004 | 0.0083 | <MDL | 0.0185 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.1886 | 0.0082 |
| Caland (x-1)m | fall | 2004 | 0.0076 | <MDL | 0.0170 | <MDL | <MDL | 0.0115 | <MDL | <MDL | 0.0036 | 0.2552 | 0.0052 |
| Caland (x-1)m | winter | 2005 | 0.0943 | <MDL | 0.0163 | <MDL | <MDL | 0.0135 | <MDL | <MDL | 0.1577 | 0.4615 | 0.0069 |
| Caland (x-1)m | spring | 2005 | 0.0086 | <MDL | 0.0158 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0024 | 0.4421 | 0.0057 |
| Caland (x-1)m | summer | 2005 | 0.0100 | 0.0070 | 0.0220 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.7369 | 0.0110 |
| Caland (x-1)m | winter | 2006 | 0.0130 | <MDL | 0.0210 | <MDL | <MDL | <MDL | <MDL | 0.0030 | 0.0230 | 0.5193 | 0.0080 |
| Caland (x-1)m | spring | 2006 | 0.0110 | <MDL | 0.0210 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0130 | 0.0141 | 0.0060 |
| Caland (x-1)m | summer | 2006 | 0.4460 | 0.2220 | 0.4450 | 0.2190 | 0.2210 | 0.2260 | 0.2270 | 0.2280 | 0.2130 | 0.2240 | 0.2260 |

| Location | Season | year | Pb | S | V | Zn | NH3 | SO4 | pH | TDS | TOTN | TOTP | TSS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Caland 1m | spring | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | 253.00 | 8.27 | 463.40 | 0.2115 | 0.0050 | <MDL |
| Caland 1m | summer | 1998 | <MDL | <MDL | <MDL | 0.0400 | <MDL | 250.81 | 8.06 | 467.33 | 0.1371 | 0.0050 | <MDL |
| Caland 1m | fall | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | 213.66 | 7.71 | 469.10 | 0.3250 | 0.0340 | <MDL |
| Caland 1m | winter | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | 232.75 | 7.22 | 507.50 | 0.2900 | 0.0050 | <MDL |

| Location | Season | year | Pb | S | V | Zn | SO4 | NH3 | pH | TDS | TOTN | TOTP | TSS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Caland 1m | spring | 1999 | <MDL | <MDL | <MDL | <MDL | 197.85 | <MDL | 7.83 | 446.00 | 0.3330 | 0.0073 | <MDL |
| Caland 1m | summer | 1999 | <MDL | <MDL | <MDL | <MDL | 230.65 | <MDL | 8.02 | 442.19 | 0.3539 | 0.0103 | <MDL |
| Caland 1m | fall | 1999 | <MDL | <MDL | <MDL | <MDL | 216.75 | <MDL | 7.64 | 477.90 | 0.4835 | 0.0150 | <MDL |
| Caland 1m | winter | 2000 | <MDL | <MDL | <MDL | <MDL | 222.30 | <MDL | 7.07 | 466.40 | 0.4000 | 0.0240 | <MDL |
| Caland 2m | spring | 2002 | <MDL | 74.37 | <MDL | <MDL | 214.56 | <MDL | 7.95 | 430.20 | 0.4767 | 0.0130 | 3.87 |
| Caland 2m | summer | 2002 | <MDL | 74.71 | 0.1246 | 0.0025 | 201.73 | <MDL | 7.95 | 426.07 | 0.1930 | <MDL | 2.47 |
| Caland 2m | summer | 2003 | <MDL | 86.42 | <MDL | 0.0017 | 248.58 | 0.1040 | 7.22 | 487.45 | 0.2675 | 0.0290 | <MDL |
| Caland 2m | spring | 2004 | <MDL | 75.75 | <MDL | 0.0048 | 222.39 | <MDL | 8.09 | 449.67 | 0.2260 | <MDL | <MDL |
| Caland 2m | summer | 2004 | <MDL | 77.31 | <MDL | 0.0027 | 216.67 | <MDL | 8.35 | 447.67 | 0.2000 | <MDL | <MDL |
| Caland 2m | fall | 2004 | 0.0298 | 73.07 | <MDL | 0.0015 | 216.63 | <MDL | 8.04 | 495.30 | 0.2050 | 0.0070 | <MDL |
| Caland 2m | winter | 2005 | 0.0415 | 72.42 | <MDL | <MDL | 225.37 | <MDL | 7.94 | 479.90 | 0.1215 | <MDL | <MDL |
| Caland 2m | spring | 2005 | <MDL | 71.33 | <MDL | <MDL | 216.70 | 0.0560 | 8.23 | 446.40 | 0.2220 | <MDL | <MDL |
| Caland 2m | summer | 2005 | <MDL | 73.46 | <MDL | <MDL | 236.20 | <MDL | 8.33 | 452.40 | 0.0955 | 0.0110 | <MDL |
| Caland 2m | winter | 2006 | <MDL | 85.11 | <MDL | <MDL | 237.05 | <MDL | 6.84 | 476.00 | 0.3680 | 0.0130 | <MDL |
| Caland 2m | spring | 2006 | <MDL | 83.99 | <MDL | <MDL | 205.21 | 0.0470 | 8.34 | 458.60 | 0.0680 | 0.0465 | <MDL |
| Caland 2m | summer | 2006 | <MDL | 81.69 | <MDL | <MDL | 210.68 | 0.1200 | 8.41 | 505.00 | <MDL | 0.0480 | <MDL |
| Caland 18m | spring | 1998 | <MDL | <MDL | <MDL | <MDL | 256.00 | <MDL | 7.93 | 479.50 | 0.1860 | 0.0050 | <MDL |
| Caland 18m | summer | 1998 | <MDL | <MDL | <MDL | <MDL | 241.54 | <MDL | 7.69 | 484.83 | 0.2585 | 0.0102 | <MDL |
| Caland 18m | fall | 1998 | <MDL | <MDL | <MDL | <MDL | 218.67 | <MDL | 7.55 | 491.00 | 0.2850 | 0.0140 | <MDL |
| Caland 18m | winter | 1999 | <MDL | <MDL | <MDL | <MDL | 249.60 | <MDL | 6.90 | 536.10 | 0.3550 | 0.0055 | <MDL |
| Caland 18m | spring | 1999 | <MDL | <MDL | <MDL | <MDL | 208.20 | <MDL | 7.48 | 467.90 | 0.4533 | 0.0070 | <MDL |
| Caland 18m | summer | 1999 | <MDL | <MDL | <MDL | <MDL | 232.14 | <MDL | 7.70 | 444.74 | 0.4824 | 0.0197 | <MDL |
| Caland 18m | fall | 1999 | <MDL | <MDL | <MDL | <MDL | 218.55 | <MDL | 7.62 | 471.40 | 0.4830 | 0.0150 | <MDL |
| Caland 18m | winter | 2000 | <MDL | <MDL | <MDL | <MDL | 222.20 | <MDL | 7.09 | 471.70 | 0.3900 | 0.0175 | <MDL |
| Caland 18m | spring | 2002 | <MDL | 80.36 | <MDL | <MDL | 225.88 | <MDL | 7.46 | 463.20 | 0.4895 | 0.0140 | 4.00 |
| Caland 18m | summer | 2002 | <MDL | 76.00 | 0.1650 | 0.0020 | 199.57 | <MDL | 7.73 | 431.25 | 0.2715 | <MDL | 3.45 |
| Caland 18m | summer | 2003 | <MDL | 84.56 | <MDL | 0.0014 | 229.09 | 0.0655 | 6.76 | 494.40 | 0.1873 | 0.0125 | <MDL |
| Caland 18m | spring | 2004 | <MDL | 80.53 | <MDL | 0.0025 | 243.64 | <MDL | 7.70 | 505.33 | 0.2357 | <MDL | <MDL |
