The Effectiveness of Self-Restoration for Two Small Mine Impacted Shield Lakes

by

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Abstract

Two lakes in the Whitesand Watershed, Cleaver and Horneblende, were impacted by mining and milling activities that occurred at the headwaters for over a decade. These lakes, both exhibiting varying degrees of meromixis, were examined for their water quality and potential for natural restoration for brook trout habitat. Detailed sampling took place from October 1999 to March 2001.

With the termination of discharge from the mine in the fall of 1999, the lakes were able to experience relaxation of input from the mine. Cleaver Lake had a well established monimolimnion at 6m, which dropped to 7m during fall turnover in 2000, although no discernable trend in water quality could be detected. An experiment was conducted with Cleaver lake sediments to determine the effect of sediment aeration. No release of zinc, copper, iron, or manganese was detected in aerated sediment samples. Horneblende Lake had a much weaker chemocline that eroded continually throughout the study period. There were more significant reductions in metals, sulphate, calcium, and conductivity, reflecting the eroding stratification. With the improvement of meromixis and stability of zinc levels, brook trout sustainability in Cleaver Lake appears possible.

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GENERAL INTRODUCTION

With increasing degradation of our natural resources and environment, there is an ever-increasing need for protection, maintenance and rehabilitation of our natural ecosystems. Lakes are examples of natural systems that are often put under pressure by human activities. Many recreational and industrial activities can contribute to lake degradation. These activities usually add nutrients that can lead to eutrophication, or toxic chemicals that can harm aquatic organisms. Industrial activities, such as mining, may add trace metals and other by-products of mining processes into aquatic systems.

Over the past century, industrial activities have led to an increase in trace metal mobilization. This mobilization can occur directly through activities such as mining or smelting, or indirectly through increased weathering due to acid rain. This increased release of trace metals amplifies fluxes into the aquatic environment. Since these habitats are constantly changing, it is imperative to understand the interactions of trace metals with their associated aquatic environments.

Factors Affecting Metal Availability

Vertical and Horizontal Mixing

Most historic research on trace element distribution and movement has been done in oceans. Compared to lakes, they are considered more open for vertical transport of trace elements. Vertical water movement occurs when the water column has a uniform temperature (typically 4°C in temperate lakes) or salinity. This movement can be reduced or eliminated through changes in density if salinity or temperature gradients are established. Lakes that have a permanent layer that inhibits whole water column mixing are termed meromictic, with a monimolimnion, located in the deep water that is incapable of mixing with the upper mixolimnion, which periodically circulates. A stratum termed the chemolimnion separates the mixolimnion and monimolimnion, which is called the chemocline (Wetzel, 2001). Biological, chemical, and anthropogenic factors can influence salinity concentrations thereby inducing a meromictic condition, termed meromixis. Ectogenic meromixis occurs when an external event beings in saltwater into a freshwater lake, or conversely, freshwater into a saline lake. The result of either interaction is less dense, less saline water that overlays a layer of more dense saline water. This has been observed in both Mono Lake, California and the Dead Sea where both experienced events of high runoff periods that inputted high levels of freshwater that formed a mixolimnion on the surface of both water bodies. Meromictic conditions persisted on both until evaporation eventually concentrated the saline levels in the mixolimnion to levels near the monimolimnion, reducing the density between the layers, allowing wind action to induce a mixing event (Steinhorn, 1985; Jellison & Melack, 1993).

In many lake systems, horizontal transport must be included due to the significant role that the sediment plays and the vastly higher sediment:water ratio compared to oceans. Since horizontal water movement is approximately 100 times faster than vertical movement in stratified lakes, the interaction with lateral sediments is increased (Davison & Tipping, 1984).

Redox Effects

Redox cycling is one of the largest influences on the availability of metals in natural waters. Elements themselves can undergo redox transformations directly [e.g. Cu(II) – Cu(I)] or can be involved indirectly where they are affected by redox cycling, but in themselves are not transformed (e.g. Zn) (Hamilton-Taylor & Davison, 1995). One factor in influencing redox cycling is photosynthesis, which produces reduced states of high free energy resulting in non-equilibrium concentrations of C, N, and S compounds (Stumm, 1966). Respiration, fermentation, and other non-photosynthetic reactions restore equilibrium by decomposing the products of photosynthesis (Wetzel, 2001). Organic matter decay proceeds through a series of redox reactions in which oxidants (including Fe(III) and Mn(IV)) are consumed in order of theoretical decreasing free energy yield. This reaction sequence is subject to the availability of particular oxidants and kinetic constraints, including the dominance of particular microbial populations. These processes may affect metals in a variety of different ways. They may be adsorbed or assimilated by various planktonic organisms in surface waters and released back into deeper waters upon decay, possibly in a different redox state (Sigg, 1985; Sigg *et al*, 1987). Metals may also be mobilized through the reductive dissolution of oxides or the oxidation of sulphides (Hamilton-Taylor & Davison, 1995).

pH Effects

Another important factor controlling trace metal availability in lakes is pH. pH may vary temporally and vertically by more than three pH units in productive, poorly buffered lakes, due to the effects of photosynthesis and respiration (Talling, 1976). Thus, the sorption of elements by Fe and Mn oxides may vary substantially due to such pH changes. Mobilization of heavy metals will occur in low pH conditions. Cadmium and zinc are strongly released compared to copper and lead with a pH decrease from 7 to 3.4. Under controlled pH values, more metals are released in oxidized sediment below a pH of 4.5 (Calmano *et al*, 1992).

With respect to zinc, Tessier *et al* (1989) showed that in oxic water, most mobile zinc will be found in the water column at pH < 5 and in the surficial sediments at pH 7. Hydrous ferrous oxides strongly sorb zinc over calcium or cadmium, with increased sorption from pH 5 to 7. Phosphate can be concurrently sorbed at a different site on the iron oxide (Kuo, 1986). Hydrous manganese oxides can also be effective scavengers of zinc at higher pH levels (Zasoski & Burau, 1988).

Iron and Manganese Cycling

The behaviour of Iron (Fe) and manganese (Mn) in lakes has been very well studied (Davison *et al*, 1982; Balistrieri *et al*, 1992) and comprehensively reviewed (Davison, 1993). Mortimer (1941) first studied iron cycling of Esthwaite Waters in England in 1939, and came up with a simple seasonal model: He found that in well-oxygenated water, the higher forms of Fe and Mn [Fe(III) and Mn(III/IV)] are favoured, and are present as colloids or particles. When anoxic conditions predominated, lower redox states [Fe(II) and Mn(II)] are favoured. Iron cycling throughout the year was dependent on the redox condition of the lake, which was seasonally anoxic. During the winter months when oxygen was present throughout the water column, iron oxide reduction only occurred in the sediment column. When reduced iron reached the sediment water interface, it was immediately oxidized. This resulted in no iron build-up in the water column during the winter months. Once the lake became stratified in the summer and biological processes began consuming oxygen in the hypolimnion, anoxia resulted. Reduction of iron oxide continued in the sediments and diffused through the anoxic water until it reached the oxic/anoxic boundary where iron formed a peak in particulate matter. Below this point, the reducing water increased in Fe(II) concentration over time. With a mixing event (i.e. fall turnover) oxygen was replenished to the entire water column, re-oxidizing and precipitating Fe(II).

Mortimer (1941) assumed that a lake acted like a cylinder with sediments on the bottom, which mimics marine conditions, and failed to take into account horizontal transport of iron, which has been shown to be as important as, if not more important than vertical transport (Davison, 1981; Davison & Tipping, 1984). In the hypolimnion of seasonally anoxic lakes, the majority of iron is supplied from the sediments while manganese is supplied via the settling and dissolution of particles in the water column (Davison, 1981). Sediment release of Fe and Mn in anoxic conditions is typically due to the dissolution of oxides and hydroxides (Sakata, 1985). This biogeochemical cycling of iron and manganese has been well established in seasonally anoxic lakes (Hamilton-Taylor *et al*, 1996).

Iron, and to a lesser extent manganese, play an important role in the geochemical cycling of other elements. Coupled with redox conditions, they can give clues as to whether or not they have the potential to transport other elements. Iron is capable of noticeably influencing the concentration of humic substances, which can increase in the anoxic waters of a seasonally stratified lake due to release from dissolving Fe oxides (Davison, 1993). Because humic substances are well known for their metal complexing ability, the mobility of other metals may be increased. Under oxic conditions, Fe and Mn oxides, along with organic matter, are considered among the most important scavengers for trace elements in aquatic environments (Förstner, 1982; Sigg, 1985). The amounts of many metals that are bound through coprecipitation with Fe oxide are greater than through adsorption alone (Laxen, 1984).

Zinc and Copper Cycling

Zinc cycling in the water column is not strongly related to iron and manganese cycling. Balistrieri *et al.* (1992) showed a strong correlation between Zn and reactive Si, which indicates a relationship with seasonal diatom growth and die-off. Positive correlations were found between dissolved Zn and phosphate, silicate, and a negative correlation with chlorophyll a during a spring diatom bloom (Reynolds & Hamilton-Taylor, 1992). In anoxic conditions, ZnS species are dominant. Tessier *et al* (1989) have proposed that many lakes studied in Ontario and Quebec are undersaturated with respect to many solid phases of zinc, some by many orders of magnitude.

Copper is usually scavenged or adsorbed to suspended matter and has been shown to have a strong correlation with suspended matter. Although colloidal iron can make up a large portion of suspended solids in the water column, colloids may not be a large contributor for copper suspension (Sigg, 1994). In anoxic conditions, iron can incorporate copper into iron sulphide precipitates, although copper sulphides are more common (Hamilton-Taylor *et al*, 1996). Balistrieri *et al.* (1992) noted supersaturation with respect to $Cu_2S(s)$ in sediments of a seasonally anoxic lake.

Both Cu and Zn have shown a high affinity to dissolved organic carbon (DOC) (Cabaniss & Shuman, 1988; Shafer *et al*, 1999). Shafer *et al* (1999) showed strong correlations between Cu and DOC, and that filterable zinc levels showed a significant relationship to DOC.

Two small mine-impacted meromictic lakes, Cleaver and Horneblende, located on the Precambrian Shield in Northwestern Ontario were studied. Both lakes are in the Whitesand River watershed which until the fall of 1999 was the location of a zinc-copper mine and mill site. Both lakes exhibited varying degrees of meromixis, and were monitored after the closure of the mine and mill, and cessation of mine effluent entering the Whitesand River. Brook trout (*Salvelinus fontinalis*) were once thought to occupy the lake, but have not been found in surveys since 1992 (Laine, 1994). This study will focus on the improvement of meromixis in Cleaver and Horneblende Lakes for fish habitat, and observe potential zinc toxicity in these water bodies.

1.0 INTRODUCTION

Mine and milling wastes produced through ore processing can have lasting environmental impacts (Förstner & Wittmann, 1981; Arnesen *et al*, 1997). Research over the last few decades has shown that by treating tailings disposal sites by depositing them under water in lakes or ponds minimizes metal release into the environment when compared to traditional methods of disposal (MEND, 1995; Arnesen *et al*, 1997). Subaqueous disposal of mine tailings suppresses the production of acid generation as exposure to oxygen and bacterial degradation is minimized. Sulphide-rich wastes may also be stored underwater without significant release of metals into the overlying waters (MEND, 1989). This method is relatively new with few long-term studies, but Benson Lake (British Columbia), which received tailings for a copper mine between 1962-73, showed a remarkable recovery in less than 20 years with little evidence that it was a recipient of mine waste. All metal concentrations in fish from the lake fell within the range of values recorded from fish tissues and livers from unpolluted Canadian waters (MEND 1991, 1992).

During mining activities, sulphates and sulphides rich mine wastes can leach into aquatic systems. As well, calcium from treatment of waters to reduce acid production may also enter receiving water bodies. These compounds will increase salinity of the water, and have the potential to cause density gradients in receiving water bodies. If these density gradients are strong enough to persist through turnover periods, meromixis can develop. Oxygen depletion will occur in the monimolimnion, creating an anoxic environment. Sulphate reduction by anaerobic genera such as *Desulfovibrio* and *Desulfotomaculum* will form hydrogen sulphide, which will consume any oxygen entering the monimolimnion, perpetuating anoxia (Wetzel, 2001). Hydrogen sulphide even at low concentrations is acutely toxic to aquatic organisms. Acute toxicity to rainbow trout occurs at 0.20 mg/L and 0.0087 mg/L for sensitive macroinvertebrates (Dunnette *et al*, 1985).

Zinc toxicity to aquatic organisms is well documented (EPA, 1987; Erten-Unal, 1998; Muyssen, 2002). Variation in toxic levels depends on many factors such as water hardness, temperature, pH, or the presence of other elements (Irwin *et al*, 1997). In insects, Mayfly (*Epeorus latifolium*) larvae experienced 100% mortality with exposure to levels greater than 0.1mg/L. Mosquito (*Aedes aegypti*) pupae suffered an increased mortality in levels of 0.5mg/L. Midge (*Chironomus tentans*) larvae experienced detrimental effects at zinc levels of 8.2mg/L. Gastropods have been found to experience growth and reproductive inhibitions at levels >0.18mg/L, and increased mortality at levels >0.5mg/L (USDI, 1998). Rainbow trout (*Oncorhynchus mykiss*) experience low mortality rates (10%) at levels >0.14mg/L, and will reach LC50 concentrations at2.6-3.5mg/L (Finlayson & Aschuckian, 1979; Irwin *et al*, 1997). Many studies have found zinc tolerance and acclimation in a wide variety of organisms (Admiraal *et al*, 1999; Muyssen *et al*, 2002).

The cessation of mining operations at a zinc/copper mine located in Northwestern Ontario, Canada, provided an opportunity to examine the effects of mining operations. The effects of meromictic conditions developing during mining and milling efforts are detrimental, but may not be permanent. For lake systems, natural restoration may be a preferred rehabilitation strategy when mine related inputs are eliminated. Active rehabilitation strategies for meromictic lakes such as hypolimnetic withdrawl or hypolimnetic aeration may not be desirable as potentially toxic water in the monimolimnion has built up and a sudden release may be detrimental to the water body.

The objective of this study was to observe the effectiveness of self-restoration from meromictic conditions in Cleaver and Horneblende Lakes following the termination of discharge into the Whitesand River.

1.1 METHODOLOGY

1.1.1 Study Site

The study site was located at the Inmet Winston Lake mine, approximately 200 km east of Thunder Bay near Schreiber, Ontario (Figure 1.1). The mine and milling sites were formerly located around the headwaters of the Whitesand River. The area was sporadically mined for zinc over the last century until the development of the Winston Lake mine commenced in 1986, complete with the construction of a mill, catchment pond, tailings dam, sedimentation pond and polishing pond. This mine was the first to process ore on-site starting in 1988 with tailings waste deposited in the tailings pond for the life of the mine, which operated until 1998. The effluent discharge from the tailings pond flowed into the Whitesand River until October of 1999 (SENES, 2001). During periods of discharge since October 1999, the tailings have been treated with lime and pumped into the underground mine workings to assist in the flooding of the mine and to eliminate the large volume of high total dissolved solids (TDS) water from entering the Whitesand River.

Cleaver Lake is a small lake at the head of the Whitesand River system and is the receiving water body for the mine effluent (Figure 1.1). It has an area of approximately 12ha, volume of about 573 000m^3 with a mean depth of 4.9m, a maximum depth of 19m and a water residence time of 0.09 years (Inmet & SENES, 1999). Meromictic conditions were first observed in Cleaver Lake in 1991. The lake has remained permanently stratified to varying degrees since this time mainly due to the high TDS loadings to the system from the mining operations. Horneblende Lake, with a similar morphometry and size to Cleaver Lake, is located 6 km downstream from Cleaver Lake

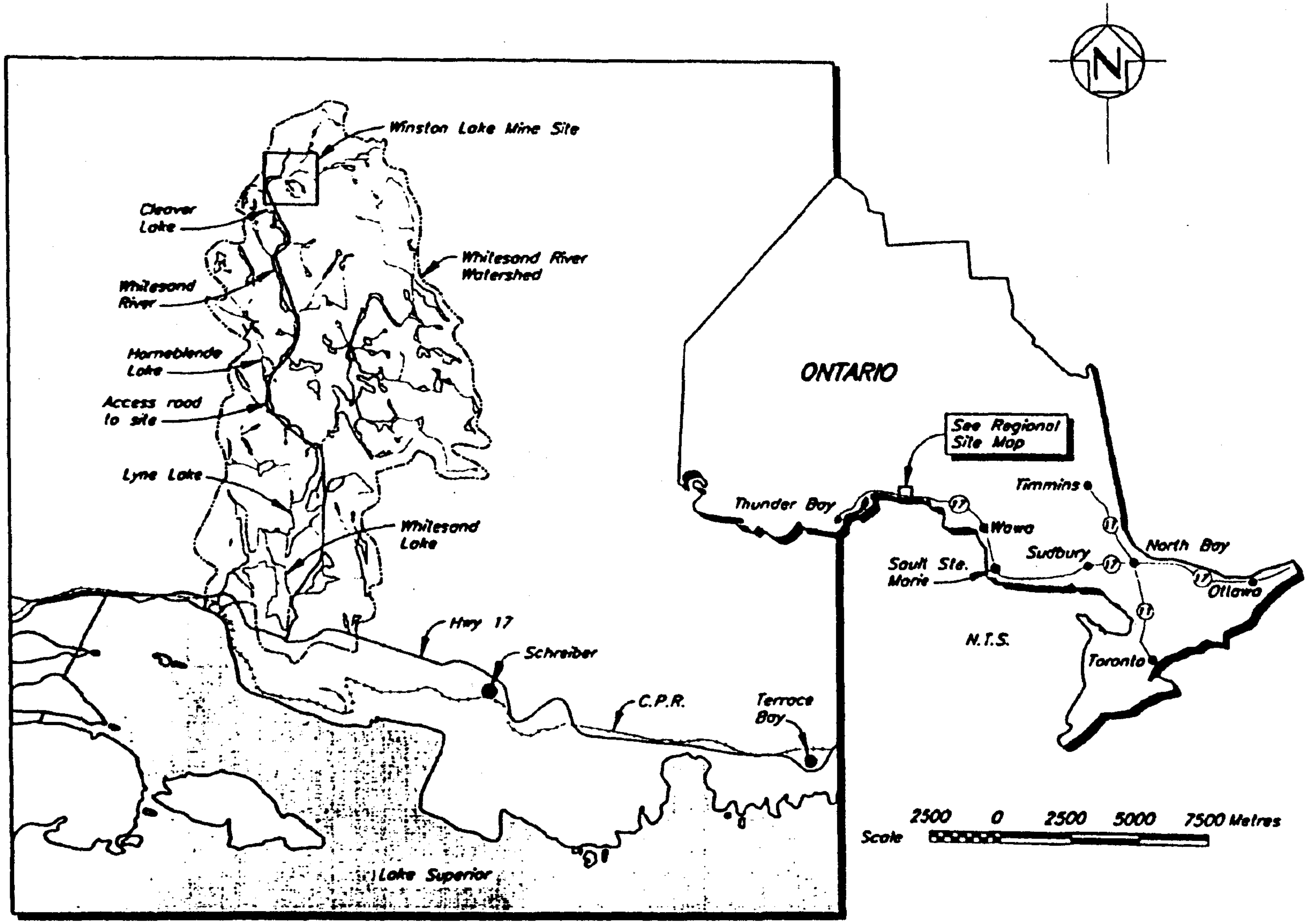


Figure 1.1: Location of Cleaver Lake, Horneblende Lake, and the Winston Mine site.

with a chemocline that has varied over the last decade. Prior to 1998, the chemocline was consistently below 10 metres. Between 1998 and 2000 however, the chemocline has varied between 4 and 16 metres. Such drastic variances in a short time period may be correlated to flow levels of the watershed or historically high TDS water flowing from Cleaver Lake (SENES, 2001). River sites included the inflow and outflow of Cleaver and Horneblende Lakes. Lake samples were taken at the deepest points of Cleaver and Horneblende Lakes.