| Caland 18m | summer | 2004 | <MDL | 78.75 | <MDL | 0.0025 | 227.27 | <MDL | 7.72 | 470.07 | 0.1587 | <MDL | <MDL |
| Caland 18m | fall | 2004 | 0.0319 | 76.11 | <MDL | <MDL | 222.85 | <MDL | 7.84 | 480.00 | 0.2173 | <MDL | <MDL |
| Caland 18m | winter | 2005 | 0.0402 | 71.70 | <MDL | <MDL | 229.53 | <MDL | 7.83 | 482.80 | 0.0835 | <MDL | <MDL |
| Caland 18m | spring | 2005 | <MDL | 76.17 | <MDL | <MDL | 235.80 | 0.0375 | 7.82 | 480.20 | 0.2270 | <MDL | <MDL |

| Location | Season | year | Pb | S | V | Zn | SO4 | NH3 | pH | TDS | TOTN | TOTP | TSS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Caland 18m | summer | 2005 | <MDL | 79.06 | <MDL | <MDL | 254.36 | <MDL | 7.44 | 478.40 | 0.0880 | 0.0170 | <MDL |
| Caland 18m | winter | 2006 | <MDL | 84.82 | <MDL | 0.0010 | 241.10 | <MDL | 6.71 | 494.00 | 0.3850 | 0.0150 | <MDL |
| Caland 18m | spring | 2006 | <MDL | 92.01 | <MDL | <MDL | 224.89 | 0.0480 | 7.82 | 501.30 | 0.0515 | 0.0475 | <MDL |
| Caland 18m | summer | 2006 | <MDL | 88.87 | <MDL | <MDL | 217.90 | 0.1060 | 7.80 | 481.00 | <MDL | 0.0420 | <MDL |
| Caland 30m | spring | 1998 | <MDL | <MDL | <MDL | <MDL | 486.50 | <MDL | 7.17 | 810.70 | 0.2780 | 0.0050 | <MDL |
| Caland 30m | summer | 1998 | <MDL | <MDL | <MDL | <MDL | 478.53 | <MDL | 7.01 | 770.83 | 0.2517 | 0.0078 | <MDL |
| Caland 30m | fall | 1998 | <MDL | <MDL | <MDL | <MDL | 362.36 | <MDL | 6.99 | 765.90 | 0.3400 | 0.0050 | <MDL |
| Caland 30m | winter | 1999 | <MDL | <MDL | <MDL | <MDL | 376.25 | <MDL | 6.77 | 765.50 | 0.4900 | 0.0050 | <MDL |
| Caland 30m | spring | 1999 | <MDL | <MDL | <MDL | <MDL | 336.03 | <MDL | 7.16 | 673.05 | 0.3708 | 0.0050 | <MDL |
| Caland 30m | summer | 1999 | <MDL | <MDL | <MDL | <MDL | 358.32 | <MDL | 7.28 | 718.70 | 0.3423 | 0.0095 | <MDL |
| Caland 30m | fall | 1999 | <MDL | <MDL | <MDL | <MDL | 330.40 | <MDL | 7.21 | 717.60 | 0.3780 | 0.0140 | <MDL |
| Caland 30m | winter | 2000 | <MDL | <MDL | <MDL | <MDL | 332.35 | <MDL | 6.87 | 695.50 | 0.2600 | 0.0200 | <MDL |
| Caland 40m | spring | 2004 | <MDL | 108.47 | <MDL | 0.0037 | 339.91 | <MDL | 7.43 | 688.30 | 0.1555 | <MDL | <MDL |
| Caland 40m | summer | 2004 | <MDL | 126.59 | <MDL | 0.0023 | 355.55 | <MDL | 7.29 | 728.20 | 0.1125 | 0.0080 | <MDL |
| Caland 40m | fall | 2004 | 0.0390 | 107.69 | <MDL | <MDL | 300.04 | <MDL | 7.38 | 630.50 | 0.2630 | 0.0080 | <MDL |
| Caland 40m | winter | 2005 | 0.0518 | 108.30 | <MDL | 0.0014 | 332.13 | <MDL | 7.50 | 703.40 | 0.0800 | <MDL | <MDL |
| Caland 40m | spring | 2005 | <MDL | 110.68 | <MDL | 0.0010 | 348.33 | 0.0435 | 7.35 | 731.33 | 0.0880 | <MDL | <MDL |
| Caland 40m | summer | 2005 | <MDL | 111.90 | <MDL | 0.0010 | 356.19 | <MDL | 7.22 | 668.20 | 0.1780 | 0.0070 | 5.00 |
| Caland 40m | winter | 2006 | <MDL | 120.36 | <MDL | 0.0130 | 337.64 | <MDL | 6.63 | 680.80 | 0.4030 | 0.0110 | <MDL |
| Caland 40m | spring | 2006 | <MDL | 125.17 | <MDL | <MDL | 306.75 | 0.0460 | 7.51 | 684.10 | 0.0910 | 0.1180 | <MDL |
| Caland 40m | summer | 2006 | <MDL | 104.47 | <MDL | <MDL | 267.72 | 0.1180 | 7.43 | 720.80 | <MDL | 0.0660 | <MDL |
| Caland (x-1)m | spring | 1998 | <MDL | <MDL | <MDL | <MDL | 491.50 | <MDL | 7.11 | 842.30 | 0.3375 | 0.0050 | <MDL |
| Caland (x-1)m | summer | 1998 | <MDL | <MDL | <MDL | 0.0100 | 539.88 | <MDL | 7.00 | 887.20 | 0.2053 | 0.0050 | <MDL |
| Caland (x-1)m | fall | 1998 | <MDL | <MDL | <MDL | <MDL | 376.37 | <MDL | 7.13 | 774.30 | 0.2250 | 0.0050 | <MDL |
| Caland (x-1)m | winter | 1999 | <MDL | <MDL | <MDL | <MDL | 461.30 | <MDL | 6.78 | 905.30 | 0.3800 | 0.0060 | <MDL |
| Caland (x-1)m | spring | 1999 | <MDL | <MDL | <MDL | <MDL | 407.95 | <MDL | 7.04 | 882.80 | 0.3378 | 0.0098 | <MDL |
| Caland (x-1)m | summer | 1999 | <MDL | <MDL | <MDL | <MDL | 430.75 | <MDL | 7.22 | 835.16 | 0.3239 | 0.0307 | <MDL |
| Caland (x-1)m | fall | 1999 | <MDL | <MDL | <MDL | <MDL | 413.25 | <MDL | 7.17 | 856.50 | 0.3620 | 0.0185 | <MDL |
| Caland (x-1)m | winter | 2000 | <MDL | <MDL | <MDL | <MDL | 409.40 | <MDL | 6.87 | 811.80 | 0.2550 | 0.0280 | <MDL |
| Caland (x-1)m | spring | 2002 | <MDL | 116.62 | <MDL | 0.0050 | 334.53 | <MDL | 7.20 | 690.80 | 0.1660 | 0.0080 | 3.10 |
| Caland (x-1)m | summer | 2002 | <MDL | 125.28 | 0.2621 | 0.0030 | 324.38 | <MDL | 7.21 | 690.30 | 0.1040 | 0.0060 | 3.20 |
| Caland (x-1)m | summer | 2003 | <MDL | 133.76 | <MDL | 0.0025 | 379.55 | 0.0787 | 6.71 | 748.35 | 0.1865 | 0.0168 | 43.80 |

| Location | Season | year | Pb | S | V | Zn | SO4 | NH3 | pH | TDS | TOTN | TOTP | TSS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Caland (x-1)m | spring | 2004 | <MDL | 128.22 | <MDL | 0.0033 | 383.67 | <MDL | 7.42 | 760.40 | 0.1560 | 0.0070 | <MDL |
| Caland (x-1)m | summer | 2004 | <MDL | 117.26 | <MDL | 0.0022 | 330.19 | <MDL | 7.32 | 667.70 | 0.1170 | 0.0150 | <MDL |
| Caland (x-1)m | fall | 2004 | 0.0420 | 122.91 | <MDL | 0.0011 | 351.87 | <MDL | 7.38 | 753.80 | 0.2490 | 0.0095 | <MDL |
| Caland (x-1)m | winter | 2005 | 0.0526 | 118.51 | <MDL | 0.0014 | 380.82 | <MDL | 7.48 | 792.80 | 0.0390 | 0.0100 | 10.70 |
| Caland (x-1)m | spring | 2005 | <MDL | 131.34 | <MDL | 0.0010 | 412.07 | 0.0310 | 7.37 | 800.10 | 0.0975 | 0.0130 | <MDL |
| Caland (x-1)m | summer | 2005 | <MDL | 147.76 | <MDL | 0.0010 | 443.27 | <MDL | 7.27 | 811.20 | 0.0720 | 0.0180 | <MDL |
| Caland (x-1)m | winter | 2006 | <MDL | 144.80 | <MDL | 0.0070 | 403.32 | 0.0550 | 6.71 | 772.00 | 0.4080 | 0.0480 | <MDL |
| Caland (x-1)m | spring | 2006 | <MDL | 102.44 | <MDL | <MDL | 247.18 | <MDL | 7.60 | 563.00 | 0.0400 | 0.0410 | <MDL |
| Caland (x-1)m | summer | 2006 | 0.2220 | 0.17 | 0.2230 | 0.2240 | 360.25 | 0.1090 | 7.45 | 664.80 | <MDL | 0.0250 | <MDL |

| Location | Season | year | Ca | K | Mg | Na | ALK | Cond | Hardness | DOC | Cl | NO3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hogarth 1m | spring | 1998 | 325.75 | 7.15 | 202.64 | 24.41 | 91.55 | 2425.00 | 1662.02 | 3.8300 | 17.5150 | 1.3900 |
| Hogarth 1m | summer | 1998 | 353.94 | 7.40 | 217.72 | 25.68 | 94.30 | 2506.67 | 1795.59 | 1.7717 | 18.6033 | 1.4033 |
| Hogarth 1m | fall | 1998 | 334.38 | 6.70 | 215.32 | 25.94 | 94.95 | 2285.00 | 1736.69 | 0.8850 | 14.5315 | 0.9610 |
| Hogarth 1m | winter | 1999 | 346.23 | 6.60 | 204.35 | 23.97 | 98.47 | 2115.00 | 1720.34 | 1.1600 | 15.2500 | 1.1220 |
| Hogarth 1m | spring | 1999 | 308.51 | 5.88 | 187.94 | 21.75 | 81.05 | 1983.75 | 1557.42 | 2.9125 | 13.1750 | 0.8873 |
| Hogarth 1m | summer | 1999 | 294.63 | 6.03 | 190.42 | 21.96 | 70.00 | 2037.29 | 1533.18 | 1.6529 | 12.9186 | 0.8593 |
| Hogarth 1m | fall | 1999 | 307.58 | 6.40 | 198.54 | 22.79 | 82.45 | 2140.00 | 1599.51 | 0.9500 | 13.8000 | 0.9070 |
| Hogarth 1m | winter | 2000 | 316.22 | 6.10 | 207.48 | 24.11 | 98.35 | 2110.00 | 1658.49 | 0.6490 | 14.8000 | 1.0340 |
| Hogarth 2m | spring | 2002 | 291.51 | 5.65 | 166.25 | 22.41 | 89.20 | 2170.00 | 1424.16 | 0.5700 | 13.0300 | 0.8410 |
| Hogarth 2m | summer | 2002 | 269.38 | 5.65 | 162.26 | 19.31 | 64.85 | 2137.50 | 1352.15 | 0.7750 | 9.5700 | 0.6005 |
| Hogarth 2m | summer | 2003 | 265.22 | 6.06 | 168.02 | 20.66 | 84.48 | 2080.00 | 1365.92 | 0.8918 | 10.2100 | 0.4520 |
| Hogarth 2m | spring | 2004 | 271.82 | 5.53 | 163.75 | 19.20 | 92.10 | 2140.00 | 1364.54 | 0.8313 | 9.1533 | 0.5243 |
| Hogarth 2m | summer | 2004 | 246.23 | 5.51 | 156.13 | 19.00 | 89.83 | 2143.33 | 1268.73 | 1.7560 | 11.2633 | 0.4687 |
| Hogarth 2m | fall | 2004 | 284.50 | 5.85 | 171.10 | 20.14 | 96.30 | 2290.00 | 1426.96 | 2.0645 | 6.5650 | 0.4455 |
| Hogarth 2m | winter | 2005 | 292.25 | 6.16 | 178.30 | 22.13 | 102.65 | 2319.00 | 1476.47 | 1.3015 | 11.4900 | 0.5860 |
| Hogarth 2m | spring | 2005 | 274.45 | 5.55 | 161.40 | 18.56 | 85.25 | 2078.00 | 1361.24 | 1.2250 | 10.0750 | 0.5155 |
| Hogarth 2m | summer | 2005 | 267.90 | 5.43 | 157.85 | 18.67 | 75.60 | 2074.00 | 1330.02 | 0.8575 | 11.3550 | 0.4540 |
| Hogarth 2m | winter | 2006 | 283.00 | 5.72 | 170.90 | 20.88 | 96.60 | 2120.00 | 1422.38 | 1.0000 | 10.5100 | 0.5640 |
| Hogarth 2m | spring | 2006 | 253.80 | 5.34 | 155.40 | 18.43 | 87.80 | 2000.00 | 1284.68 | 1.4000 | 8.9400 | 0.4615 |
| Hogarth 2m | summer | 2006 | 261.20 | 5.72 | 153.60 | 18.02 | 88.10 | 2024.00 | 1295.49 | 1.2000 | 8.9100 | 0.4670 |
| Hogarth 18m | spring | 1998 | 331.40 | 7.00 | 208.81 | 25.01 | 98.70 | 2455.00 | 1701.97 | 3.7050 | 17.5950 | 1.4400 |
| Hogarth 18m | summer | 1998 | 351.63 | 7.10 | 213.82 | 25.31 | 97.83 | 2511.67 | 1773.48 | 1.3983 | 19.0817 | 1.4832 |
| Hogarth 18m | fall | 1998 | 335.28 | 6.85 | 214.08 | 25.89 | 98.30 | 2270.00 | 1733.75 | 0.9700 | 15.0780 | 1.0240 |
| Hogarth 18m | winter | 1999 | 348.49 | 6.85 | 212.01 | 25.42 | 97.77 | 2115.00 | 1758.08 | 1.2650 | 13.7000 | 1.0565 |
| Hogarth 18m | spring | 1999 | 321.82 | 6.13 | 195.76 | 22.70 | 90.75 | 2145.00 | 1623.41 | 2.6500 | 14.6250 | 0.9690 |
| Hogarth 18m | summer | 1999 | 311.43 | 6.28 | 203.29 | 23.80 | 89.11 | 2153.29 | 1629.00 | 1.8143 | 14.0829 | 1.0100 |
| Hogarth 18m | fall | 1999 | 305.51 | 5.90 | 197.54 | 22.70 | 82.10 | 2145.00 | 1590.12 | 0.9600 | 14.7500 | 0.8780 |
| Hogarth 18m | winter | 2000 | 327.10 | 6.30 | 210.09 | 24.50 | 98.65 | 2125.00 | 1696.60 | 0.6250 | 14.9500 | 1.0415 |
| Hogarth 18m | spring | 2002 | 324.25 | 6.42 | 177.55 | 25.15 | 108.00 | 2370.00 | 1553.23 | 0.5700 | 13.7400 | 0.8700 |
| Hogarth 18m | Summer | 2002 | 308.80 | 6.41 | 187.40 | 22.77 | 93.05 | 2345.00 | 1555.89 | 0.6000 | 11.5750 | 0.8260 |
| Hogarth 18m | Summer | 2003 | 307.43 | 6.99 | 197.83 | 25.08 | 112.70 | 2365.00 | 1596.15 | 0.7330 | 14.5000 | 0.9078 |
| Hogarth 18m | spring | 2004 | 313.81 | 6.15 | 185.29 | 22.13 | 115.75 | 2420.00 | 1559.57 | 0.8270 | 14.0800 | 0.9395 |

| Location | Season | year | Ca | K | Mg | Na | ALK | Cond | Hardness | DOC | Cl | NO3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hogarth 18m | summer | 2004 | 285.20 | 6.21 | 178.97 | 22.38 | 119.47 | 2383.33 | 1461.66 | 1.1607 | 14.6400 | 0.8350 |