1.1.2 Field Procedures

Location and Frequency of Sampling

Water samples were taken at the deepest points of Cleaver (19m) and Horneblende (18m) Lakes, and at the inflow and outflow of both lakes. The lakes were sampled at monthly intervals From October 1999 to March 2001, except during October and November 1999, when Cleaver was sampled weekly until ice cover, to observe any change during the anticipated turnover period. Cleaver was again sampled on a weekly basis in May of 2000, during the expected spring turnover time. Cleaver inflow and outflow were sampled weekly from October 1999 until November 2000 to meet regulatory sampling, after which, they were sampled monthly. The inflow and outflow of Horneblende Lake were sampled monthly.

Sampling Technique

For the inflow and outflow sites, three water samples were taken. One 1.0L polyethylene bottle was filled, and two 250mL bottles were filled; one preserved with nitric acid (HNO_3) for metals, and the other with sulphuric acid (H_2SO_4) for nutrients. The temperature and dissolved oxygen was also taken at these points using a YSI-51B probe. The lake samples were taken at the deepest area of the respective lakes, where anchored buoys were already in place. Using a Kemmerer Bottle, water samples were taken at two metres below the surface (2m), at an eight-metre depth (mid), which approximated the thermocline/chemocline location, and 16m (deep). Bottles were filled and preserved as per the roadside samples. Dissolved oxygen, conductivity and temperature profiles were also taken at one metre intervals from the surface to the bottom for both lakes for each sampling date using YSI-51B (dissolved oxygen, temperature) and YSI 33 SCT (conductivity) probes. Samples were kept cool during transport, and stored at 4° once at Lakehead University. Travel and field blanks were carried in the cooler with the rest of the sample bottles, and duplicate samples were taken for every tenth sample for quality control protocols.

Hydrogen Sulphide (H_2S) Profiling

On March 31, 2000 and August 9, 2000, detailed hydrogen sulphide profiles were made of Cleaver Lake and Horneblende Lake (August 9, 2000 only). Samples were collected at 1m intervals on the lakes from the centre of the deepest basin, and preserved immediately upon collection with 2N zinc acetate. Once filled, the bottles were loosely capped and then gently squeezed until sample started overflowing at which point they were tightly capped to ensure no air remained in the bottle. The samples were kept cool during transport and stored at 4°C until analysis. Analysis was based on the EPA Method 376.1 NS (titrimetric, iodine) (EPA, 1988) using a Cary SE UV-Vis-NIR Varian Spectrophotometer.

1.1.3 Laboratory Procedures

All laboratory procedures were conducted at the Lakehead University Environmental Laboratory (LUEL), located on the Lakehead University campus. The parameters examined are listed in Table 1.1.

Table 1.1: Parameters examined in Cleaver and Horneblende Lakes and detection limit.

Parameter	Detection Limit
Alkalinity	1mg/L
Conductivity	0.2 µS/cm
Dissolved Inorganic Carbon	0.2 mg/L
Dissolved Organic Carbon	0.5 mg/L
Dissolved Oxygen	0.05 mg/L
Calcium	0.01 mg/L
Sulphate	0.05 mg/L
Aluminum	0.025 mg/L
Cadmium	0.004 mg/L
Chromium	0.005 mg/L
Copper	0.005 mg/L
Iron	0.005 mg/L
Manganese	0.001 mg/L
Nickel	0.005 mg/L
Lead	0.01 mg/L
Zinc	0.005 mg/L
Ammonia	0.025 mg/L
pH	N/A
Temperature	°C
Total Suspended Solids	5 mg/L
Total Nitrogen	0.015 mg/L
Total Phosphorous	0.005 mg/L
Hydrogen Sulphide	0.2 mg/L

Lab Quality Assurance and Quality Control Procedures

All laboratory procedures adhered to strict Quality Assurance / Quality Control (QA/QC) protocols. For every parameter, a blank was run first followed by a certified reference (QC) sample. The succeeding field sample was one of the field duplicates, one of which was split to assess any potential variation in in-lab sample handling. After this, every tenth sample was a field duplicate and again split with another QC sample run with it. Each test followed LUEL Standard Operating Procedures (LUEL, 1999, 2000, 2001) which were modified from Standard Methods for the Examination of Water and Wastewater 18th Edition (Greenberg *et al*, 1992).

The lake samples were examined for all parameters with the exception of H_2S, which was only done twice over the course of sampling (see below). Cleaver outflow and Horneblende inflow and outflow were examined for all parameters except chlorophyll, DIC, DOC, and H_2S. Cleaver inflow was analysed for MISA parameters (Conductivity, Dissolved Oxygen, Calcium, Sulphate, Copper, Nickel, Lead, Zinc, Ammonia, pH, Temperature, and Total Suspended Solids).

Alkalinity, pH and conductivity were measured within 24 hours of sampling once the samples had reached ambient room temperature. A 50mL aliquot sample was used for pH and alkalinity determination using an automated Mettler DL20 Compact Titrator. Conductivity was measured with a VWR digital conductivity meter with automated temperature compensation, which was calibrated at either 200 or 2000 μS/cm, depending on the level of the sample.

Dissolved organic and inorganic carbon (DOC and DIC) were measured by converting carbonate and bicarbonate into carbon dioxide. DOC was measured by introducing the sample into the SKALAR spectrophotometric analyzer where it was purged with acid and flushed with nitrogen gas to remove inorganic carbon. The sample was then oxidized with a UV digester in an acid-persulphate medium. Again, the carbon was converted to CO_2 and following dialysis, was measured by determining the loss in absorbance of a weakly buffered alkaline solution containing phenolphthalein indicator. Acidifying the sample and passing it over a carbon dioxide permeable membrane measured DOC. The CO_2 gas passed through the membrane and was absorbed in a weakly buffered alkaline solution containing phenolphthalein indicator. The Skalar San^{PLUS} System detected the decrease.

Aliquots of sample for anions (SO_4) and cations (Ca, NH_4) were filtered through 0.45μm membrane glass fibre filters prior to analysis. Concentrations were determined using a Dionex DX-120 ion chromatograph in conjunction with an AS40 automated sampler.

Metals determination was performed after microwave aided nitric acid digest at 85-95°C using LUEL protocols that followed a modified EPA method (EPA, 1992; LUEL, 2000). The samples were then analysed using a Jarrell Ash Inductively Coupled Argon Plasma 9000 Spectrophotometer (ICP).

Total suspended solids were gravimetrically determined and reported as weight/volume of sample. Suspended solids refer to all material removed by filtration through a 0.45μm glass fibre filter and then dried at 103°C.

Total phosphorous and total Kjeldahl nitrogen (TKN) samples were first digested stepwise to 400°C with sulphuric acid to achieve a three-fold preconcentration. The samples were then restored to their original volume. Total phosphorous concentrations were determined via the ascorbic acid procedure where all forms of phosphorous are converted to orthophosphate and determined colorimetrically at 880nm (Greenberg *et al*, 1992). TKN concentrations, determined simultaneously with total phosphorous, were determined spectrophotometrically at 660nm based on a modified Berthelot reaction (Greenberg *et al*, 1992).

Metals Profiling

On March 26 2001, detailed metals profiles were taken of Cleaver and Horneblende Lakes. Samples were taken at one-metre intervals and preserved with nitric acid in the field. Upon return to the laboratory, the samples were examined for all metals indicated in Table 1.1.

Toxicity Testing

On December 3, 2000, 100L of water was collected from Cleaver Lake (13m depth) for toxicity testing following the procedure outlined in Environmental Protection Services (1996). The Lakehead University Aquatic toxicology Research Centre (ATRC) conducted toxicity LD50 on *Daphnia magna* and rainbow trout (*Oncorhynchus mykiss*) (Environment Canada, 1990, 2000 a,b,c), as well as chronic fathead minnow (*Pimephales promelas*) and *Ceriodaphnia dubia* testing (Environment Canada, 1992, 1997).

1.1.4 Data Analysis

A multivariate statistical program (SPSS) was used for data analysis. Water quality parameters were summarized using means and standard deviations. A Friedman Test was performed between ice cover seasons (Nov 1999-Mar 2000 vs. Nov 2000-Mar 2001) to detect changes in parameters between the two years. A hierarchal cluster analysis with a Pearson correlation matrix was used on the December data to group the variables in 1999 and 2000 together to provide groupings for Cleaver and Horneblende Lakes.

1.2 RESULTS

1.2.1 Cleaver Lake

1.2.1.1 Meromixis

The mean and standard deviation for the water chemistry parameters for Cleaver Lake with the exception of hydrogen sulphide separated by inflow, outflow, and depths (shallow, mid, and deep) are found in Table 1.2. Cleaver Lake profiles exhibited a sharp chemocline with abrupt changes in conductivity, dissolved oxygen and temperature that remained consistent at a depth of 6m, until October 2000 when fall turnover lowered the chemocline to 7m (Figure 1.2). Most water quality parameters indicated meromictic conditions with elevated levels of alkalinity, Ca, SO_4, Cr, Fe, Mn, NH_4, TKN, TP, DIC, and TSS below the chemocline. Al, Zn, Cu, and DOC decreased with depth. Many of the heavy metals (As, Cd, Ni, Pb) were very low in concentration, or only detected sporadically, throughout the water column, and, along with pH, varied very little with depth.

An apparent flushing event occurred in February 2000 that destabilized the top layer of the monimolimnion. As an early spring melt event, the inflowing water was warmer (1.25°C) and had higher conductivity levels than the 2m depth of Cleaver Lake, causing it to be denser and sink upon entering the lake. This caused a seiche-like response in the basin, as the ice cover prevented water levels from rising, forcing the water down and allowing the water entering the lake to flow towards the chemocline and build up. This caused a temporary destabilization of the chemocline, resulting in a mixing event at a depth of 6m, which cumulated as a lowering of the monimolimnion in October 2000.

Table 1.2: Means, Minimums, Maximums, and Standard Deviations of Cleaver Inflow (n=62) Cleaver 2m (n=26), Cleaver Mid (n=26), Cleaver Deep (n=26) and Cleaver Outflow (n=62). n = number of samples. Grey areas indicate analytes not tested for various locations. DL = Detection Limit; <DL represents no values over detection limits. All values in mg/L except for alkalinity (mEq/L), conductivity (µs/cm), temperature (°C) and pH.

		Cleaver Inflow				**Cleaver 2m**				**Cleaver Mid**				**Cleaver Deep**				**Cleaver Outflow**			
Parameter	DL	**Mean**	Min	Max	Std Dev	**Mean**	Min	Max	Std Dev	**Mean**	Min	Max	Std Dev	**Mean**	Min	Max	Std Dev	**Mean**	Min	Max	Std Dev
Alkalinity	1					**10**	5	19	4	**48**	29	124	18	**54**	12	65	10	**10**	4	24	5
Cond.	0.2	**132.0**	21.8	426.0	103.7	**175.0**	35.2	368.0	100.0	**1528.9**	1271.0	1711.0	103.6	**1618.6**	1325.0	1760.0	89.7	**128.9**	34.5	359.0	84.3
DIC	0.2					**1.7**	0.5	3.7	0.9	**10.6**	8.1	13.7	1.7	**13.3**	10.3	17.9	2.1				
Diss. O2	0.05	**11.3**	0.0	14.9	2.8	**11.1**	8.8	13.4	1.3	**0.5**	0.0	1.8	0.3	**0.4**	0.0	0.9	0.2	**10.6**	2.1	14.5	2.3
DOC	0.5					**12.0**	8.9	16.5	2.1	**8.6**	7.3	10.4	0.8	**9.6**	8.5	11.5	0.8				
Ca	0.01	**16.5**	2.3	55.4	13.2	**23.3**	4.0	51.1	14.4	**276.4**	30.2	312.8	53.4	**299.3**	31.7	359.4	63.3	**16.8**	4.2	49.7	12.1
SO4	0.05	**31.7**	3.9	113.7	27.5	**54.1**	8.1	130.2	35.8	**793.9**	667.4	926.5	61.4	**857.8**	446.6	1341.0	133.2	**36.6**	6.9	134.7	31.6
Al	0.025					**0.28**	0.15	0.40	0.08	**0.16**	0.11	0.20	0.02	**0.16**	0.12	0.21	0.02	**0.30**	0.15	0.44	0.08
Cd	0.004					**<DL**				**<DL**				**<DL**				**<DL**			
Cr	0.005					**<DL**				**0.014**	<DL	0.017	0.003	**0.019**	0.007	0.022	0.003	**<DL**			
Cu	0.005	**0.007**	<DL	0.025	0.005	**0.008**	<DL	0.018	0.003	**0.005**	<DL	0.008	0.002	**0.005**	<DL	0.007	0.001	**0.007**	<DL	0.017	0.003
Fe	0.005					**0.39**	0.26	0.52	0.07	**3.50**	0.46	5.04	1.06	**4.67**	1.01	5.59	0.96	**0.42**	0.23	0.60	0.09
Mn	0.001					**0.05**	0.03	0.09	0.02	**0.47**	0.24	0.53	0.05	**0.42**	0.32	0.49	0.04	**0.05**	0.02	0.09	0.02
Ni	0.005	**0.01**	0.01	0.02	0.00	**0.01**	0.01	0.01	0.00	**0.01**	0.01	0.01	0.00	**0.01**	0.01	0.02	0.00	**0.01**	0.01	0.02	0.00
Pb	0.01	**0.01**	<DL	0.01	0.00	**<DL**				**<DL**				**0.01**	0.01	0.01	-	**0.01**	<DL	0.02	0.01
Zn	0.005	**0.93**	0.04	5.76	0.90	**0.62**	0.22	1.46	0.27	**0.23**	0.16	0.44	0.06	**0.15**	0.11	0.22	0.04	**0.72**	0.22	1.86	0.34
NH4	0.025	**0.131**	0.025	0.326	0.069	**0.203**	0.025	0.375	0.115	**4.666**	0.443	7.15	1.403	**5.725**	0.489	10.383	1.950	**0.161**	0.027	0.89	0.129
pH	n/a	**6.5**	6.0	7.3	0.3	**6.3**	6.1	6.7	0.2	**6.3**	6.2	6.5	0.1	**6.4**	6.3	6.6	0.1	**6.3**	6.1	6.7	0.2
Temp	Celclus	**4.7**	0.0	16.0	5.6	**7.0**	0.0	20.7	5.8	**3.8**	3.0	4.7	0.5	**3.5**	3.0	3.9	0.2	**5.7**	0.0	19.6	6.5
TKN	0.015					**0.61**	0.35	0.91	0.17	**4.12**	1.02	7.29	1.34	**4.84**	1.82	7.73	1.32	**0.56**	0.13	0.97	0.17
Total P	0.005					**0.016**	0.009	0.026	0.006	**0.062**	0.008	0.236	0.053	**0.090**	0.014	0.414	0.092	**0.021**	0.005	0.156	0.025
TSS	5	<DL				<DL				**7.7**	5.4	12.8	1.9	**8.0**	5.0	13.9	3.0	<DL			