| Hogarth 18m | fall | 2004 | 317.57 | 6.31 | 188.97 | 21.69 | 119.20 | 2470.00 | 1584.36 | 1.4757 | 5.7467 | 0.8000 |
| Hogarth 18m | winter | 2005 | 312.17 | 6.37 | 187.93 | 23.62 | 120.97 | 1713.00 | 1566.54 | 1.2587 | 12.3233 | 0.8503 |
| Hogarth 18m | spring | 2005 | 324.30 | 6.42 | 188.57 | 22.37 | 119.33 | 2426.00 | 1599.49 | 1.3833 | 13.8467 | 0.9300 |
| Hogarth 18m | summer | 2005 | 315.23 | 6.25 | 183.63 | 22.82 | 119.07 | 2428.67 | 1556.19 | 0.6853 | 15.3600 | 0.9113 |
| Hogarth 18m | winter | 2006 | 310.60 | 6.13 | 185.70 | 23.32 | 123.20 | 2307.00 | 1553.28 | 1.1000 | 13.2500 | 0.9030 |
| Hogarth 18m | spring | 2006 | 297.00 | 6.07 | 180.10 | 22.11 | 122.90 | 2350.00 | 1495.87 | 1.1000 | 12.2300 | 0.8690 |
| Hogarth 18m | summer | 2006 | 295.10 | 6.11 | 168.70 | 20.17 | 115.40 | 2266.50 | 1443.38 | 1.0000 | 12.1850 | 0.8785 |
| Hogarth 30m | spring | 1998 | 335.96 | 6.70 | 207.81 | 25.16 | 94.75 | 2475.00 | 1709.18 | 3.7900 | 18.3400 | 1.5500 |
| Hogarth 30m | summer | 1998 | 356.47 | 6.98 | 210.27 | 24.75 | 95.42 | 2500.00 | 1770.72 | 1.6083 | 19.2133 | 1.5760 |
| Hogarth 30m | fall | 1998 | 334.34 | 6.25 | 210.73 | 25.55 | 97.10 | 2285.00 | 1717.35 | 0.9100 | 15.2160 | 1.0520 |
| Hogarth 30m | winter | 1999 | 351.56 | 6.80 | 214.16 | 25.75 | 98.52 | 2075.00 | 1774.73 | 1.1900 | 14.7000 | 1.1325 |
| Hogarth 30m | spring | 1999 | 332.09 | 6.55 | 200.57 | 23.40 | 95.53 | 2197.50 | 1669.21 | 2.6675 | 15.4250 | 1.0285 |
| Hogarth 30m | summer | 1999 | 319.84 | 6.70 | 208.55 | 24.99 | 96.33 | 2210.00 | 1672.05 | 1.7283 | 14.7333 | 1.0483 |
| Hogarth 30m | fall | 1999 | 318.25 | 6.35 | 204.18 | 24.11 | 97.80 | 2210.00 | 1649.76 | 0.9600 | 15.7000 | 1.0100 |
| Hogarth 30m | winter | 2000 | 331.88 | 6.65 | 211.48 | 25.03 | 101.25 | 2155.00 | 1714.35 | 0.5950 | 15.7000 | 1.0710 |
| Hogarth 40m | spring | 2005 | 293.42 | 5.85 | 174.24 | 20.65 | 103.75 | 2295.00 | 1462.37 | 0.8270 | 12.5000 | 0.7910 |
| Hogarth 40m | summer | 2004 | 284.90 | 6.29 | 180.30 | 22.73 | 118.65 | 2400.00 | 1466.49 | 1.1360 | 14.6750 | 0.8475 |
| Hogarth 40m | fall | 2004 | 322.95 | 6.44 | 192.30 | 22.12 | 118.35 | 2475.00 | 1611.76 | 1.0200 | 8.9050 | 0.8275 |
| Hogarth 40m | winter | 2005 | 319.40 | 6.47 | 190.90 | 23.81 | 120.25 | 1710.00 | 1597.03 | 1.0900 | 12.5100 | 0.8790 |
| Hogarth 40m | spring | 2005 | 301.35 | 6.01 | 176.10 | 20.62 | 102.85 | 2215.50 | 1489.98 | 1.7750 | 12.3900 | 0.7190 |
| Hogarth 40m | summer | 2005 | 318.80 | 6.25 | 184.30 | 22.78 | 121.70 | 2446.00 | 1567.89 | 0.7105 | 15.2600 | 0.9575 |
| Hogarth 40m | winter | 2006 | 316.50 | 6.19 | 187.60 | 23.51 | 124.30 | 2331.00 | 1575.97 | 1.3500 | 13.6600 | 0.9205 |
| Hogarth 40m | spring | 2006 | 291.15 | 5.94 | 176.70 | 21.32 | 114.10 | 2200.00 | 1467.02 | 1.1000 | 11.4050 | 0.7670 |
| Hogarth 40m | summer | 2006 | 301.70 | 6.45 | 175.60 | 21.49 | 125.20 | 2331.00 | 1488.76 | 0.8000 | 12.8400 | 0.9810 |
| Hogarth(x-1)m | spring | 1998 | 333.83 | 6.95 | 207.26 | 25.16 | 95.00 | 2455.00 | 1701.56 | 3.8750 | 18.2700 | 1.5500 |
| Hogarth(x-1)m | summer | 1998 | 355.04 | 7.08 | 211.09 | 25.02 | 95.32 | 2500.00 | 1770.58 | 1.6633 | 18.7750 | 1.5185 |
| Hogarth(x-1)m | fall | 1998 | 335.01 | 6.60 | 210.87 | 25.53 | 96.90 | 2280.00 | 1719.63 | 0.9700 | 15.2830 | 1.0790 |
| Hogarth(x-1)m | winter | 1999 | 349.96 | 6.65 | 209.98 | 24.95 | 98.19 | 2065.00 | 1753.23 | 0.9100 | 14.8500 | 1.1165 |
| Hogarth(x-1)m | spring | 1999 | 333.24 | 6.43 | 201.94 | 23.62 | 96.50 | 2200.00 | 1677.83 | 2.8925 | 15.3500 | 1.0308 |
| Hogarth(x-1)m | summer | 1999 | 324.72 | 6.74 | 211.14 | 25.34 | 96.96 | 2208.57 | 1695.09 | 1.7786 | 15.0157 | 1.0714 |
| Hogarth(x-1)m | fall | 1999 | 319.81 | 6.60 | 206.51 | 24.51 | 98.90 | 2210.00 | 1663.40 | 0.8450 | 15.5500 | 0.9885 |

| Location | Season | year | Ca | K | Mg | Na | ALK | Cond | Hardness | DOC | Cl | NO3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hogarth(x-1)m | winter | 2000 | 329.36 | 6.65 | 212.90 | 25.17 | 101.25 | 2155.00 | 1714.01 | 0.6070 | 15.6500 | 1.0400 |
| Hogarth(x-1)m | spring | 2002 | 312.89 | 5.77 | 170.50 | 24.17 | 107.35 | 2365.00 | 1495.33 | 0.7300 | 15.1500 | 1.0675 |
| Hogarth(x-1)m | summer | 2002 | 318.12 | 6.35 | 190.03 | 23.07 | 101.63 | 2392.50 | 1590.20 | 0.8200 | 12.5575 | 0.9280 |
| Hogarth(x-1)m | summer | 2003 | 306.10 | 7.14 | 201.01 | 25.97 | 114.67 | 2400.00 | 1606.16 | 0.6655 | 13.9400 | 0.9443 |
| Hogarth(x-1)m | spring | 2004 | 314.39 | 6.16 | 185.18 | 22.08 | 116.40 | 2410.00 | 1560.55 | 0.7745 | 14.1250 | 0.9525 |
| Hogarth(x-1)m | summer | 2004 | 283.65 | 6.36 | 180.75 | 22.95 | 119.05 | 2395.00 | 1465.26 | 0.9775 | 14.7150 | 0.8670 |
| Hogarth(x-1)m | fall | 2004 | 310.50 | 6.16 | 183.55 | 21.15 | 109.15 | 2385.00 | 1544.03 | 1.8915 | 7.5450 | 0.6580 |
| Hogarth(x-1)m | winter | 2005 | 312.65 | 6.35 | 187.60 | 23.55 | 121.35 | 1719.50 | 1566.36 | 1.2015 | 12.4350 | 0.8915 |
| Hogarth(x-1)m | spring | 2005 | 326.20 | 6.49 | 190.05 | 22.63 | 119.65 | 2458.00 | 1610.45 | 1.9000 | 13.6350 | 0.9185 |
| Hogarth(x-1)m | summer | 2005 | 317.25 | 6.16 | 182.65 | 22.45 | 121.50 | 2450.00 | 1557.11 | 0.7960 | 15.3300 | 0.9290 |
| Hogarth(x-1)m | winter | 2006 | 314.90 | 6.20 | 187.50 | 23.56 | 124.50 | 2343.00 | 1571.56 | 1.1000 | 13.3000 | 0.8800 |
| Hogarth(x-1)m | spring | 2006 | 304.30 | 5.89 | 177.80 | 21.31 | 123.20 | 2450.00 | 1504.46 | 1.1000 | 12.3300 | 0.8850 |
| Hogarth(x-1)m | summer | 2006 | 288.40 | 6.71 | 178.60 | 22.52 | 124.10 | 2327.00 | 1468.11 | 2.4000 | 12.6200 | 0.9640 |

| Location | Season | year | Al | As | Ba | Be | Cd | Co | Cr | Cu | Fe | Mn | Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hogarth 1m | spring | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.4535 | 0.2130 | 0.0810 |
| Hogarth 1m | summer | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.2453 | 0.1420 | 0.0545 |
| Hogarth 1m | fall | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.3915 | 0.1885 | 0.0530 |
| Hogarth 1m | winter | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.1065 | 0.0755 | 0.0620 |
| Hogarth 1m | spring | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.4103 | 0.3465 | 0.0613 |
| Hogarth 1m | summer | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.4237 | 0.4257 | 0.0627 |
| Hogarth 1m | fall | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.4095 | 0.3940 | 0.0680 |
| Hogarth 1m | winter | 2000 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.1235 | 0.3770 | 0.0710 |
| Hogarth 2m | spring | 2002 | 0.0290 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0020 | 0.1120 | 0.6070 | 0.0710 |
| Hogarth 2m | summer | 2002 | 0.0493 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0015 | 0.0770 | 0.8223 | 0.0788 |
| Hogarth 2m | summer | 2003 | 0.0662 | <MDL | 0.0083 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.1573 | 0.2770 | 0.0288 |
| Hogarth 2m | spring | 2004 | 0.0595 | <MDL | 0.0083 | <MDL | <MDL | <MDL | <MDL | 0.0037 | 0.1422 | 0.3552 | 0.0424 |
| Hogarth 2m | summer | 2004 | 0.0745 | <MDL | 0.0088 | <MDL | 0.0014 | <MDL | <MDL | 0.0020 | 0.0521 | 0.3745 | 0.0398 |
| Hogarth 2m | fall | 2004 | 0.0397 | <MDL | 0.0069 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.1501 | 0.2102 | 0.0254 |
| Hogarth 2m | winter | 2005 | 0.0423 | <MDL | 0.0077 | <MDL | <MDL | 0.0225 | <MDL | <MDL | 0.2247 | 0.2354 | 0.0282 |
| Hogarth 2m | spring | 2005 | 0.0644 | <MDL | 0.0057 | <MDL | <MDL | 0.0237 | <MDL | <MDL | 0.1868 | 0.4027 | 0.0367 |
| Hogarth 2m | summer | 2005 | 0.0710 | 0.0185 | 0.0125 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0565 | 0.5285 | 0.0530 |
| Hogarth 2m | winter | 2006 | 0.0450 | <MDL | 0.0090 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.1770 | 0.3289 | 0.0340 |

| Location | Season | year | Al | As | Ba | Be | Cd | Co | Cr | Cu | Fe | Mn | Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hogarth 2m | spring | 2006 | 0.0395 | <MDL | 0.0070 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0755 | 0.3393 | 0.0350 |
| Hogarth 2m | summer | 2006 | 0.0370 | 0.0080 | 0.0100 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0350 | 0.2264 | 0.0250 |
| Hogarth 18m | spring | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.4205 | 0.2750 | 0.0760 |
| Hogarth 18m | summer | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.3202 | 0.2525 | 0.0673 |
| Hogarth 18m | fall | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.2485 | 0.1575 | 0.0610 |
| Hogarth 18m | winter | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.1195 | 0.0745 | 0.0585 |
| Hogarth 18m | spring | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.7133 | 0.2920 | 0.0633 |
| Hogarth 18m | summer | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.4316 | 0.3424 | 0.0616 |
| Hogarth 18m | fall | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.3815 | 0.3905 | 0.0680 |
| Hogarth 18m | winter | 2000 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0820 | 0.3380 | 0.0725 |
| Hogarth 18m | spring | 2002 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0730 | 0.1410 | 0.0500 |
| Hogarth 18m | Summer | 2002 | 0.0185 | <MDL | 0.0055 | <MDL | <MDL | <MDL | <MDL | 0.0013 | 0.0458 | 0.3363 | 0.0595 |
| Hogarth 18m | Summer | 2003 | 0.0176 | <MDL | 0.0055 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0415 | 0.0309 | 0.0383 |
| Hogarth 18m | spring | 2004 | 0.0263 | <MDL | 0.0052 | <MDL | 0.0014 | <MDL | <MDL | <MDL | 0.0496 | 0.0683 | 0.0429 |
| Hogarth 18m | summer | 2004 | 0.0150 | <MDL | 0.0041 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0309 | 0.0542 | 0.0387 |
| Hogarth 18m | fall | 2004 | 0.0119 | <MDL | 0.0048 | <MDL | <MDL | 0.0221 | <MDL | <MDL | 0.0295 | 0.0447 | 0.0312 |
| Hogarth 18m | winter | 2005 | 0.0123 | <MDL | 0.0034 | <MDL | <MDL | 0.0226 | <MDL | <MDL | 0.0726 | 0.0390 | 0.0331 |
| Hogarth 18m | spring | 2005 | 0.0171 | <MDL | 0.0073 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0579 | 0.0642 | 0.0314 |
| Hogarth 18m | summer | 2005 | 0.0193 | 0.0127 | 0.0060 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0813 | 0.0400 |