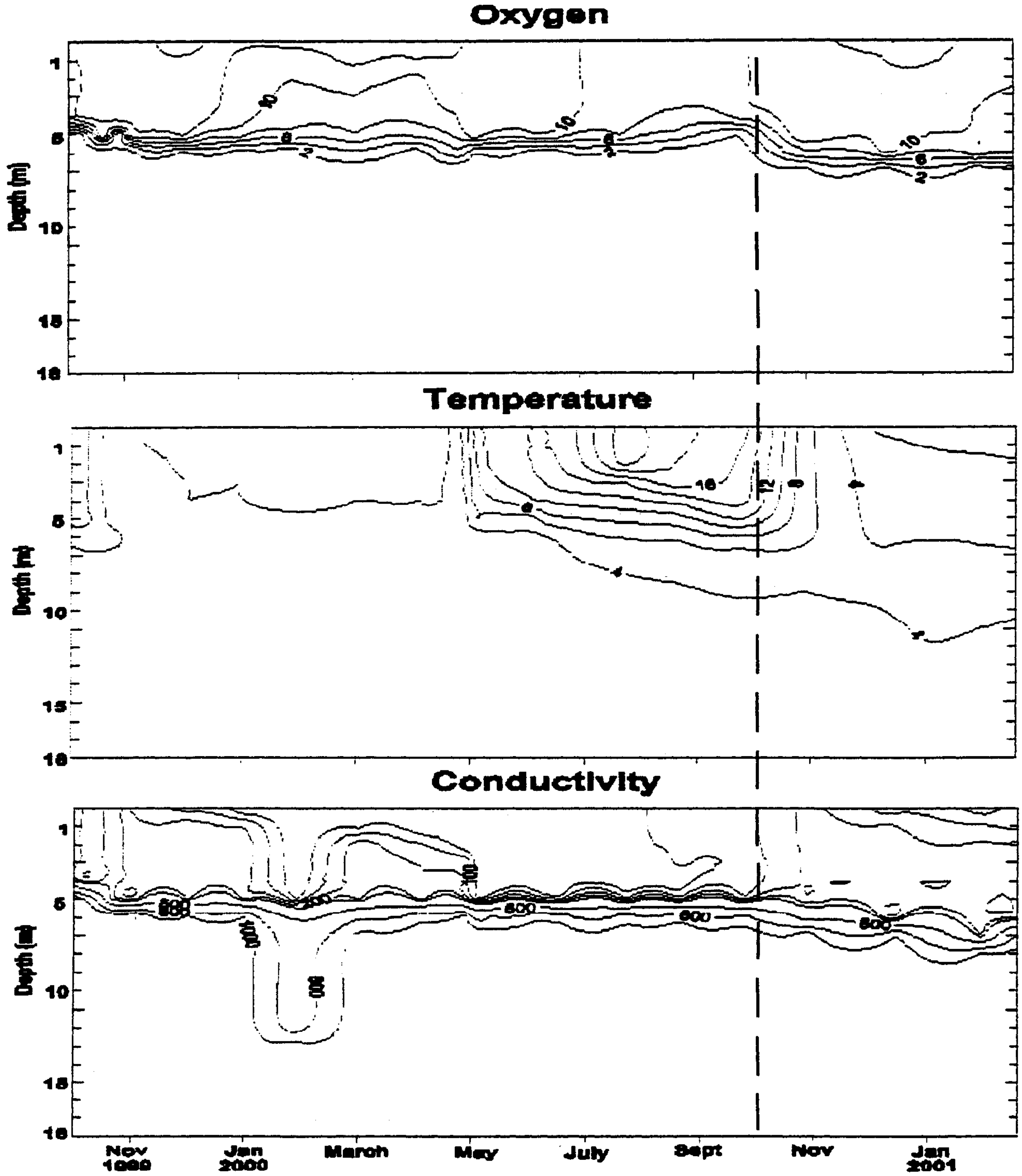


Figure 1.2: Dissolved oxygen, temperature, and conductivity isopleths of Cleaver Lake. The dashed line represents the turnover of October 2000, which resulted in the lowering of the monimolimnion by one metre.

1.2.1.2 Profiles

The two hydrogen sulphide profiles reached detectable levels below the chemocline, and maximum concentrations near the bottom of the lake, reaching maximum concentrations of 6mg/L on March 31, 2000 and 2.5mg/L on August 9, 2000 (Figure 1.3).

The metal profile of March 26, 2001 (Figure 1.4) showed elevated levels of iron and manganese below the chemocline. Zinc levels dropped below the chemocline and copper levels dropped below detection limits below the chemocline. Chromium levels became detectable below the chemocline, but remained constant between 0.014 and 0.021 mg/L. Aluminum and Ni levels fluctuated with respect to depth, but did not show any discernable gradient. Lead, As and Cd were not detected with any regularity.

96 hour acute toxicity testing resulted in 100% survival of rainbow trout and *Daphnia magna* acute testing. Seven day chronic testing yielded a 100% survival rate for both fathead minnow and *Ceriodaphnia dubia*.

1.2.1.3 Variation Between Years

The Friedman Test (Table 1.3) revealed significant increases between the two years at the 2m depth for alkalinity, Ca, Fe, and Mn; significant decreases in conductivity, Al, and TKN. SO_4 significantly increased while Fe and temperature decreased in the mid depth. Alkalinity, Ca, Mn, and temperature all showed significant increase in the deep waters between the two ice-cover seasons. In the 2000 ice-cover months, Cu was only sporadically detected in the mid and deep depths, which could be interpreted as a significant decline, but statistical testing was not done due to the missing data points. The Pearson correlation hierarchical cluster analysis grouped the analytes into two very similar clusters in both years (Figure 1.5). For both years, the first cluster containing most of the variables represents analytes that were elevated in the hypolimnion. The correlations were stronger in 1999 than in 2000. The second cluster, which was comprised of dissolved oxygen, DOC, Al, Zn, Cu, and pH in 1999 remained the same with the loss of pH to the first cluster in 2000.

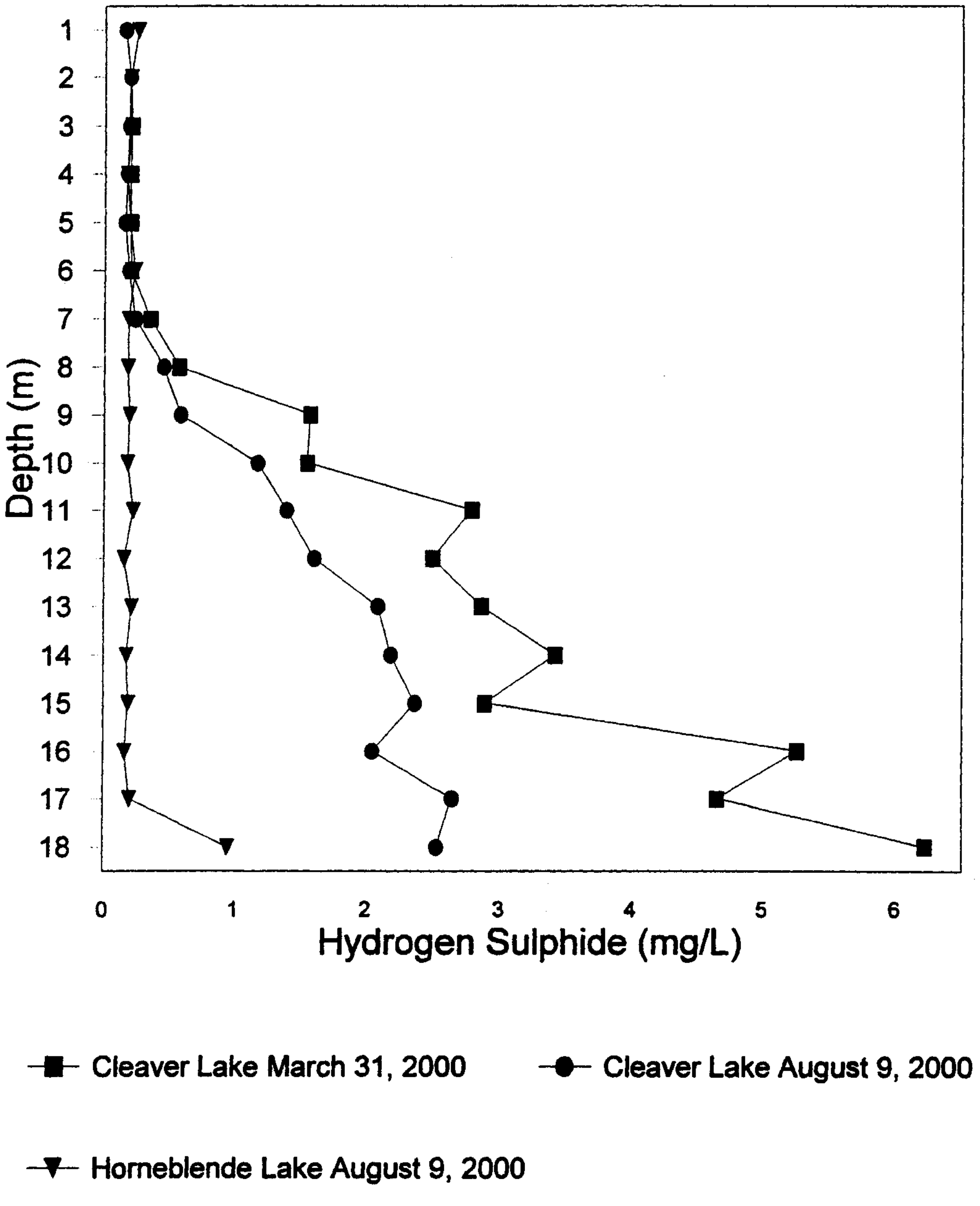
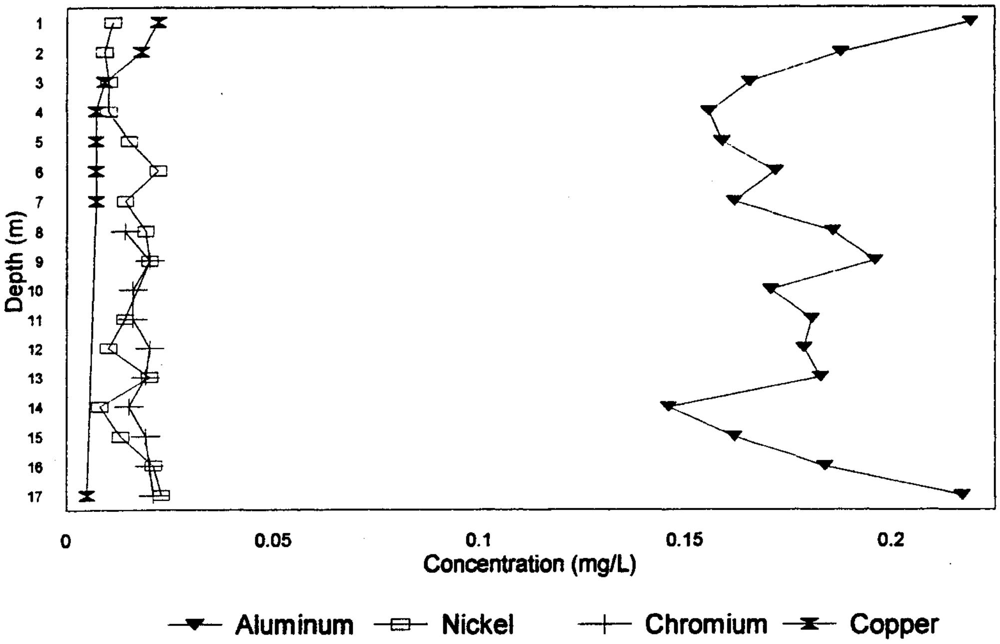


Figure 1.3: Hydrogen sulphide profiles of Cleaver Lake (March 31 and August 9, 2000) and Horneblende Lake (August 9, 2000). Method detection limit was 0.2 mg/L.



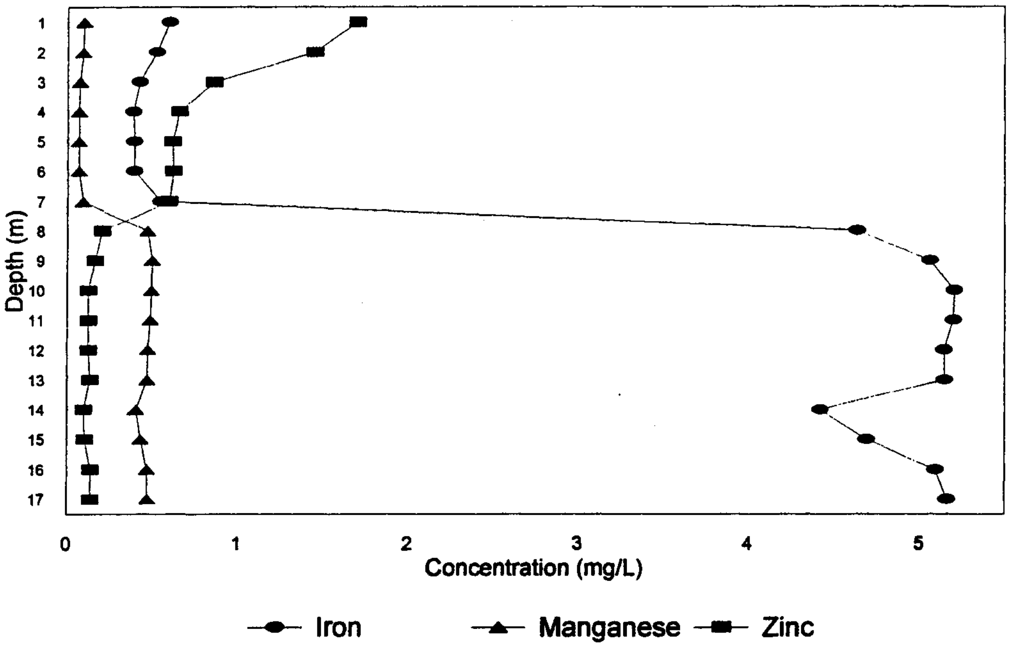


Figure 1.4 Metal profiles from Cleaver Lake, March 26, 2001

Table 1.3: Means and significant Friedman results of Cleaver Lake ice-cover data (Nov-Mar of 1999-2000 and 2000-2001). <DL = majority of values below detection limits for both years and not tested.

	Cleaver 2m			**Cleaver Mid**			**Cleaver Deep**		
	Means			Means			Means		
	1999-00	2000-01	Friedman	1999-00	2000-01	Friedman	1999-00	2000-01	Friedman
Alkalinity	8.5	17.5	p<0.05	41.7	68.5		46.1	61.8	p<0.05
Conductivity	204.4	247.2	p<0.05	1509	1531		1595	1691.6	
D.O.	11.6	10.7		0.4	0.3		0.3	0.1	
Ca	26.2	35.2	p<0.05	234.1	296.1		225.3	335.7	p<0.05
Sulphate	66.1	73.6		807.5	729.3	p<0.05	783.5	826.0	
Al	0.354	0.163	p<0.05	0.160	0.171		0.169	0.1584	
Cu	0.008	0.010			<DL			<DL	
Fe	0.422	0.465	p<0.05	3.413	4.629	p<0.05	5.055	3.636	
Mn	0.058	0.078	p<0.05	0.482	0.483		0.395	0.47	p<0.05
Zn	0.757	0.889		0.237	0.203		0.180	0.118	
Ammonia	0.277	0.301		3.470	5.367		4.318	7.789	
pH	6.4	6.2		6.4	6.3		6.5	6.4	
Temperature	1.3	2.4		3.3	4.4	p<0.05	3.4	3.8	
TKN	0.749	0.588	p<0.05	3.264	4.489		3.647	5.581	
Total P	0.017	0.015		0.074	0.075		0.133	0.098	
DIC	1.2	3.1	p<0.05	10.1	12.1		12.9	15.4	
DOC	14.6	10.6	p<0.05	8.9	9.0		9.9	9.8	

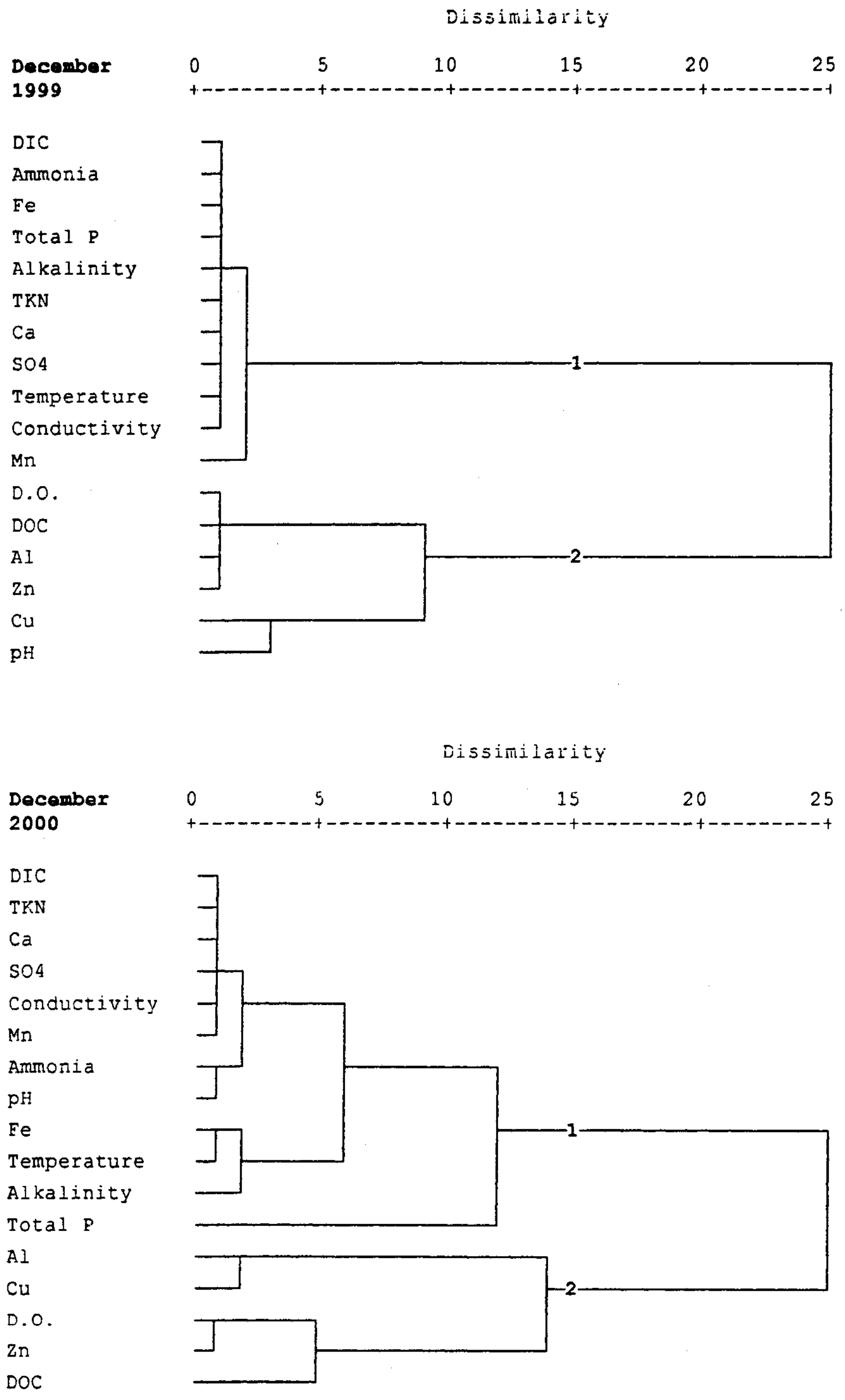


Figure 1.5: Hierarchical cluster analysis using the Pearson correlation average linkage between groups for water quality parameters measured in December 1999 and 2000 in Cleaver Lake.