| Hogarth 18m | winter | 2006 | 0.0190 | <MDL | 0.0050 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0210 | 0.0611 | 0.0350 |
| Hogarth 18m | spring | 2006 | 0.0120 | <MDL | 0.0065 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0300 | 0.0636 | 0.0370 |
| Hogarth 18m | summer | 2006 | 0.0100 | 0.0100 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0070 | 0.1077 | 0.0335 |
| Hogarth 30m | spring | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.2500 | 0.0395 | 0.0695 |
| Hogarth 30m | summer | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.2050 | 0.0658 | 0.0727 |
| Hogarth 30m | fall | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0860 | 0.0315 | 0.0630 |
| Hogarth 30m | winter | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.3520 | 0.1030 | 0.0630 |
| Hogarth 30m | spring | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.1685 | 0.1780 | 0.0588 |
| Hogarth 30m | summer | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.2468 | 0.1402 | 0.0595 |
| Hogarth 30m | fall | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.1985 | 0.0580 | 0.0675 |
| Hogarth 30m | winter | 2000 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.1060 | 0.0330 | 0.0650 |
| Hogarth 40m | spring | 2005 | 0.0414 | <MDL | 0.0068 | <MDL | 0.0014 | <MDL | <MDL | <MDL | 0.1127 | 0.2006 | 0.0418 |
| Hogarth 40m | summer | 2004 | 0.0141 | <MDL | 0.0053 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0607 | 0.0377 | 0.0395 |

| Location | Season | year | Al | As | Ba | Be | Cd | Co | Cr | Cu | Fe | Mn | Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hogarth 40m | fall | 2004 | 0.0102 | <MDL | 0.0039 | <MDL | <MDL | 0.0219 | <MDL | <MDL | 0.0212 | 0.0176 | 0.0305 |
| Hogarth 40m | winter | 2005 | 0.0086 | <MDL | 0.0046 | <MDL | <MDL | 0.0225 | <MDL | <MDL | 0.0265 | 0.0080 | 0.0327 |
| Hogarth 40m | spring | 2005 | 0.0360 | <MDL | 0.0042 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0811 | 0.2135 | 0.0329 |
| Hogarth 40m | summer | 2005 | 0.0190 | 0.0180 | 0.0070 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0124 | 0.0415 |
| Hogarth 40m | winter | 2006 | 0.0205 | <MDL | 0.0060 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0215 | 0.0114 | 0.0340 |
| Hogarth 40m | spring | 2006 | 0.0145 | <MDL | 0.0060 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.1025 | 0.1762 | 0.0370 |
| Hogarth 40m | summer | 2006 | <MDL | 0.0080 | 0.0060 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0041 | 0.0340 |
| Hogarth(x-1)m | spring | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 1.0295 | 0.1770 | 0.0750 |
| Hogarth(x-1)m | summer | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.5213 | 0.1308 | 0.0762 |
| Hogarth(x-1)m | fall | 1998 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.1020 | 0.0375 | 0.0650 |
| Hogarth(x-1)m | winter | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.4170 | 0.1130 | 0.0630 |
| Hogarth(x-1)m | spring | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.3525 | 0.2228 | 0.0623 |
| Hogarth(x-1)m | summer | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.4793 | 0.1633 | 0.0603 |
| Hogarth(x-1)m | fall | 1999 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.2435 | 0.0850 | 0.0670 |
| Hogarth(x-1)m | winter | 2000 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.1380 | 0.0390 | 0.0710 |
| Hogarth(x-1)m | spring | 2002 | 0.0120 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0010 | 0.0515 | 0.0660 | 0.0525 |
| Hogarth(x-1)m | summer | 2002 | 0.2388 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0080 | 1.4445 | 0.2893 | 0.0638 |
| Hogarth(x-1)m | summer | 2003 | 0.0390 | <MDL | 0.0051 | <MDL | <MDL | <MDL | 0.0110 | <MDL | 0.2147 | 0.0329 | 0.0400 |
| Hogarth(x-1)m | spring | 2004 | 0.0305 | <MDL | 0.0055 | <MDL | 0.0014 | <MDL | <MDL | <MDL | 0.1800 | 0.0720 | 0.0425 |
| Hogarth(x-1)m | summer | 2004 | 0.0147 | <MDL | 0.0056 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0205 | 0.0264 | 0.0417 |
| Hogarth(x-1)m | fall | 2004 | 0.0236 | <MDL | 0.0054 | <MDL | <MDL | 0.0224 | <MDL | <MDL | 0.1056 | 0.1098 | 0.0274 |
| Hogarth(x-1)m | winter | 2005 | 0.1935 | <MDL | 0.0054 | <MDL | <MDL | 0.0245 | 0.0045 | 0.0029 | 1.4086 | 0.1159 | 0.0357 |
| Hogarth(x-1)m | spring | 2005 | 0.0193 | <MDL | 0.0033 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0623 | 0.0599 | 0.0307 |
| Hogarth(x-1)m | summer | 2005 | 0.0365 | 0.0155 | 0.0075 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.1230 | 0.1002 | 0.0480 |
| Hogarth(x-1)m | winter | 2006 | 0.0180 | <MDL | 0.0060 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0630 | 0.0141 | 0.0310 |
| Hogarth(x-1)m | spring | 2006 | 0.0140 | <MDL | 0.0050 | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0400 | 0.0459 | 0.0330 |
| Hogarth(x-1)m | summer | 2006 | <MDL | <MDL | 0.0060 | <MDL | <MDL | <MDL | <MDL | <MDL | <MDL | 0.0288 | 0.0310 |