1.2.2 Horneblende Lake

1.2.2.1 Meromixis

The mean and standard deviation for the water chemistry parameters for Horneblende Lake with the exception of hydrogen sulphide separated by inflow, outflow, and depths (2m, mid, and deep) can be found in Table 1.4. Conductivity, temperature, and dissolved oxygen isopleths are shown in Figure 1.6. Horneblende Lake showed a much weaker and deeper chemocline compared to Cleaver lake. Increased alkalinity, DIC, Ca, SO4, Al, Fe, Mn, Zn, NH4, TKN, TP, and TSS were found in the hypolimnion. DOC, Al, As, Cd, Cr, Cu, Ni, Pb, and pH levels remained fairly constant through the water column.

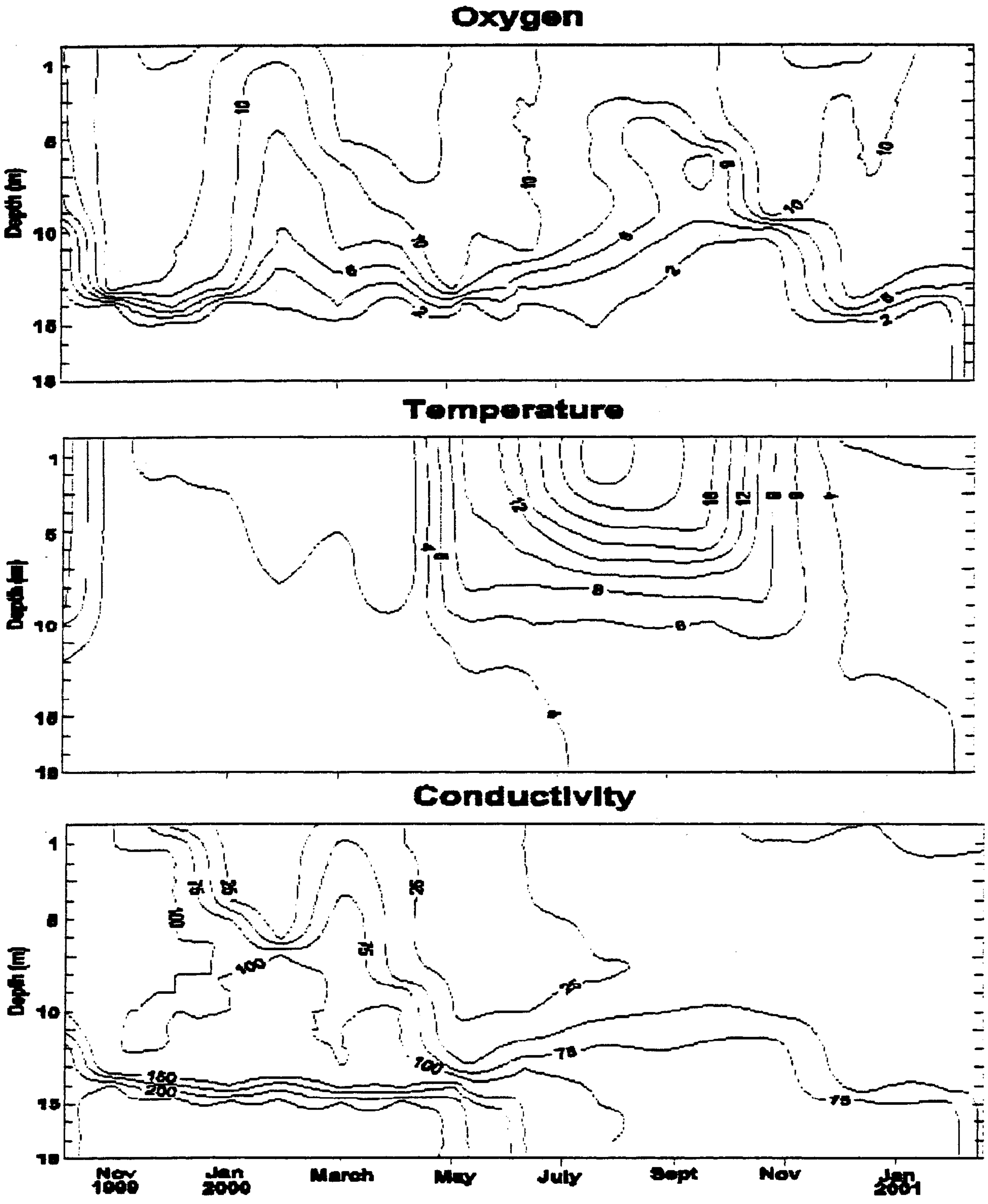
1.2.2.2 Profiles

The hydrogen sulphide profile of August 9, 2001 (Figure 1.3) showed no detectable levels of hydrogen sulphide until 18m, which was due to the Kemmerer sampler hitting the bottom and stirring the sediments, possibly releasing hydrogen sulphide that was in sediment pore water, or adding turbidity interference in the colorimetric test.

The metals survey of March 26, 2001 (Figure 1.7) reflected the weaker chemocline of Horneblende Lake. Iron, manganese and aluminum levels increased at the 16th meter, while nickel remained fairly constant throughout the water column. Zinc was very low on the surface, reaching a level just over 0.1mg/L at 3m and remained at that level for the entire column.

Table 1.4: Means, Minimums, Maximums, and Standard Deviations of Horneblende Inflow (n=18) Horneblende 2m (n=21), Horneblende Mid (n=21), Horneblende Deep (n=21) and Horneblende Outflow (n=18). n represents sample frequency over the course of the study. Grey areas indicate analates not tested for various locations. <DL represents no values over detection limits. All vlaues in mg/L except for alkalinity (mEq/L), conductivity (μs/cm), temperature (°C) and pH.

	Horneblende Inflow				Horneblende 2m				Horneblende Mid				Horneblende Deep				Horneblende Outflow			
Parameter	**Mean**	Min	Max	Std Dev	**Mean**	Min	Max	Std Dev	**Mean**	Min	Max	Std Dev	**Mean**	Min	Max	Std Dev	**Mean**	Min	Max	Std Dev
Alkalinity	**12.788**	5.1	24.3	5.299	**9.219**	4.7	21.4	3.542	**9.238**	4.6	26.4	4.769	**18.186**	8	24.6	3.788	**9.288**	4.9	13.2	2.586
Cond.	**86.935**	26	169.8	47.116	**60.371**	25.2	129	34.856	**75.33**	25.7	279	60.508	**200.09**	72	342	85.865	**66.969**	26.8	134.3	33.751
DIC					**1.568**	0.72	2.36	0.521	**1.508**	0.43	2.62	0.647	**4.181**	0.28	6.72	1.575				
Diss. O2	**11.207**	7	14.1	2.037	**10.889**	8.5	13.8	1.439	**9.317**	2.4	12.9	2.722	**0.706**	0.2	1.9	0.479	**11.136**	8.2	13.5	1.882
DOC					**9.469**	7.64	11.5	1.204	**9.558**	7.93	12.41	1.310	**10.849**	8.02	11.86	0.939				
Ca	**11.446**	3	24.13	6.149	**7.958**	2.8	17.47	4.572	**10.235**	2.75	38.07	8.216	**26.272**	9.28	46.16	11.717	**8.811**	3.5	16.12	4.125
SO4	**19.466**	4.67	49.5	15.064	**13.348**	4.2	37.6	11.762	**19.401**	4.75	97.45	22.535	**57.650**	10.9	119.78	33.676	**14.791**	4.21	37.73	11.360
Al	**0.231**	0.103	0.3724	0.079	**0.221**	0.108	0.3378	0.070	**0.240**	0.113	0.3401	0.075	**0.284**	0.116	0.3394	0.043	**0.233**	0.115	0.3433	0.076
As	**0.027**	0.0274	0.0274	0.000	**0.016**	0.0155	0.0155	-	**0.015**	0.0152	0.0152	0.000	**0.017**	0.0155	0.0183	0.001	**0.009**	0.0094	0.0094	-
Cd	**0.002**	0.0016	0.0016	-	**0.002**	0.0013	0.002	0.000	**0.002**	0.0022	0.0022	-	**0.001**	0.0007	0.0023	0.001	**0.001**	0.0007	0.001	0.000
Cr	**0.002**	0.0013	0.002	0.000	**0.001**	0.0005	0.0018	0.000	**0.001**	0.0009	0.0025	0.001	**0.001**	0.001	0.0016	0.000	**0.001**	0.0005	0.0012	0.000
Cu	**0.003**	0.0016	0.0057	0.001	**0.005**	0.0026	0.0083	0.001	**0.005**	0.0038	0.0083	0.001	**0.006**	0.004	0.012	0.002	**0.002**	0.0012	0.0028	0.001
Fe	**0.304**	0.145	0.897	0.157	**0.213**	0.112	0.2937	0.056	**0.233**	0.1376	0.429	0.066	**1.914**	0.262	4.2127	1.162	**0.237**	0.141	0.3058	0.049
Mn	**0.025**	0.01	0.042	0.008	**0.021**	0.0088	0.06	0.013	**0.039**	0.0109	0.235	0.049	**0.341**	0.024	0.798	0.187	**0.025**	0.0114	0.056	0.011
Ni	**0.013**	0.008	0.02	0.005	**0.009**	0.005	0.014	0.003	**0.008**	0.006	0.0125	0.002	**0.011**	0.006	0.0292	0.007	**0.007**	0.005	0.012	0.003
Pb	**0.014**	0.0086	0.0185	0.005		<DL			**0.010**	0.01	0.01	-	**0.013**	0.0122	0.0128	0.000	**0.008**	0.0082	0.0086	0.000
Zn	**0.186**	0.039	0.5019	0.127	**0.114**	0.056	0.3162	0.065	**0.120**	0.061	0.3202	0.061	**0.182**	0.086	0.3344	0.073	**0.124**	0.062	0.2683	0.063
NH4	**0.130**	0.027	0.272	0.077	**0.083**	0.029	0.172	0.044	**0.078**	0.025	0.161	0.044	**0.228**	0.04	0.586	0.134	**0.096**	0.026	0.172	0.052
pH	**6.407**	6.12	6.87	0.186	**6.280**	6.02	6.75	0.203	**6.154**	5.89	6.47	0.145	**6.145**	6	6.41	0.100	**6.319**	6.1	6.66	0.189
Temp	**6.220**	0	20	6.997	**8.122**	0	20.9	6.616	**5.622**	0.5	9	2.713	**3.761**	3	4.8	0.572	**6.929**	0	20.5	7.272
TKN	**0.529**	0.33	0.819	0.125	**0.394**	0.203	0.573	0.091	**0.395**	0.247	0.589	0.100	**0.619**	0.207	1.029	0.202	**0.426**	0.267	0.602	0.096
Total P	**0.044**	0.006	0.358	0.088	**0.017**	0.007	0.028	0.006	**0.018**	0.005	0.109	0.023	**0.033**	0.007	0.147	0.034	**0.014**	0.006	0.039	0.009
TSS		<DL				<DL				<DL			**8.150**	5.1	12.3	2.155	**5.900**	5.9	5.9	-

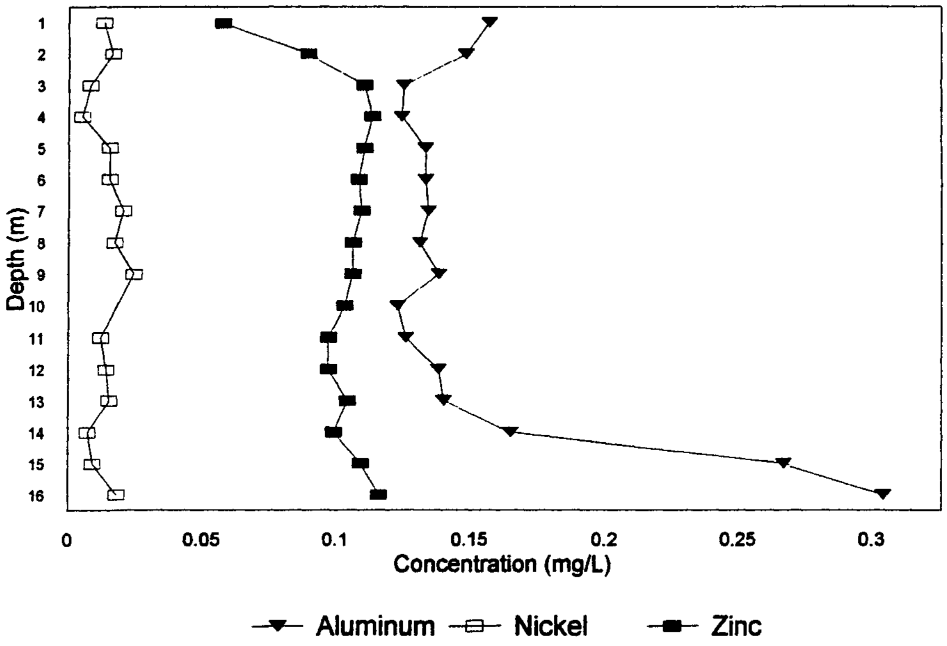


Oxygen

Temperature

Conductivity

Figure 1.6: Dissolved oxygen, temperature and conductivity isopleths of Horneblende Lake.



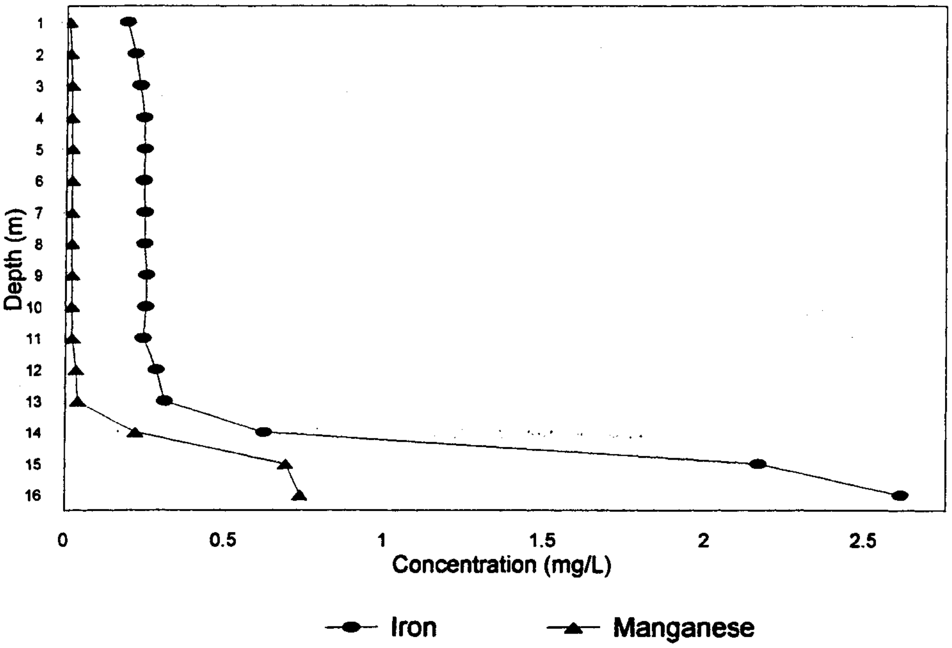


Figure 1.7 Metal profiles from Horneblende Lake, March 26, 2001

Arsenic, cadmium, chromium, copper and lead were not detected with any regularity through the water column.

1.2.2.3 Variation Between Years

The Friedman Test (Table 1.5) revealed significant increases at the 2m depth for alkalinity and temperature, and significant declines of Ca, Zn, conductivity, SO_4, TKN, and Al. In the mid depth there were significant increases in alkalinity, temperature and Fe with significant declines of Ca, Zn, conductivity, SO_4, TKN, and Al. The deep water experienced significant increases in alkalinity and temperature with significant declines in Ca, Zn, conductivity, SO_4, and NH_4. As with copper in Cleaver Lake, detection in 2000 was mostly below detection and not included in the analysis. Ammonia levels in Horneblende 2m and mid were similarly excluded from analysis due to levels all being below detection. These observations may also be interpreted as a decline over the two years of study. Total P in Horneblende 2m was sporadically detected over the ice-cover period for both years and excluded from the analysis. The Pearson hierarchical cluster analysis discriminated between three clusters in 1999 which became two in 2000 (Figure 1.8). The first cluster contained the majority of the parameters which were associated with elevated levels in the hypolimnion of the lake. The second cluster in 1999 contained DOC, Cu, and Al, and was absorbed by the first cluster in 2000. The third cluster of 1999 and the second cluster of 2000 both contained pH and dissolved oxygen.

Table 1.5: Means and significant Friedman results of Horneblende Lake ice-cover data (Nov-Mar of 1999-2000 and 2000-2001). <DL = majority of values below detection limits for both years; <DL in 2000-01 = majority of values below detection in 2000-2001, and not tested.

	Horneblende 2m			**Horneblende Mid**			**Horneblende Deep**		
	Means			Means			Means		
	1999-00	2000-01	Friedman	1999-00	2000-01	Friedman	1999-00	2000-01	Friedman
Alkalinity	8.6	13.8	p<0.05	7.6	15.2	p<0.05	15.2	21.6	p<0.05
Conductivity	105.84	57.18	p<0.05	131.22	64.52	p<0.05	290.6	117.1	p<0.05
D.O.	11.8	9.9		10.4	8.5		0.6	0.2	
Ca	13.6	8.1	p<0.05	16.8	9.1	p<0.05	37.8	16.0	p<0.05
Sulphate	29.2	9.3	p<0.05	40.3	10.8	p<0.05	94.9	24.7	p<0.05
Al	0.295	0.128	p<0.05	0.303	0.122	p<0.05	0.303	0.255	
Cu		<DL		<DL in 2000-01			<DL in 2000-01		
Fe	0.268	0.234		0.239	0.271	p<0.05	1.329	2.268	
Mn	0.025	0.019		0.030	0.028		0.285	0.516	
Zn	0.215	0.068	p<0.05	0.177	0.079	p<0.05	0.267	0.115	p<0.05
Ammonia		<DL		<DL in 2000-01			0.145	0.246	p<0.05
pH	6.5	6.1		6.4	6.1		6.2	6.1	
Temperature	1.4	2.8	p<0.05	2.8	3.7	p<0.05	3.3	4.3	p<0.05
TKN	0.512	0.335	p<0.05	0.507	0.353	p<0.05	0.719	0.571	
Total P		<DL		0.031	0.011		0.076	0.020	
DIC	1.9	2.1		1.7	2.3		4.4	4.1	
DOC	11.1	8.2	p<0.05	11.6	8.3	p<0.05	11.5	10.0	p<0.05

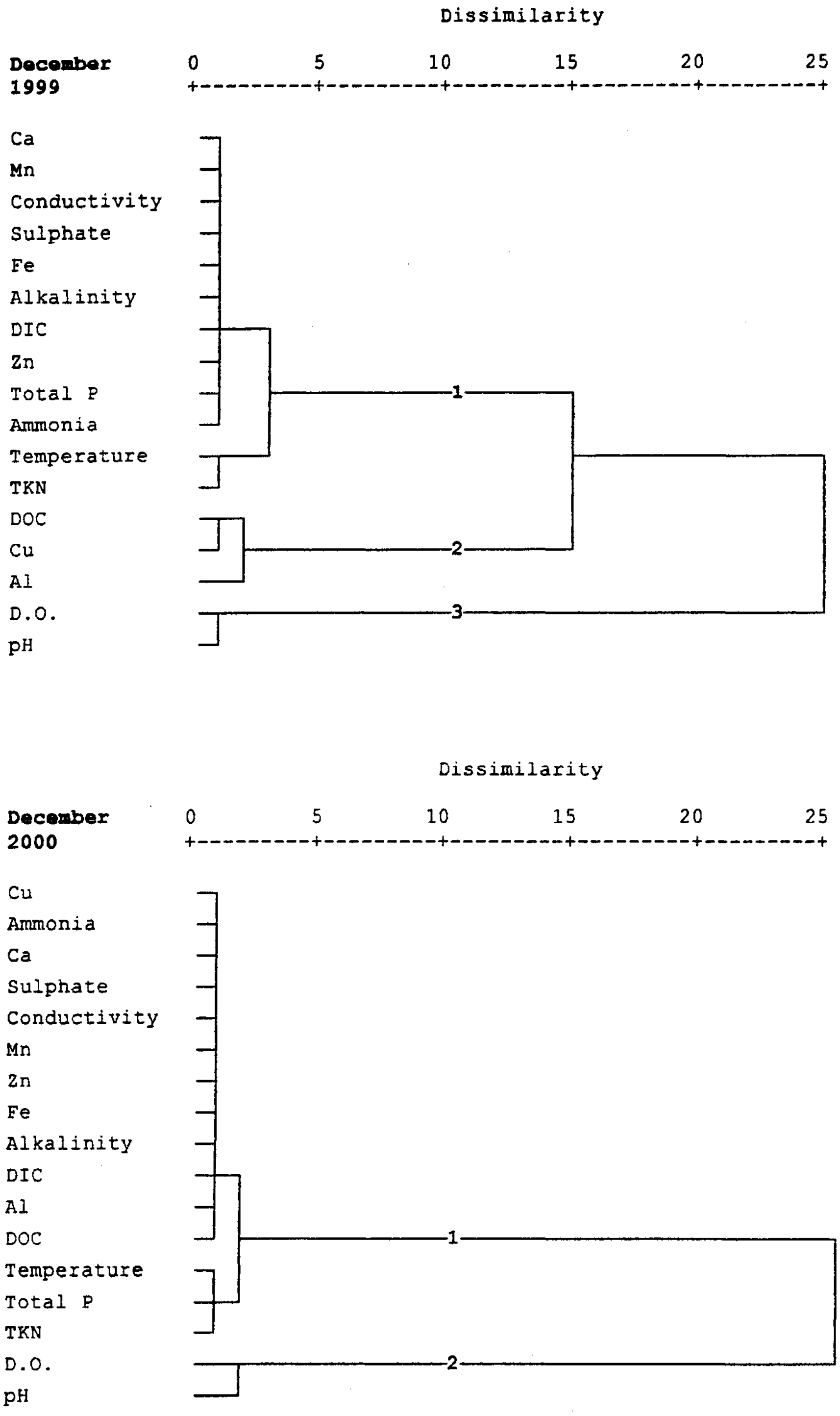


Figure 1.8: Hierarchical cluster analysis using the Pearson correlation average linkage between groups for water quality parameters measured in December 1999 and 2000 in Horneblende Lake.

Data from the Cleaver and Horneblende isopleths can be found in Appendix A, plots of Cleaver Lake analytes can be found in Appendix B, and plots of Horneblende Lake analytes can be found in Appendix C.

1.3 DISCUSSION

Along with general size and morphometry, Cleaver and Horneblende Lakes showed many similar characteristics that made them ideal to compare different stages of meromixis. Nutrient levels were very similar with total phosphorous concentrations in the epilimnion of both Cleaver and Horneblende being at the meso-eutrophic production level (16μg/L and 17μg/L, respectively) and nitrogen levels falling into the oligo-mesotrophic level of productivity (Wetzel, 2001). In Cleaver Lake, meromixis has resulted in high levels of nutrients in the hypolimnion. Similar conditions are exhibited in oceans and in Lake Baikal where hypolimnetic renewal time is almost a decade (Weiss *et al*, 1991). The pH levels in both lakes remained relatively similar to each other and throughout the water column. They were stable through the course of the study, varying between 6.0 and 6.7 spatially and temporally. The inflow of Cleaver Lake had a higher pH, which was due to the addition of lime in the treatment of tailings water upstream. A stable pH throughout the water column of Cleaver Lake during the recovery process is a good indication that no pH-driven releases of zinc through desorption from ligands or organic particles in the oxic sediments will occur (Tessier *et al*, 1989). Metals release from Horneblende Lake is not as great a concern since it is farther downstream and has lower concentrations of metals. Low alkalinity levels in the surface waters (10 mEq/L) of both lakes indicate low acid neutralizing capacity and any loss may result in a precipitous drop in pH. Higher alkalinity levels built up in the monimolimnion of both lakes will be lost seasonally as the lakes turn over and the heavier TDS laden water is mixed and flushed downstream.

1.3.1 Meromixis in Cleaver and Horneblende Lakes

Throughout the study, Cleaver Lake was in a state of meromixis, and Horneblende exhibited weak meromixis. Horneblende Lake showed dimictic tendencies with regular turnover in both the falls of 1999 and 2000 and springs of 2000, eroding the weakly established monimolimnion (Figure 1.6). Cleaver Lake may be monomictic due to ice cover persisting into the spring turnover time when the mixolimnion is at an equal temperature and density, preventing wind-aided overturn, as was observed in the spring of 2000. Spring melt events during ice cover such as that observed in February 2000 may assist Cleaver Lake overturn. By forcing warmer water (1-4°C) down to interact with the chemocline, destabilize may occur, easing fall overturn.

The Friedman test showed significant declines of conductivity, calcium, and sulphate in all depths of Horneblende Lake. Since Ca and SO_4 are the major contributors to salinity in the system, their decreased presence in the lake basin will reduce the stratification observed in the hypolimnion of the lake, allowing for the quick elimination of the meromictic tendencies exhibited by Horneblende Lake.

Horneblende had little high-TDS laden water left in the hypolimnion, which is expected to flush away in one to two years of regular cycling. Cleaver Lake will undoubtedly take longer with the observed drop from 6m to 7m which occurred in the fall of 2000. With the reduction of input to the system from the mine, Cleaver Lake may eventually exhibit the weaker stratification levels of current Horneblende Lake, making the elimination of the monimolimnion much easier. With the small amount of monimolimnion waters that were removed from the system (a one metre layer), the impact on Cleaver Lake from sulphide or metal release appeared to be minimized, as no corresponding spikes in metals was observed in the outflow of Cleaver Lake during the turnover period.

1.3.2 Metals in Cleaver and Horneblende Lakes

The distribution of zinc, copper, and aluminium in Cleaver Lake is what would be expected in high-sulphide conditions. Zinc and copper depletion due to sulphide precipitation in the hypolimnion is well known, and is an important control for many metals (Matisoff *et al*, 1980; Förstner, 1982; Frevert, 1987; Davison *et al*, 1992). High sulphide (>2mg/L) levels in the monimolimnion should provide ample sources for precipitation of all metals that sink to the chemocline. High levels of sulphate (>700mg/L) will give a large supply of sulphur for reduction. Precipitation as a pure sulphide or coprecipitation with FeS can be an important removal mechanism for both Cu and Zn under anoxic conditions (Hamilton-Taylor *et al*, 1996). The higher levels for these metals in the epilimnion was likely due to the low residence time of the water and any metals penetrating the chemocline quickly being sequestered by sulphides. Increased Fe and Mn levels in Cleaver Lake are likely due to re-release from sediments, as most Fe probably originated from allochthonous particles from the inflow incorporated in clay minerals or oxyhydroxides, which may have been reduced and released into solution after settling onto the sediments (Davison, 1993). The increased levels of Fe over the ice-cover periods may be due to an increased input, which would increase epilimnion concentrations. Subsequent sinking into the anoxic region would expose Fe to oxidation-reduction cycling and keep elevated levels near the anoxic boundary, of which the mid (8m) depth is representative

(Davison, 1993). As iron was not tested in the Cleaver inflow, this cannot be definitely ascertained.

In contrast, metals in Horneblende Lake (Figure 1.7) show elevated levels in the hypolimnion that are typical patterns of seasonal anoxia (Sigg *et al*, 1991; Balistrieri *et al*, 1992). With the lack of hydrogen sulphide and much lower levels of sulphate as compared to Cleaver Lake, there is no indication that sulphide sequestering of metals is occurring in the hypolimnion. A drop of zinc throughout the water column over the study period (Table 1.5) is most likely indicative of the effects of the mine closure and decreased input to the system.

Toxicity testing revealed that the water from the monimolimnion posed little danger to the aquatic life of Cleaver Lake. Any hydrogen sulphide present in the water was oxygenated to below toxic levels. With the slow reversal of meromixis (1m/year), the monimolimnion water would be quickly diluted upon reaching the epilimnion or outflow of the lake. Organisms in Cleaver Lake would also likely build up tolerance to the high zinc levels. It has been shown that with time, *Daphnia magna, Ceriodaphnia dubia*, and many algal species will develop a higher tolerance for zinc (Admiraal *et al*, 1999; Muyssen & Janssen, 2001; Muyssen & Janssen, 2002; Muyssen *et al*, 2002). In surveys of Cleaver Lake where brook trout were found, zinc levels were in the order of 0.5mg/L, indicating that these levels may not be toxic for populations acclimated to the lake (SENES, 2001).

1.3.3 Management Implications

Since closure of the mine and cessation of effluent entering the Whitesand River, Cleaver and Horneblende Both appear to be recovering from meromixis. The monimolimnion of Cleaver Lake was reduced by one metre during the study period. The much weaker stratification in Horneblende Lake eroded considerably during the study. Neither Lake showed any negative impact in water quality in out-flowing water. With the increasing oxygenated volume of water, fish habitat will be similarly increased.

With the decrease in size of the monimolimnion of Cleaver Lake, the sediments will again be exposed to oxygenated water. Effects of sediment oxygenation will be studied in the following chapter.

INTRODUCTION

Throughout the past century, industrial activity has increased the amount of trace metals entering aquatic environments (Förstner & Wittmann, 1979). A large fraction of metals introduced into aquatic environments are associated with the sediments.

It is well known that many heavy metals, including Co, Cu, Fe, Mn, Mo, Ni, Pb, Zn, can become effectively immobilized by the formation of precipitated sulphide minerals in anoxic conditions (Balistrieri *et al*, 1994; Hamilton-Taylor *et al*, 1996; Petersen *et al*, 1997; Harrington *et al*, 1998). As long as the sediments remain anoxic and undisturbed, the metals will remain fixed in the sediments. If they become disturbed in some fashion, and the sediments are exposed to oxygenated water, the sulphide minerals may oxidize resulting in the re-release of the trapped trace metals (Lithner *et al*, 2000). In oxic sediments, particulate organic matter and iron and manganese oxyhydroxides are the dominant binding phases of metals (Tessier *et al*, 1996, Chapman *et al*, 1998). Particulate organic carbon, usually in the form of humic substances, is capable of binding metals through Langmuir adsorption (Mahoney *et al*, 1996), surface complexation (Davis, 1984), or ion binding (Marinsky & Ephraim, 1986). Humic substances have also been shown to be effective scavengers of metals in anoxic sediments when sulphide availability has been exhausted (Mahoney *et al*, 1996)

Many studies on trace element release in lakes have focused on seasonally anoxic waters (Balistrieri *et al*, 1992; Harrington, *et al* 1998). Other studies have centered around meromictic lakes and cycling of metals in them (Balistrieri *et al*, 1994; Viollier *et al*, 1995; Hongve, 2002)

Further studies focus on trace element behaviour in rivers or impoundments that have been anthropogenically affected that may be subjected to catastrophic disturbance events which could potentially mobilize metals (Dadea *et al*, 2001; Zoumis *et al*, 2001; Akcay *et al*, 2003). Sequential extractions (Tessier *et al*, 1979) are often preferred to discern metal distribution (Dadea *et al*, 2001).

In this study, a small meromictic lake on the Precambrian Shield in Northern Ontario near a former zinc-copper mine was examined. Meromictic conditions have been present since 1991, and with the closing of the mine in the fall of 1999, the lake has not received input from the mine/milling site. The greatest concern with the remediation of the lake is that with the disappearance of the monimolimnion, sediments that have been anoxic for almost a decade will once again be exposed to oxygen, resulting in a possible release of metals. An understanding of the forms of trace metals that may be released from the sediments is needed to ensure that any potential change in metal concentration that occurs in the water column will not be detrimental to the system. The objective of this study was to assess possible change of metal concentrations in the water column during the potential oxidation of the sediments.

2.2 METHODOLOGY

2.2.1 Study Site

The study site was at Cleaver Lake, located near the headwaters of the Whitesand River. The characteristics of Cleaver Lake are presented in section 1.2.1, and in Figure 1.1.

2.2.2 Sediment Aeration Experiment

2.2.2.1 Field Procedures

Sediment was collected from Cleaver Lake (Figure 2.1) with a sediment core sampler from the deepest location of the lake (19m), midway to shore (8m), and in the littoral area of the lake (3m). The deep sediment samples were located below the redox boundary, and represented anoxic sediments; the midway sediment represented a transition area near the redox boundary; and the littoral sediment represented oxic conditions, above the redox boundary. Six cores were taken at each location, spaced 1-2 metres apart to avoid obtaining samples from areas that may have been disturbed from previous coring efforts. Cores were immediately capped upon retrieval and placed into a bag purged with nitrogen. Once all cores were collected, the bag was placed into a cooler that had also been purged with nitrogen. The cores were then transported upright to the laboratory, where they were stored in a nitrogen bag until sorted.

Water samples were collected from a depth of 13m. The containers used for water collection were purged with nitrogen gas prior to filling, and the gas was continually flowed into the container while being displaced by the water. The containers were filled to overflowing for several minutes to ensure no air remained inside. All samples were kept cool during transport and refrigerated at 4°C upon arrival in the laboratory.

2.2.2.2 Laboratory Procedures

The top five centimetres of each core from each of the locations in the lake (deep, midway and littoral) were collected and placed into a beaker, where they were thoroughly mixed. These conglomerates were divided into 40cc samples and placed into ultra-pure cellulose dialysis membranes that were sealed at both ends by polypropylene clamps. Six sediment-filled membranes were filled for each depth, with three replicates for the oxic and anoxic components of the experiment. The membranes, which measured approximately 2cm in diameter by 12cm in length, were placed into 1L polyethylene bottles filled with the 13m Cleaver Lake water. Approximately 5cm of water was above the top of the membrane, minimizing the interaction between the membrane-bound sediment and the external atmosphere. A network of tubing was built to pump air into each individual bottle with gages on the tubes to regulate the flow of air into each bottle. For quality control, two bottles containing Cleaver Lake water and two bottles containing distilled, de-ionized water samples were also run with no sediment filled membranes. Figure 2.1 shows the apparatus used.