| Location | Season | year | Pb | S | V | Zn | SO4 | NH3 | pH | TDS | TOTN | TOTP | TSS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hogarth 1m | spring | 1998 | <MDL | <MDL | <MDL | 0.0240 | 1894.00 | <MDL | 8.05 | 2383.20 | 0.0685 | <MDL | 10.00 |
| Hogarth 1m | summer | 1998 | <MDL | <MDL | <MDL | 0.0113 | 1982.69 | <MDL | 7.67 | 2432.00 | 0.0723 | <MDL | 10.70 |
| Hogarth 1m | fall | 1998 | <MDL | <MDL | <MDL | 0.0135 | 1451.98 | <MDL | 7.24 | 2608.60 | 0.0500 | <MDL | 10.50 |
| Hogarth 1m | winter | 1999 | <MDL | <MDL | <MDL | 0.0130 | 1532.90 | <MDL | 6.53 | 2520.10 | 0.0320 | <MDL | 10.30 |

| Location | Season | year | Pb | S | V | Zn | SO4 | NH3 | pH | TDS | TOTN | TOTP | TSS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hogarth 1m | spring | 1999 | <MDL | <MDL | <MDL | 0.0103 | 1364.25 | <MDL | 7.30 | 2224.05 | 0.1070 | <MDL | 10.42 |
| Hogarth 1m | summer | 1999 | <MDL | <MDL | <MDL | 0.0106 | 1222.78 | <MDL | 7.47 | 2146.61 | 0.1219 | <MDL | 9.65 |
| Hogarth 1m | fall | 1999 | <MDL | <MDL | <MDL | 0.0100 | 1378.40 | <MDL | 7.32 | 2245.20 | 0.1110 | <MDL | 10.45 |
| Hogarth 1m | winter | 2000 | <MDL | <MDL | <MDL | 0.0240 | 1488.85 | <MDL | 6.78 | 2264.20 | 0.1250 | <MDL | 9.25 |
| Hogarth 1m | spring | 2002 | <MDL | 467.91 | <MDL | 0.0100 | 1435.31 | <MDL | 7.54 | 2317.60 | 0.1100 | <MDL | 6.80 |
| Hogarth 2m | summer | 2002 | <MDL | 463.76 | 0.5161 | 0.0055 | 1236.53 | <MDL | 7.21 | 1986.70 | 0.0190 | 0.0230 | 7.35 |
| Hogarth 2m | summer | 2003 | <MDL | 413.25 | <MDL | 0.0020 | 1276.85 | 0.0733 | 6.98 | 1946.85 | 0.0530 | 0.0330 | 5.20 |
| Hogarth 2m | spring | 2004 | <MDL | 466.54 | <MDL | 0.0043 | 1335.21 | <MDL | 7.78 | 2040.73 | 0.0610 | <MDL | <MDL |
| Hogarth 2m | summer | 2004 | <MDL | 460.67 | <MDL | 0.0033 | 1319.79 | <MDL | 7.96 | 2024.33 | 0.0320 | <MDL | <MDL |
| Hogarth 2m | fall | 2004 | 0.0749 | 433.20 | <MDL | <MDL | 1339.80 | <MDL | 7.77 | 2060.30 | 0.0810 | <MDL | <MDL |
| Hogarth 2m | winter | 2005 | 0.0885 | 452.12 | <MDL | 0.0015 | 1452.90 | <MDL | 7.72 | 2150.00 | 0.0340 | <MDL | <MDL |
| Hogarth 2m | spring | 2005 | <MDL | 400.91 | <MDL | 0.0017 | 1324.67 | 0.0525 | 7.61 | 1973.70 | 0.1995 | <MDL | 2.40 |
| Hogarth 2m | summer | 2005 | 0.0100 | 475.00 | <MDL | 0.0020 | 1445.29 | 0.0305 | 7.82 | 1963.40 | 0.0440 | 0.0070 | <MDL |
| Hogarth 2m | winter | 2006 | <MDL | 447.94 | <MDL | 0.0030 | 1465.97 | 0.0800 | 6.59 | 2104.20 | 0.1110 | <MDL | <MDL |
| Hogarth 2m | spring | 2006 | <MDL | 459.34 | <MDL | 0.0020 | 1258.59 | 0.0585 | 8.10 | 2031.20 | 0.0290 | 0.0625 | 9.10 |
| Hogarth 2m | summer | 2006 | <MDL | 467.56 | <MDL | <MDL | 1227.37 | 0.1780 | 8.10 | 1806.60 | <MDL | 0.0440 | 9.90 |
| Hogarth 18m | spring | 1998 | <MDL | <MDL | <MDL | 0.0230 | 1920.00 | <MDL | 7.42 | 2388.10 | 0.0605 | <MDL | 10.00 |
| Hogarth 18m | summer | 1998 | <MDL | <MDL | <MDL | 0.0107 | 1982.15 | <MDL | 6.68 | 2469.83 | 0.0567 | <MDL | 11.22 |
| Hogarth 18m | fall | 1998 | <MDL | <MDL | <MDL | 0.0110 | 1479.33 | <MDL | 6.62 | 2692.70 | 0.0600 | <MDL | 9.40 |
| Hogarth 18m | winter | 1999 | <MDL | <MDL | <MDL | 0.0110 | 1376.55 | <MDL | 6.55 | 2494.90 | 0.0240 | <MDL | 9.10 |
| Hogarth 18m | spring | 1999 | <MDL | <MDL | <MDL | 0.0115 | 1452.68 | <MDL | 6.70 | 2373.90 | 0.1283 | <MDL | 9.90 |
| Hogarth 18m | summer | 1999 | <MDL | <MDL | <MDL | 0.0109 | 1295.74 | <MDL | 6.88 | 2305.84 | 0.1546 | <MDL | 10.52 |
| Hogarth 18m | fall | 1999 | <MDL | <MDL | <MDL | 0.0100 | 1423.45 | <MDL | 7.30 | 2307.10 | 0.1090 | <MDL | 10.55 |
| Hogarth 18m | winter | 2000 | <MDL | <MDL | <MDL | 0.0245 | 1537.15 | <MDL | 6.74 | 2362.40 | 0.1300 | <MDL | 9.83 |
| Hogarth 18m | spring | 2002 | <MDL | 518.02 | <MDL | 0.0040 | 1397.52 | <MDL | 6.76 | 2125.60 | 0.0830 | 0.0100 | 4.90 |
| Hogarth 18m | Summer | 2002 | <MDL | 518.05 | 0.6199 | 0.0055 | 1359.15 | <MDL | 6.75 | 2199.15 | <MDL | <MDL | 7.30 |
| Hogarth 18m | Summer | 2003 | <MDL | 487.40 | <MDL | 0.0029 | 1390.91 | 0.0913 | 6.47 | 2316.80 | 0.2825 | 0.0570 | 76.00 |
| Hogarth 18m | spring | 2004 | <MDL | 515.24 | <MDL | 0.0040 | 1543.96 | <MDL | 6.97 | 2365.50 | 0.0465 | <MDL | <MDL |
| Hogarth 18m | summer | 2004 | <MDL | 502.73 | <MDL | 0.0059 | 1517.04 | <MDL | 6.88 | 2361.67 | 0.0230 | <MDL | 3.30 |
| Hogarth 18m | fall | 2004 | 0.0782 | 474.47 | <MDL | 0.0013 | 1488.77 | <MDL | 7.00 | 2260.67 | 0.0970 | <MDL | <MDL |
| Hogarth 18m | winter | 2005 | 0.0908 | 468.74 | <MDL | 0.0016 | 1542.23 | <MDL | 7.02 | 2289.13 | <MDL | <MDL | <MDL |
| Hogarth 18m | spring | 2005 | <MDL | 474.29 | <MDL | 0.0019 | 1605.37 | 0.0357 | 6.87 | 2358.60 | 0.1490 | <MDL | <MDL |

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| Location | Season | year | Pb | S | V | Zn | SO4 | NH3 | pH | TDS | TOTN | TOTP | TSS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hogarth 18m | summer | 2005 | 0.0140 | 113.11 | <MDL | 0.0030 | 1717.57 | <MDL | 6.79 | 2335.00 | 0.0400 | 0.0070 | <MDL |
| Hogarth 18m | winter | 2006 | <MDL | 480.61 | <MDL | 0.0030 | 1577.12 | 0.0620 | 6.45 | 2295.80 | 0.1020 | 0.0150 | <MDL |