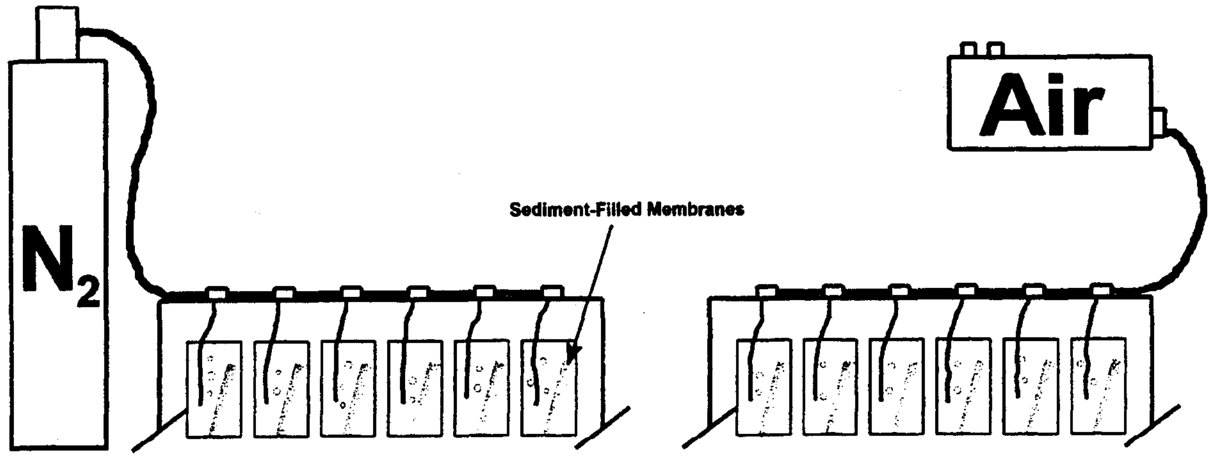


Figure 2.1: Apparatus set-up used for the Sediment Aeration Experiment.

At the beginning of the experiment, water samples were taken from each bottle and tested for Zn, Cu, Fe, Mn and SO_4 for baseline levels. All of the bottles were then placed into a nitrogen filled glove bag and bubbled with nitrogen gas for three days. At day three, samples were taken and tested for the same analytes, and three of the littoral, midway, and deep bottles along with one of each control were removed and placed in an oxic environment, where air replaced the nitrogen gas. Water samples were subsequently removed on days 5, 9, 24, and 31 and tested for the same parameters.

Aliquots of samples for SO_4 were filtered through 0.45µm membrane glass fibre filters prior to analysis. Concentrations were determined using a Dionex DX-120 ion chromatograph equipped with an AS40 automated sampler.

Metals determination was performed after microwave aided nitric acid digest at 85-95°C using LUEL protocols that followed a modified EPA method (EPA, 1992; LUEL, 2000). The samples were then analysed using a Jarrell Ash Inductively Coupled Argon Plasma 9000 Spectrophotometer (ICP).

A one-step aqua regia digestion was performed on the sediments from the three locations to give total metal content.

2.2.3 Sequential Extraction

The Cleaver Lake sediments used in this procedure were collected by BEAK Environmental Inc. in October 2000. The sequential extraction was carried out by PSC Analytical Services, which included two deep samples (anoxic) and a shallow sample (oxic). Following the procedure from Tessier *et al.* (1979), the following metal fractions were determined: (1) exchangeable (magnesium chloride); (2) carbonate bound (sodium acetate); (3) bound to Mn-Fe (hydroxylamine hydrochloride); (4) bound to organic (ammonium acetate); and (5) residual (aqua regia). Each extract was examined for Zn, Cu, Fe and Mn. The five reactions were compared to a one-step aqua regia digestion to give an indication of the loss of any metal traces between digestions.

2.2.4 Data Analysis

A Repeated Measures ANOVA was used to determine the effect of the treatments (air vs. nitrogen) on metal concentrations (air vs. nitrogen) as well as changes during the course of the sediment aeration experiment. A Huyhn-Feldt correction was used during the Repeated Measures analysis when the sphericity assumption was violated.

RESULTS

2.3.1 Sediment Aeration Experiment

The sediment experiment results are shown graphically in Figure 2.2, with the exception of copper, which had many concentrations at or below detection limit, and were not included in further analysis. For metals, neither the oxic nor anoxic littoral, midway, and deep replicates were statistically different ($p<0.05$) from each other, with the exception of manganese on days 9 and 31. The three locations for each treatment were subsequently grouped together to provide sufficient degrees of freedom for the Repeated Measures ANOVA. For sulphate, the triplicates of air for days 9 and 24 and nitrogen day 9 were significantly different, but included in the time series analysis.

The Repeated Measures ANOVA results can be found in Table 2.1. The zinc levels of the aeration experiment were significantly different between the two treatments ($F(1,16)=62.346$, $p<0.05$). The anoxic samples showed a steady decline from 0.08mg/L to 0.02 mg/L, while the samples exposed to air varied from 0.08 mg/L to 0.06 mg/L before beginning a climb to pre-experiment levels. Iron was significant between the treatments ($F(1,16)=34.084$, $p<0.05$). Iron samples all began at a level approximating 3.5 mg/L and declined throughout the experiment. The level of dissolved iron in the oxic samples did not drop as much as the anoxic samples, remaining at a level around 2 mg/L compared to just below 1 mg/L. Manganese showed a slight split in the samples over the course of the experiment. Differences in levels were also significant between treatments ($F(1,16)=36.932$, $p<0.05$). All samples had an initial concentration of 0.425 mg/L and over time the anoxic samples dropped slightly to 0.4 mg/L while the air samples

Table 2.1: Results of repeated measures ANOVA, including repeated measures t-tests to detect significance (Y) between testing days. F statistic refers to overall significance.

Treatment	Statistic Between Treatments	Significance Between Days				Statistic Between Days
		3-5	5-9	9-24	24-31	3-31
Zinc air	F(1,16)=62.346 p<0.05		Y	Y		F(4, 32)=12.49 p<0.05
Zinc N			Y	Y	Y	F(4, 32)=142.56 p<0.05
Iron air	F(1,16)=34.084 p<0.05		Y	Y		F(2.04, 16.34)=100.74 p<0.05; with Huynh-Feldt Correction
Iron N		Y	Y	Y	Y	F(4, 32)=493.99 p<0.05
Manganese air	F(1,16)=36.932 p<0.05		Y	Y		F(1.95, 15.64)=15.3 p<0.05; with Huynh-Feldt Correction
Manganese N						F(1.81, 14.47)=5.96 p<0.05; with Huynh-Feldt Correction
Sulphate air	F(1,15)=4.854 p<0.05	Y	Y	Y	Y	F(4, 32)=146.70 p<0.05
Sulphate N		Y			Y	F(4, 28)=65.87 p<0.05

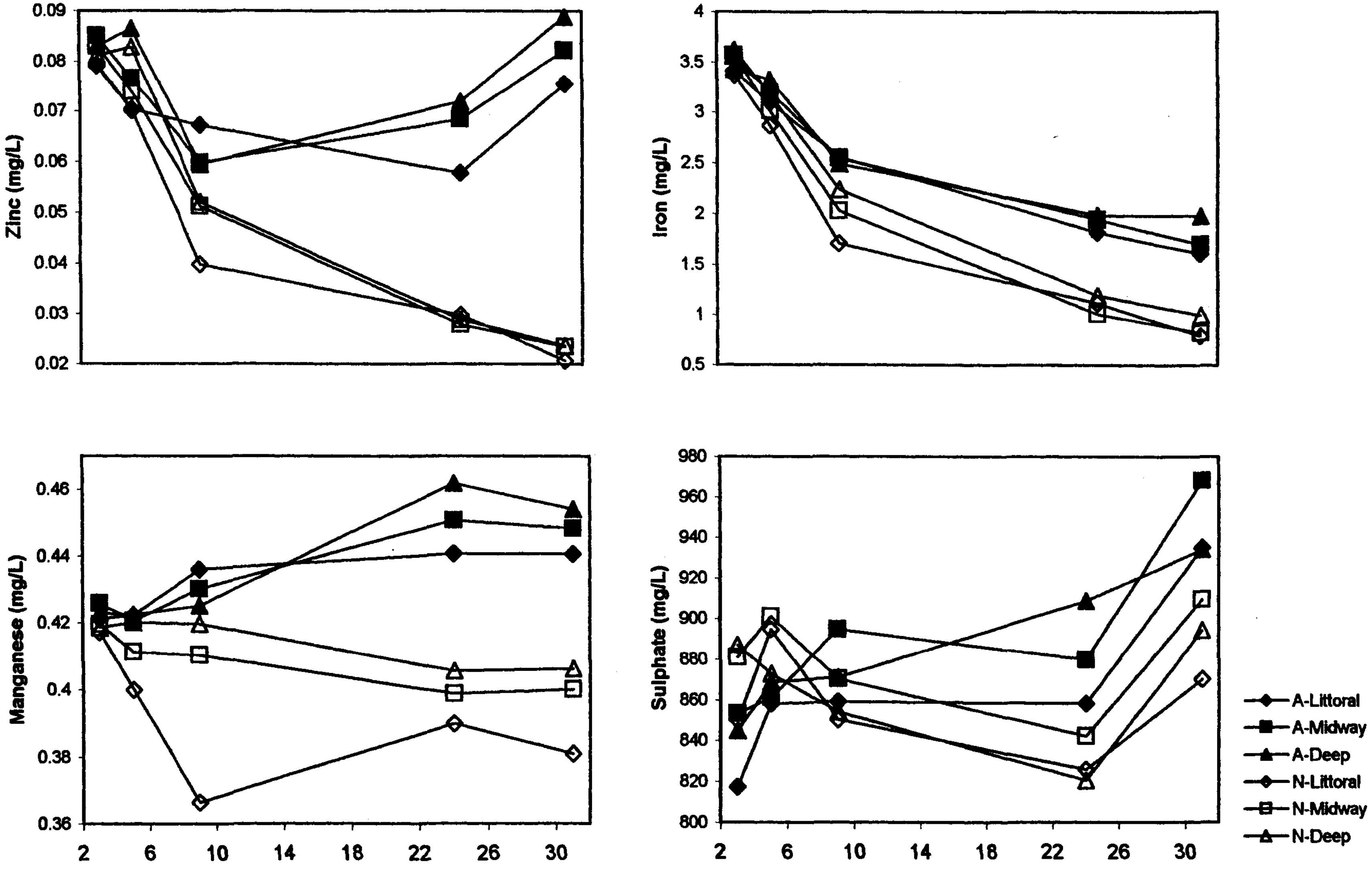


Figure 2.2: Results of zinc, iron, manganese, and sulphate from the sediment experiment for the A (air) and the N (nitrogen) treatments.

increased in a similar fashion to 0.45 mg/L. Sulphate levels were approximately 850 mg/L at the beginning of the experiment with little variation until the last sampling period where there was a slight increase in levels of all the samples. At the end of the sampling, oxic samples were roughly 40 mg/L higher than the anoxic samples, finishing at 934 mg/L compared to 894 mg/L. The treatments were significant different ($F(1,15)=4.584$ $p<0.05$).

During the disassembly of the aeration experiment, a precipitate formed in the bottom of each bottle containing Cleaver Lake water, which was likely due to the length of the experiment.

Table 2.2 shows the results of the aqua regia digestion of the Cleaver Lake sediments. The littoral sediments contained the lowest amounts of metals, while the midway contained the highest amount of Zn, Cu, and Mn. The deep sediments contained the highest iron content. Metal levels were significant ($p<0.05$) between the sites.

Table 2.2: Metal content of Cleaver Lake sediment used for the sediment aeration experiment. All values in mg/kg. * denotes a significant ($p<0.05$) difference between sites.

Sample	Zn*	Cu*	Fe*	Mn*
Littoral 1	1357.3	88.6	7993.8	88.6
Littoral 2	1364.8	85.8	7882.6	85.8
Littoral 3	1582.3	86.7	8087.5	86.7
Average	**1434.8**	**87.0**	**7988.0**	**87.0**
Midway 1	2226.5	132.3	10073.1	132.3
Midway 2	2385.6	145.6	11308.3	145.6
Midway 3	2016.7	121.5	8948.6	121.5
Average	**2209.6**	**133.1**	**10110.0**	**133.1**
Deep 1	1727.2	134.3	15635.1	134.3
Deep 2	1226.9	96.7	12509.2	96.7
Deep 3	1486.0	115.5	13907.7	115.5
Average	**1480.0**	**115.5**	**14017.3**	**115.5**

2.3.2 Sequential Extraction

The results of the sequential extraction are in Table 2.3, including each extractable fraction, the sum of the five extractions, a one-step regia digestion, and a comparison between the sum of the five extractions and one-step regia digestion to check for accuracy. There was good agreement between the one step digestion and five extractions, with only three samples falling outside of 10% agreement. Figure 2.3 shows a graphical representation of the percentage of each fraction in each of the sediment samples.

Manganese was the only metal that showed a high fraction (~20%) in the exchangeable form. No metals showed a significant portion bound to carbonates, and zinc showed the largest fraction bound to Fe-Mn oxyhydroxides, with the shallow sample at nearly 60%. Zinc and copper were the only metals with large fractions bound to organics. All metals had significant portions in the residual fraction with Zn averaging nearly 40% and Cu, Fe, and Mn nearing 60%.

Table 2.3: Sequential extraction results for zinc, copper, iron, and manganese. All values are in mg/kg.

Sample	Exchangeable (1)		Carbonate Bound (2)		Fe-Mn Bound (3)		Organic Bound (4)		Residual (5)		Sum of 1 to 5	One Step Aqua Regia Digestion	Ratio of one stage and five stage
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%			
Zn													
Shallow	<0.6	<1	38	2	1150	61	500	26	210	11	1898	2000	1.05
Deep #1	5	0	38	1	950	36	850	32	800	30	2643	2500	0.95
Deep #2	21	1	50	2	175	6	850	30	1700	61	2796	2900	1.04
Cu													
Shallow	<0.7	<1	<0.5	<1	3	2	120	67	55	31	178	180	1.01
Deep #1	<0.7	<1	<0.5	<1	<1.1	<1	135	49	140	51	275	220	0.80
Deep #2	<0.7	<1	<0.5	<1	<1.2	<1	36	25	110	75	146	140	0.96
Fe													
Shallow	750	3	2100	7	8000	27	2450	8	16500	55	29800	30000	1.01
Deep #1	155	1	550	3	3150	16	2950	15	13500	66	20305	18000	0.89
Deep #2	120	1	26	0	440	4	900	8	9500	86	10986	12000	1.09
Mn													
Shallow	44	19	9	4	36	16	6	2	135	59	228.5	240	1.05
Deep #1	44	23	8	4	31	16	7	4	105	54	194	190	0.98
Deep #2	28.5	29	3	3	4	4	7	7	55	56	97.5	110	1.13

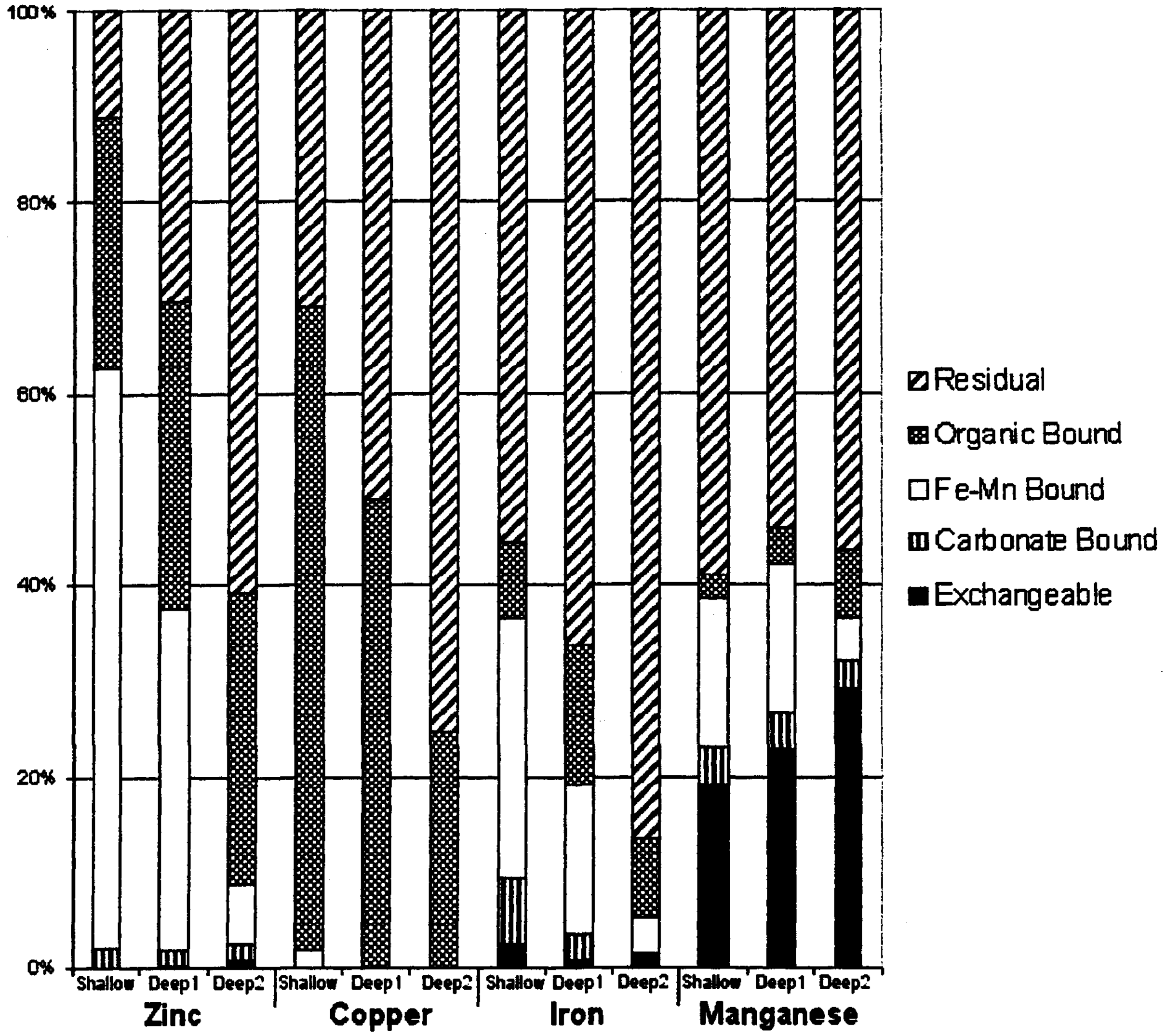


Figure 2.3: Percent fractions from the sequential extraction.