| Hogarth 18m | spring | 2006 | <MDL | 553.33 | <MDL | 0.0030 | 1486.94 | 0.0470 | 7.04 | 2011.00 | <MDL | 0.0260 | <MDL |
| Hogarth 18m | summer | 2006 | <MDL | 516.89 | <MDL | <MDL | 1455.75 | 0.1565 | 7.04 | 2139.20 | <MDL | 0.0380 | <MDL |
| Hogarth 30m | spring | 1998 | <MDL | <MDL | <MDL | 0.0200 | 1914.00 | <MDL | 7.15 | 2397.90 | 0.0710 | <MDL | 9.00 |
| Hogarth 30m | summer | 1998 | <MDL | <MDL | <MDL | 0.0117 | 1991.63 | <MDL | 6.60 | 2420.40 | 0.0653 | <MDL | 11.48 |
| Location | Season | year | Pb | S | V | Zn | SO4 | NH3 | pH | TDS | TOTN | TOTP | TSS |
| Hogarth 30m | fall | 1998 | <MDL | <MDL | <MDL | 0.0120 | 1451.82 | <MDL | 6.56 | 2533.90 | 0.0400 | <MDL | 8.80 |
| Hogarth 30m | winter | 1999 | <MDL | <MDL | <MDL | 0.0100 | 1505.90 | <MDL | 6.56 | 2526.50 | 0.0270 | <MDL | 10.45 |
| Hogarth 30m | spring | 1999 | <MDL | <MDL | <MDL | 0.0100 | 1504.03 | <MDL | 6.69 | 2374.45 | 0.1950 | <MDL | 10.58 |
| Hogarth 30m | summer | 1999 | <MDL | <MDL | <MDL | 0.0100 | 1298.82 | <MDL | 6.88 | 2348.30 | 0.1245 | <MDL | 9.10 |
| Hogarth 30m | fall | 1999 | <MDL | <MDL | <MDL | 0.0100 | 1464.60 | <MDL | 6.79 | 2425.20 | 0.0885 | <MDL | 10.00 |
| Hogarth 30m | winter | 2000 | <MDL | <MDL | <MDL | 0.0165 | 1549.55 | <MDL | 6.58 | 2360.80 | 0.1050 | <MDL | 9.67 |
| Hogarth 40m | spring | 2005 | <MDL | 492.74 | <MDL | 0.0038 | 1435.93 | <MDL | 7.36 | 2199.40 | 0.0800 | <MDL | <MDL |
| Hogarth 40m | summer | 2004 | <MDL | 521.90 | <MDL | 0.0028 | 1517.20 | <MDL | 6.87 | 2380.60 | <MDL | <MDL | <MDL |
| Hogarth 40m | fall | 2004 | 0.0776 | 464.10 | <MDL | <MDL | 1491.50 | <MDL | 7.02 | 2280.70 | 0.0930 | <MDL | <MDL |
| Hogarth 40m | winter | 2005 | 0.0908 | 463.23 | <MDL | 0.0016 | 1552.85 | <MDL | 7.01 | 2350.90 | <MDL | <MDL | <MDL |
| Hogarth 40m | spring | 2005 | <MDL | 433.45 | <MDL | 0.0014 | 1382.90 | 0.0515 | 7.27 | 2169.60 | 0.1715 | <MDL | <MDL |
| Hogarth 40m | summer | 2005 | 0.0080 | 528.30 | <MDL | 0.0025 | 1710.97 | 0.0275 | 6.80 | 2205.30 | <MDL | 0.0095 | <MDL |
| Hogarth 40m | winter | 2006 | <MDL | 493.28 | <MDL | 0.0040 | 1582.77 | 0.0600 | 6.47 | 2314.20 | 0.1510 | 0.0135 | <MDL |
| Hogarth 40m | spring | 2006 | <MDL | 524.89 | <MDL | 0.0015 | 1455.61 | 0.0465 | 7.03 | 2353.20 | <MDL | 0.0915 | <MDL |
| Hogarth 40m | summer | 2006 | <MDL | 533.33 | <MDL | <MDL | 1496.07 | 0.1630 | 6.97 | 2225.40 | <MDL | 0.0320 | <MDL |
| Hogarth(x-1)m | spring | 1998 | <MDL | <MDL | <MDL | 0.0255 | 1920.00 | <MDL | 7.44 | 2442.70 | 0.0765 | <MDL | 10.50 |
| Hogarth(x-1)m | summer | 1998 | <MDL | <MDL | <MDL | 0.0137 | 1937.40 | <MDL | 6.62 | 2376.47 | 0.0728 | <MDL | 11.22 |
| Hogarth(x-1)m | fall | 1998 | <MDL | <MDL | <MDL | 0.0130 | 1462.10 | <MDL | 6.55 | 2529.30 | 0.0250 | <MDL | 9.15 |
| Hogarth(x-1)m | winter | 1999 | <MDL | <MDL | <MDL | 0.0105 | 1522.35 | <MDL | 6.53 | 2509.40 | 0.0290 | <MDL | 10.15 |
| Hogarth(x-1)m | spring | 1999 | <MDL | <MDL | <MDL | 0.0100 | 1497.78 | <MDL | 6.70 | 2426.90 | 0.1575 | <MDL | 10.55 |
| Hogarth(x-1)m | summer | 1999 | <MDL | <MDL | <MDL | 0.0106 | 1330.96 | <MDL | 6.99 | 2351.31 | 0.1207 | <MDL | 10.38 |
| Hogarth(x-1)m | fall | 1999 | <MDL | <MDL | <MDL | 0.0100 | 1464.60 | <MDL | 6.81 | 2410.20 | 0.0875 | <MDL | 11.42 |
| Hogarth(x-1)m | winter | 2000 | <MDL | <MDL | <MDL | 0.0215 | 1550.80 | <MDL | 6.58 | 2360.00 | 0.1400 | <MDL | 9.92 |
| Hogarth(x-1)m | spring | 2002 | <MDL | 541.50 | <MDL | 0.0030 | 1530.68 | <MDL | 6.81 | 2321.30 | 0.1260 | 0.0085 | 7.80 |
| Hogarth(x-1)m | summer | 2002 | <MDL | 524.55 | 0.6307 | 0.0068 | 1388.91 | <MDL | 6.81 | 2229.30 | 0.0640 | <MDL | 40.37 |
| Hogarth(x-1)m | summer | 2003 | <MDL | 483.66 | <MDL | 0.0035 | 1437.91 | 0.0545 | 6.46 | 2359.93 | 0.0360 | 0.0100 | 35.50 |

| Location | Season | year | Pb | S | V | Zn | SO4 | NH3 | pH | TDS | TOTN | TOTP | TSS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hogarth(x-1)m | spring | 2004 | <MDL | 522.04 | <MDL | 0.0040 | 1543.75 | <MDL | 6.96 | 2367.40 | 0.0575 | <MDL | <MDL |
| Hogarth(x-1)m | summer | 2004 | <MDL | 550.00 | <MDL | 0.0030 | 1531.76 | <MDL | 6.87 | 2374.80 | 0.0190 | <MDL | <MDL |
| Hogarth(x-1)m | fall | 2004 | 0.0773 | 458.00 | <MDL | 0.0010 | 1422.00 | <MDL | 7.37 | 2075.90 | 0.0850 | <MDL | 5.80 |
| Hogarth(x-1)m | winter | 2005 | 0.0929 | 456.34 | <MDL | 0.0029 | 1556.75 | <MDL | 7.04 | 2248.30 | <MDL | <MDL | <MDL |
| Hogarth(x-1)m | spring | 2005 | <MDL | 477.05 | <MDL | 0.0017 | 1589.13 | 0.0400 | 7.04 | 2372.20 | 0.1345 | <MDL | 2.00 |
| Hogarth(x-1)m | summer | 2005 | 0.0090 | 521.65 | <MDL | 0.0020 | 1714.04 | 0.0430 | 6.84 | 2382.80 | <MDL | 0.0060 | 34.30 |
| Hogarth(x-1)m | winter | 2006 | <MDL | 484.50 | <MDL | 0.0020 | 1559.26 | 0.0490 | 6.48 | 2346.60 | <MDL | 0.0180 | <MDL |
| Hogarth(x-1)m | spring | 2006 | <MDL | 531.56 | <MDL | <MDL | 1502.80 | 0.0460 | 7.02 | 2394.40 | <MDL | 0.0500 | <MDL |
| Hogarth(x-1)m | summer | 2006 | <MDL | 542.67 | <MDL | <MDL | 1476.74 | 0.2000 | 7.00 | 2316.20 | <MDL | 0.0760 | <MDL |