2.4 DISCUSSION

2.4.1 Aeration Effects

Copper and Zinc

In anoxic lake sediments, Zn and Cu sulphide precipitation as a pure sulphide or as coprecipitation with an iron sulphide species has been widely reported (Carignan & Nriagu, 1985; Carignan & Tessier, 1985; Pederson *et al*, 1993; Hamilton-Taylor *et al*, 1996). Cu, Zn, and As have been shown to favour the sulphide phase over the oxyhydroxide phase in sulphide rich sediments (Moore *et al*, 1988). In this experiment, there was no noticeable release of copper or zinc, which would be expected with the dissolution of sulphides.

In the anoxic treatment, the steep drop in Zn levels was most likely due to sulphide precipitation, or coprecipitation with FeS, as humic binding is insignificant (Tessier *et al*, 1989; Hamilton-Taylor *et al*, 1996). In anoxic waters, zinc-sulphide precipitation as a monosulphide is nearly 80% (O'Day *et al*, 2000). Since in the oxic treatment, there appeared to be no significant release or removal of zinc during the experiment, dissolution of ZnS may have been offset by zinc combining with Fe-Mn oxyhydroxides. The shallow Zn sample showed the highest percentage bound to Fe-Mn oxides (60%), which gives credence to the fact that this phase is an important removal pathway under oxic conditions. Zinc has been known to favour this phase in oxic, circumneutral lake sediments where it is mainly bound with Mn-oxyhydroxides (Tessier *et al*, 1989; Young & Harvey, 1992). The dissolution of ZnS was greater than the formation of Fe-Mn oxyhydroxides in the aeration experiment, which was shown by the increase in zinc. La Force *et al* (1999) observed an increase in zinc during oxygenation of contaminated sediments and a shift from organic and residual phases to carbonate and exchangeable. They also noted a strong correlation (sigma value = 0.95) between Zn and Mn, and postulated the two metals being released from a similar source.

Copper did not show any pattern of increase or decrease throughout the sediment aeration experiment that could be linked to the sediments. The Cu fractions in the sequential extraction experiment (Figure 2.3) indicate that regardless of sediment origin, almost all copper is bound by organics or found in the residual fraction. This finding is in agreement with other studies (Sakata, 1985; Young & Harvey, 1992; Linnik & Zubenko, 2000; Dadea *et al*, 2001). With no Cu going into solution, any Cu-S species present in the sediments were likely adsorbed to newly formed Fe-Mn oxyhydroxides or bound to organic matter (Hart, 1982; Johnson & Thornton, 1987). Low levels of Cu in the sediments may not have allowed detectable changes to take place. Copper has been shown to prefer binding to organic matter even when in oxic conditions and in the presence of Fe-Mn oxides (Schintu *et al*, 1991).

Iron and Manganese

Manganese was the only metal tested that showed a significant portion in the exchangeable fraction. The release of Mn in the aerated treatment is possibly due to this fraction dissolving into solution, or dissolution of Mn-sulphide species. The minimal decline of Mn in anoxic conditions is expected as Mn has a much lower affinity for coprecipitation with FeS as compared to Cu and Zn (Morse & Arakaki, 1993). Manganese will therefore remain in solution until other metal sources are exhausted.

In sediments, most iron is present in clay minerals or unreactive oxides, and is not reduced (Hamilton-Taylor & Davison, 1996). In the aerated treatment, iron likely oxidized from Fe(II) to Fe(III), and precipitated as $Fe(OH)_3 \cdot nH_2O$ (La Force *et al*, 1999). The more significant decline of iron in the nitrogen environment is most likely due to sulphide precipitation (Davison, 1993).

Sulphate

In the anoxic treatment, sulphate levels dropped due to reduction to sulphides and subsequent binding with metals, most noticeably Fe and Zn, and to a small extent Mn. The aerated experiment showed higher levels during the experiment as no sulphate was reduced and any hydrogen sulphide present was oxidized into sulphate. Oxidation is likely to have occurred in the water itself as well as in the membrane bound sediment. The oxidation of the comparably low levels of hydrogen sulphide found in Cleaver Lake would be unlikely to give any significant increase in sulphate levels.

2.4.2 Management Implications

The water used in this experiment was taken from Cleaver Lake at 13m, well below the chemocline (6-7m). As shown in Chapter 1, the elevated levels of dissolved metals in the monimolimnion would not be what the sediments would be encountering as the chemocline lowers. Mn and Fe levels were elevated in the hypolimnion, while Zn and Cu concentrations were greater in the epilimnion. Zinc and Cu inflow levels matched the epilimnion levels and with the short residence time of water in Cleaver Lake, Zn and Cu may have been unable to penetrate the chemocline. Any Zn or Cu that did penetrate into the monimolimnion appeared to be rapidly sequestered by sulphides and removed from the water column.

If meromixis is eliminated from Cleaver Lake, there is no indication that metals will be released when exposed to an oxygenated water column, with the exception of zinc. With Zn appearing to be increasing up to the conclusion of the experiment, the experiment life may have been too short to properly determine the long-term effects of sediment aeration. The sediment aeration experiment showed no signs of metals (Zn, Cu, Fe, Mn) or sulphate increasing during the 31-day length. Very low percentages of zinc (<3%) and copper (<1%) were bound to sediments in the exchangeable or carbonate fractions that would be easily released in oxic conditions. Any Zn or Cu sulphides in the sediments that become oxidized may sorb onto oxyhydroxides or organic matter before being released into solution (Moore *et al*, 1988)

GENERAL CONCLUSIONS

Both Cleaver and Horneblende Lakes showed an impact of the mining activities conducted upstream. Both lakes were meromictic, with Cleaver Lake showing a stable monimolimnion at 6m, which dropped to 7m during the course of the study. Horneblende Lake exhibited a much weaker stratification which continued to erode away over the study period. Natural restoration appears to be working in reversing the meromixis in the two lakes, with an immediate change in Horneblende and slower restoration in Cleaver Lake. No detrimental effects of turnover were observed in either lake. Horneblende is expected to remove meromixis in one to two years, while Cleaver Lake, if staying consistent with the 1m/year drop, will take over a decade to eliminate the monimolimnion.

The examination of metals in the Cleaver Lake sediments showed no signs of becoming mobile upon oxygenation. pH effects in both lakes will be negligible as long as they remain circumneutral, with a decrease resulting in increased metal release. With oxygenation, copper and zinc, may become increasingly sorbed by Fe oxyhydroxides or organic matter.

Habitat for brook trout will be increased in Cleaver Lake as the monimolimnion is lowered and the oxygenated volume of the lake is increased. Current zinc concentrations in the epilimnion of Cleaver Lake are similar to levels found during periods of brook trout habitation, indicating acclimation to the higher levels will occur.

REFERENCES

Admiraal, W., H. Blanck, M. Buckert-de Jong, H. Guasch, N. Ivorra, V. Lehmann, B. Nyström, M Paulsson, and S. Sabater. 1999. Short-term toxicity of zinc to microbenthic algae and bacteria in a metal polluted stream. Water Research, 33:1989-1996.

Akcay, H., A. Oguz, and C. Karapire. 2003. Study of heavy metal pollution and speciation in Buyak Menderes and Gediz river sediments. Water Research, 37:813-822.

Arnesen, R., B. Bjerkeng, and E. Iversen. 1997. Comparison of model predicted and measured copper and zinc concentrations at three Norwegian underwater tailings disposal sites. In Fourth international conference on acid rock drainage, 1-6 June 1997, Vancouver, BC, Canada, 1833-1847.

Balistrieri, L. S., J. W. Murray, and B. Paul. 1992. The biogeochemical cycling of trace metals in the water column of Lake Sammamish, Washington: Response to seasonally anoxic conditions. Limnology and Oceanography, 37:529-548.

Balistrieri, L. S., J. W. Murray and B. Paul. 1994. The geochemical cycling of trace elements in a biogenic meromictic lake. Geochimica et Cosmochimica Acta, 58:3993-4008.

Cabaniss, S., and M. Shuman. 1988. Copper binding by dissolved organic matter: I. Suwannee River fluvic acid equilibria. Geochimica et Cosmochimica Acta, 52:185-193.

Calmano, W., J. Hong, and U. Förstner. 1992. Influence of pH value and redox potential on binding and mobilization of heavy metals in contaminated sediments. Vom Wasser, 78:245-257.

Carignan, R. and J. Nriagu. 1985. Trace metal deposition and mobility in the sediments of two lakes near Sudbury, Ontario. Geochimica et Cosmochimica Acta, 49: 1753-1764.

Carignan, R., and A. Tessier. 1985. Zinc deposition in acid lakes: The role of diffusion. Science, 228: 1524-1526.

Chapman, P., F. Wang, C. Janssen, G. Persoone, and H. Allen. 1998. Ecotoxicology of metals in aquatic sediments: binding and release, bioavailability, risk assessment, and remediation. Canadian Journal of Fisheries and Aquatic Sciences, 55: 2221-2243.

Dadea, C., L. Fanfani, T. Keegan, M. Farago, I. Thornton. 2001. Sequential extraction in stream sediments from the Loa basin (Northern Chile) *in* Cidu, R. (ed) Water-Rock Interaction, Swets & Zeitlinger, Lisse. p1055-1058.

Davis, J. 1984. Complexation of trace metals by adsorbed natural organic matter. Geochimica et Cosmochimica Acta, 48: 679-681.

Davison, W. 1981. Supply of iron and manganese to an anoxic lake basin. Nature, 290:241-243.

Davison, W. 1993. Iron and manganese in lakes. Earth-Science Reviews, 34: 119-163.

Davison, w., C. Woof, E. Rigg. 1982. The dynamics of iron and manganese in a seasonally anoxic lake; direct measurement of fluxes using sediment traps. Limnology and Oceanography, 27:987-1003.

Davison, W. and E. Tipping. 1984. Treading in Mortimer's footsteps: The geochemical cycling of iron and manganese in Esthwaite Water. Freshwater Biology Association Annual Report, 52:91-101.

Davison, W., G. Grime, C. Woof. 1992. Characterization of lacustrine iron sulfide particles with proton-induced X-ray emission. Limnology and Oceanography, 37:1770-1777.

Dunnette, D., D. Chynoweth, and K. Mancy. 1985. The source of hydrogen sulphide in anoxic sediment. Water Research, 7:875-884.

Environment Canada. 1990. Guidance Document on Control of Toxicity Test Precision Using Reference Toxicants. Environmental Protection Series EPS 1/RM/12, Ottawa, ON.

Environment Canada. 1992. Biological Test Method: Test of Reproduction and Survival Using the Cladoceran *Ceriodaphnia dubia* (Including Nov. 1997 Amendments). Environmental Protection Series EPS 1/RM/21, Ottawa, ON.

Environment Canada. 1997. Biological Test Method: Test of Larval Growth and Survival Using Fathead Minnows. Environmental Protection Series EPS 1/RM/22, Ottawa, ON.

Environment Canada. 2000a. Biological Test Method: Reference Method for Determining Acute Lethality of Effluents to Rainbow Trout. Environmental Protection Series EPS 1/RM/12, Ottawa, ON.

Environment Canada. 2000b. Biological Test Method: Acute Lethality Test Using *Daphnia* spp. Environmental Protection Series EPS 1/RM/11, Ottawa, ON.

Environment Canada. 2000c. Biological Test Method: Reference Method for Determining Acute Lethality of Effluents to *Daphnia magna*. Environmental Protection Series EPS 1/RM/14, Ottawa, ON.

Environmental Protection Agency. 1987. Ambient Water Quality Criteria for Zinc. EPA Publication 440587003. 213pp.

Environmental Protection Agency. 1988. Standard operating procedure for the analysis of sulfide in water, Method 376.1 NS (Titrimetric, Iodine). Region 5 Central Regional Laboratory. Illinois, USA. 14pp.

Environmental Protection Agency. 1992. Acid digestion of aqueous samples and extracts for total metals for analysis by FLAA or ICP spectroscopy, Method 3010A: Revision 1. 4pp.

Erten-Unal, M., B. Wixson, N. Gale, and J. Pitt. 1998. Evaluation of toxicity, bioavailability and speciation of lead, zinc and cadmium in mine-mill wastewaters. Chemical Speciation and Bioavailability, 10:37-46.

Finlayson, B. and S. Aschuckian. 1979. Safe zinc and copper levels from the Spring Creek drainage for steelhead trout in the Upper Sacramento River, California. California Fish and Game, 65:80-99.

Förstner, U. 1982. Accumulative phases for heavy metals in limnetic sediments. Hydrobiologia, 91:269-284.

Förstner, U. and G. Wittmann. 1981. Metal Pollution in the Aquatic Environment, 2nd Ed. Springer-Verlag, New York. 486pp.

Frevert, T. 1987. Heavy metals in Lake Kinneret (Isreal). II. Hydrogen sulfide dependent precipitation of copper, cadmium, lead and zinc. Arch Hydrobiol, 109:1-24.

Greenberg, A, L. Clesceri, and A. Eaton. 1992. Standard Methods for the Examination of Water and Wastewater, 18th Edition EPS Group Inc, Hanover Maryland.

Hamilton-Taylor, J. and W. Davison. 1995. Redox-driven cycling of trace elements in lakes. *in* A. Lerman, D. Imboden, and J. Gat. Eds. Physics and Chemistry of Lakes 2nd Edition. Springer Verlag, New York. pp 217-263.

Hamilton-Taylor, J., W. Davison, and K. Morfett. 1996. The biogeochemical cycling of Zn, Cu, Fe, Mn, and dissolved organic C in a seasonally anoxic lake. Limnology and Oceanography, 41:408-418.

Harrington, J. M. Laforce, W. Rember, S. Fendorf, and R. Rozenweig. 1998. Phase associations and mobilization of iron and trace elements in Coeur d'Alene Lake, Idaho. Environmental Science and Technology, 32:650-656.

Hart, B. 1982. Uptake of trace metals by sediments and suspended particles: a review. Hydrobiologia, 91: 299-313.

Hongve, D. 2002. Seasonal mixing and genesis of endogenic meromixis in small lakes in southeast Norway. Nordic Hydrology, 33:189-206.

Inmet Mining Corporation, and SENES Consultants, Ltd. 1999. Cleaver Lake Restoration Plan. Winston Lake Division.

Irwin, R., M VanMouwerik, L Stevens, M. Seese, and W. Basham. 1997. Environmental Contaminants Encyclopedia. National Park Service, Water Resources Division, Fort Collins, Colorado. 88pp.

Jellison, R and J Melack. 1993. Meromixis in hypersaline Mono Lake, California. 1. Stratification and vertical mixing during the onset, persistence, and breakdown of meromixis. Limnology & Oceanography, 38:1008-1019.

Johnson, C. A. and I. Thornton. 1987. Hydrological and chemical factors controlling the concentrations of Fe, Cu, Zn, and As in a river system contaminated by acid mine drainage. Water Research, 21: 359-365.

Kuo. S. 1986. Concurrent sorption of phosphate and zinc, cadmium, or calcium by a hydrous ferric oxide. Soil Science Society of America Journal, 50:1412-1419.

La Force, M. J., S Fendorf, G. Li, and R. F. Rosenweig. 1999. Redistribution of trace elements from contaminated sediments of Lake Coeur d'Alene during oxygenation. Journal of Environmental Quality, 28:1195-1200.

Laine, A. 1994. Upstream mining impacts on Cleaver Lake water quality, 1993. Ministry of Environment and Energy, Thunder Bay, ON. 6pp.

Lakehead University Environmental Laboratory. 1999. Standard Operating Procedures.

Lakehead University Environmental Laboratory. 2000. Standard Operating Procedures.

Lakehead University Environmental Laboratory. 2001. Standard Operating Procedures.

Laxen, D. 1984. Adsorption of Cd, Pb and Cu during the precipitation of hydrous ferric oxide in a natural water. Chemical Geology, 47: 321-332.

Linnik, P. and I. Zubenko. 2000. Role of bottom sediments in the secondary pollution of aquatic environments by heavy-metal compounds. Lakes & Reservoirs: Research and Management 5:11-21.

Lithner, G., H. Borg, J. Ek, E. Fröberg, K. Holm, A. Johansson, P. Kärrhage, G. Rosén, and M. Söderström. 2000. The turnover of metals in a eutrophic and an oligotrophic lake in Sweden. Ambio, 29:217-229.

Mahoney, J., D. Di Toro, A. Gonzalez, M. Curto, M. Dilg, L. De Ross, and L. Sparrow. 1996. Partitioning of metals to sediment organic carbon. Environmental and Toxicological Chemistry, 15: 2187-2197.

Marinsky, J. and J. Ephraim. 1986. A unified physiochemical description of the protonation and metal ion complexation equilibria of natural organic acids (humic and fluvic acids). 1. Analysis of the influence of polyelectrolyte properties on protonation equilibria in ionic media: fundamental concepts. Environmental Science and Technology, 20:349-354.

Matisoff, G, A. Lindsay, S. Matis, and F. Foster. 1980. Trace metal mineral equilibria in Lake Erie sediments. Journal of Great Lakes Research, 6:353-366

MEND. 1989. Subaqueous disposal of reactive mine wastes: an overview. MEND Project 2.11.1a-a.

MEND. 1991. A preliminary biological and geological assessment of subaqueous tailings disposal in Benson Lake, British Columbia. MEND Project 2.11.1c-a.

MEND. 1992. Chemical Diagenesis of submerged mine tailings in Benson Lake and natural sediments in Keogh Lake, Vancouver Island, British Columbia. MEND Project 2.11.1c-b.

MEND. 1995. Geochemical assessment of subaqueous tailings disposal in Buttle Lake, British Columbia 1993 study program. MEND Report 2.11.4a.

Moore, J., W. Ficklin, and C. Johns. 1988. Partitioning of arsenic and metals in reducing sulfidic sediments. Environmental Science and Technology 22:432-437.

Morse, J., and T Arakaki. 1993. Adsorption and coprecipitation of divalent metals with mackinawite (FeS). Geochimica et Cosmochimica Acta, 57:107-114.

Mortimer, C. 1941. The exchange of dissolved substances between mud and water in lakes: I and II. Journal of Ecology, 29:280-329.

Muyssen, B., and C. Janssen. 2001. Zinc acclimation and its effect on the zinc tolerance of *Raphidocelis supcapitata* and *Chlorella vulgaris* in laboratory experiments. Chemosphere, 45:507-514.

Muyssen, B., and C. Janssen. 2002. Tolerance and acclimation to zinc of *Ceriodaphnia dubia*. Environmental Pollution, 117:301-306.

Muyssen, B., C. Janssen, and B. Bossuyt. 2002. Tolerance and acclimation to zinc of field-collected *Daphnia magna* populations. Aquatic Toxicology, 56: 69-79.

O'Day, P., S. Carroll, S. Randall, R. Martinelli, S. Anderson, J. Jelinski, and J. Knezovich. 2000. Metal speciation and bioavailability in contaminated estuary sediments, Alameda Naval Air Station, California. Environmental Science and Technology, 34:3665-3673.

Pederson, T., B. Mueller, J. McNee, and C. Pelletier. 1993. The early diagenesis of submerged sulphide-rich mine tailings in Anderson Lake, Manitoba. Canadian Journal of Earth Sciences, 30:1099-1109.

Petersen, W., E. Willer, and C. Willamowski. 1997. Remobilization of trace elements from polluted anoxic sediments after resuspension in oxic water. Water, Air, and Soil Pollution, 99:515-522.

Reynolds, G., and J. Hamilton-Taylor. 1992. The role of planktonic algae in the cycling of Zn and Cu in a productive soft-water lake. Limnology and Oceanography, 37: 1759-1769.

Sakata, M. 1985. Diagenic remobilization of manganese, iron, copper, and lead in anoxic sediment of a freshwater pond. Water Research, 19:1033-1038.

Schintu, M., A. Kudo, G. Sarritzu, and A. Contu. 1991. Heavy metal distribution and mobilization in sediments from a drinking water reservoir near a mining area. Water, Air, and Soil Pollution, 57-58: 329-338

SENES Consultants Ltd. 2001. Cleaver and Horneblende Lakes Monitoring and Restoration Plan. Richmond Hill, ON.

Shafer, M., J. Overdier, H. Phillips, D. Webb, J. Sullivan, and D. Armstrong. 1999. Trace metal levels and partitioning in Wisconsin rivers. Water, Air, and Soil Pollution, 110: 273-311.

Sigg, L. 1985. Metal transfer mechanisms in lakes; the role of settling particles. *in* W. Stumm (ed.), Chemical processes in Lakes. John Wiley and Sons, Inc. New York, NY. pp 283-310.

Sigg, L. 1994. Regulation of trace elements in lakes: The role of sedimentation *in* J. Buffle and R. De Vitre (eds), Chemical and Biological Regulation of Aquatic Systems. Lewis, New York. pp 175-195.

Sigg, L, M. Sturm, and D. Kistler. 1987. Vertical transport of heavy metals by settling particles in Lake Zurich. Limnology and Oceanography, 32:112-130.

Sigg, L, C. Johnson, and A. Kuhn. 1991. Redoc conditions and alkalinity generation in a seasonally anoxic lake (Lake Greifen). Marine Chemistry, 36:9-26.

Steinhorn, I. 1985. The disappearance of the long-term meromictic stratification of the Dead Sea. Limnology & Oceanography, 30:451-472.

Stumm, W. 1966. Redox potential as an environmental parameter; conceptual significance and operational limitation. 3rd International Conference on Water Pollution Research, Water Pollution Control Federation. Sec. 1, Paper 13, 16pp.

Talling, J. 1976. The Depletion of carbon dioxide from lake water by phytoplankton. Journal of Ecology, 64:79-121.

Tessier, A, P. G. C. Campbell, M. Bisson. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry, 51:844-850.

Tessier, A., F. Rapin, and R. Carignan. 1985. Trace metals in oxic lake sediments: possible adsorption onto iron oxyhydroxides. Geochimica et Cosmochimica Acta, 49:183-194.

Tessier, A., R. Carignan, B. Dubreuil, and F. Rapin. 1989. Partitioning of zinc between the water column and the oxic sediments in lakes. Geochimica et Cosmochimica Acta, 53:1511-1522.

Tessier, A., A. D. Fortin, N. Belzile, R. De Vitre, and G. Leppard. 1996. Metal sorption to diagenic iron and manganese oxyhydroxides and associated organic matter: narrowing the gap between field and laboratory experiments. Geochimica et Cosmochimica Acta, 60: 387-404.

United States Department of the Interior. 1998. Guidelines for Interpretation if the Biological Effects of Selected Constituents in Biota, Water, and Sediment: Zinc. *in* National Irrigation Water Quality Program Information Report 3. 185-198.

Viollier, E., D. Jezequel, G. Michard, M. Pepe, G. Sarazin, P. Alberic. 1995. Geochemical study of a crater lake (Pavin Lake, France): Trace-element behaviour in the monimolimnion. Chemical Geology, 125: 61-72.

Weiss, R., E. Carmack, and V. Koropalov. 1991. Deep-water renewal and biological production in Lake Baikal. Nature, 349:665-669.

Wetzel, R. 2001. Limnology 3rd Edition. Academic Press: San Diego, CA. 1006pp.

Young, L., and H. Harvey. 1992. The relative importance of manganese and iron oxides and organic matter in the sorption of trace metals by surficial lake sediments. Geochimica et Cosmochimica Acta, 56:1175-1186.

Zasoski, R. J., and R. G. Bureau. 1988. Sorption and sorptive interaction of cadmium and zinc on hydrous manganese oxide. Soil Science Society of America Journal, 52:81-87.

Zoumis, T., A. Schmidt, L. Grigorova, W. Calmano. 2001. Contaminants in sediments: remobilization and demobilization. The Science of the Total Environment, 266:195-202.

Appendix

Appendix A

The following are raw data from the isopleths of Cleaver and Horneblende Lakes. Conductivity is in µs/cm, dissolved oxygen in mg/L, and temperature in °C.

Cleaver Lake Isopleth Data

Conductivity

Depth	05-Oct-99	13-Oct-99	20-Oct-99	26-Oct-99	#######	#######	#######	06-Jan-00	02-Feb-00	08-Mar-00	10-Apr-00	#######	10-May-00	17-May-00	24-May-00	31-May-00	07-Jun-00	12-Jul-00	09-Aug-00	13-Sep-00	17-Oct-00	28-Nov-00	#######	17-Jan-01	05-Feb-01	14-Mar-01
0	220	190	160	243	185	100	80	20	25	45	20	30.3	30.4	31.8	42	56.6	43	50.6	74.2	65.7	159.9	68.4	88.2	37.8	81.1	77.6
1	217	190	160	240	190	175	190	145	30	55	25	29.4	30.2	32.7	42	56.1	42.7	50.7	73.8	64.1	160.1	161	150.6	106.2	86.8	86.7
2	215	190	165	240	190	178	190	175	35	185	105	30	28.4	32.7	41.9	55.4	42.5	50.7	71.6	82.3	160	164.4	165.3	160	159.8	155.8
3	215	190	177	240	193	180	190	175	40	187	145	132.4	28.5	34.1	41.4	55.5	42.8	29.6	68.6	81	159.9	164.9	165.1	162.8	163.7	162.8
4	217	187	187	245	195	190	190	177	50	190	160	165.6	30.4	35.7	43.3	52.6	53.5	36.8	40.3	81.4	160.2	170.3	165.8	163.5	164.7	166.9
5	1200	950	750	250	200	198	190	180	55	190	165	200.2	64.3	124.6	156.6	119	90.3	105.7	113.4	112.6	160.1	166.9	166	164.3	163.5	168.3
6	1130	1150	1125	1125	1100	1200	1025	1000	440	770	950	1059	613	833	948	922	915	927	954	863	378.4	168.2	167.9	166	170.1	171.1
7	1100	1100	1100	1100	1100	1100	1100	1050	700	1050	1050	1075	1054	1062	1064	1063	1059	1059	1072	1086	1100	884	1006	181	820	928
8	1070	1100	1075	1100	1100	1100	1100	1075	700	1100	1050	1080	1071	1071	1070	1069	1066	1073	1079	1084	1093	1091	1090	1044	1072	1071
9	1070	1090	1075	1100	1100	1075	1100	1075	700	1100	1075	1088	1077	1077	1074	1066	1075	1074	1080	1083	1090	1091	1090	1072	1085	1087
10	1070	1090	1075	1100	1100	1050	1100	1075	700	1100	1075	1097	1080	1083	1076	1071	1078	1079	1080	1084	1086	1088	1086	1074	1085	1089
11	1070	1100	1100	1100	1100	1100	1100	1075	700	1100	1075	1101	1094	1089	1087	1061	1084	1082	1083	1086	1087	1085	1082	1070	1083	1087
12	1070	1100	1100	1100	1100	1100	1100	1075	700	1100	1075	1102	1097	1094	1090	1086	1087	1086	1085	1087	1087	1086	1080	1068	1083	1082
13	1070	1100	1100	1100	1100	1100	1100	1075	1075	1100	1100	1115	1098	1096	1093	1088	1089	1088	1087	1088	1088	1086	1083	1067	1080	1083
14	1070	1100	1100	1100	1100	1100	1100	1075	1100	1100	1100	1103	1100	1097	1094	1089	1092	1090	1089	1088	1088	1086	1082	1066	1080	1084
15	1070	1100	1100	1100	1100	1100	1100	1075	1100	1100	1100	1104	1100	1097	1095	1090	1092	1090	1088	1088	1088	1087	1082	1066	1081	1083
16												1102	1100	1098	1095	1090	1090	1092	1089	1088	1088	1086	1080	1066	1082	1082
17												1101	1100	1098	1095	1090	1092	1091	1089	1088	1087	1086	1083	1065	1081	1083
18												1101	1100	1098	1095	1090	1092	1090	1090	1088	1086	1086	1080	1065	1082	1082

Dissolved Oxygen

Depth	05-Oct-99	13-Oct-99	20-Oct-99	26-Oct-99	#######	#######	#######	06-Jan-00	02-Feb-00	08-Mar-00	10-Apr-00	#######	10-May-00	17-May-00	24-May-00	31-May-00	07-Jun-00	12-Jul-00	09-Aug-00	13-Sep-00	17-Oct-00	28-Nov-00	#######	17-Jan-01	05-Feb-01	14-Mar-01
0	10.4	12.4	12.75	13.3	12.9	12.8	15.4	12.4	12.6	12.8	12.4	12.2	11.5	10.9	10.6	10.1	10.5	9.1	9	9.7	11.8	12.9	14.2	11.5	11.4	10.27
1	10.4	12.4	12.5	13.2	12.9	12.9	13.8	11.5	10.8	12.8	12	11.9	11.6	10.8	10.6	10.1	10.5	9.1	9	9.7	11.8	11.8	12.5	11.2	11	10.4
2	10.3	12.1	12.5	13.2	12.9	13	13.4	11.4	10	10.4	9.5	11.9	11.7	11.1	10.6	10	10.4	9	8.8	9.5	11.8	10.8	11.2	10.7	10.3	9.71
3	10.3	12.2	12.75	13.2	13	13	13.2	11.2	9.5	10	9	11.9	11.8	11.5	10.6	10	10.6	8.8	8.6	9.6	11.5	10.4	10.9	10.2	9.7	8.24
4	10.3	12.2	12.5	13.2	13	13	13	10.8	8.7	9.1	8.7	10.1	11.6	11.8	10.6	10.3	10.5	9	7.6	9.5	11.8	10.2	10.5	9.9	9.3	8.01
5	0.8	0.75	5.8	13	0.5	11.8	12.7	9	7.5	7.9	6.6	8.95	11.1	10	9.75	10.1	9.7	8.3	5.8	2.2	11.7	10	10.4	9.8	9.1	8.02
6	0.6	0.5	0.55	0.6	0.45	0.7	0.9	0.35	0	3.4	0.6	6	1.6	2.25	0.5	0.75	0.75	0.85	0.6	0.8	7.5	10.1	10.3	9.8	9.2	7.91
7	0.5	0.43	0.45	0.5	0.4	0.55	0.5	0.35	0	0.45	0.4	0.45	0.6	2	0.3	0.5	0.6	0.6	0.45	0.6	1.1	0.8	1.25	0.4	0.2	2.62
8	0.3	0.38	0.45	0.45	0.35	0.45	0.4	0.35	0	0.45	0.4	0.45	0.55	1.75	0.25	0.4	0.55	0.5	0.4	0.45	1	0.35	0.6	0.1	0.1	0.42
9	0.4	0.35	0.4	0.45	0.35	0.45	0.4	0.35	0	0.45	0.4	0.45	0.45	1.55	0.2	0.35	0.5	0.45	0.35	0.4	0.95	0.15	0.35	0	0	0.27
10	0.4	0.35	0.4	0.45	0.35	0.4	0.3	0.4	0	0.5	0.4	0.45	0.45	1.35	0.2	0.3	0.45	0.45	0.35	0.35	0.9	0.1	0.25	0	0	0.18
11	0.3	0.35	0.35	0.4	0.35	0.4	0.3	0.45	0	0.55	0.4	0.45	0.45	1.1	0.2	0.3	0.4	0.45	0.3	0.35	0.9	0	0.15	0	0	0.13
12	0.3	0.35	0.35	0.4	0.35	0.35	0.25	0.45	0	0.55	0.4	0.45	0.45	1.05	0.2	0.3	0.4	0.4	0.3	0.35	0.9	0	0.15	0	0	0.11
13	0.3	0.35	0.35	0.4	0.35	0.35	0.25	0.45	0	0.55	0.4	0.45	0.4	0.95	0.15	0.3	0.4	0.4	0.3	0.3	0.85	0	0.15	0	0	0.1
14	0.3	0.35	0.35	0.4	0.35	0.35	0.25	0.5	0	0.45	0.45	0.45	0.4	0.9	0.15	0.3	0.4	0.4	0.3	0.3	0.85	0	0.15	0	0.1	0.09
15	0.3	0.35	0.35	0.4	0.3	0.35	0.2	0.5	0	0.45	0.45	0.45	0.4	0.85	0.15	0.25	0.35	0.4	0.3	0.3	0.85	0	0.15	0	0.1	0.08
16	0.3	0.35	0.35	0.4	0.3	0.35	0.2	0.5	0	0.4	0.5	0.45	0.4	0.8	0.15	0.25	0.35	0.4	0.3	0.3	0.85	0	0.1	0	0.1	0.08
17	0.3	0.35	0.35	0.4	0.3	0.35	0.2	0.55	0	0.4	0.5	0.45	0.4	0.75	0.15	0.25	0.35	0.4	0.3	0.25	0.85	0	0.05	0	0.1	0.07
18	0.3	0.34	0.34	0.4	0.3	0.35	0.2	0.55	0.05	0.45	0.65	0.45	0.4	0.75	0.15	0.25	0.35	0.4	0.3	0.25	0.85	0	0.05	0	0.1	0.07

Temperature

Depth	05-Oct-99	13-Oct-99	20-Oct-99	26-Oct-99	#######	#######	#######	06-Jan-00	02-Feb-00	08-Mar-00	10-Apr-00	#######	10-May-00	17-May-00	24-May-00	31-May-00	07-Jun-00	12-Jul-00	09-Aug-00	13-Sep-00	17-Oct-00	28-Nov-00	#######	17-Jan-01	05-Feb-01	14-Mar-01
0	7.9	6.75	4.9	3	2.75	2.25	0.25	0	0	0	0	4	9.8	10.3	12	14.6	14	20.7	18.3	17.1	6.9	1	0.7	0.1	0.1	0
1	7.75	6.75	4.75	3	2.75	2.25	1.75	0	0	0	0	4	9.4	10.3	12	14.3	14	20.7	18.2	16.3	6.9	2.9	2.7	1.2	0.5	0.2
2	7.75	6.75	4.75	3	2.75	2.5	1.75	1	0	1	1.25	3.75	7.9	10.3	12	13.3	13.9	20.7	17.9	15.5	6.9	3.2	3.3	2.8	2.4	1.9
3	7.75	6.75	4.75	3	2.75	2.75	2	2	0.75	1.75	1.75	3.5	7.7	9.2	11.3	12.2	13.1	14.1	17.5	15.1	6.9	3.3	3.4	3.5	3.3	3
4	7.5	6.5	4.75	3.25	3	3	2	2	1.5	2	2	3	7.3	7.6	10	10.1	10.6	11.6	12.7	14.9	6.8	3.3	3.4	3.6	3.5	3.5
5	6.5	7	5.25	3.75	3	3.25	2.5	2.25	2.25	2.25	2.25	3	6.3	5.1	5.4	7.4	7.8	8.7	9.3	12.5	6.8	3.4	3.3	3.7	3.6	3.7
6	4.25	5.75	4.75	4.5	4	3.75	3.5	3	3	2.75	2.75	2.75	3.4	3.5	3.6	4	4.4	8.2	6.3	7.8	6.5	3.5	3.7	3.9	3.8	3.9
7	3.25	3.75	3.75	3.75	3.75	3.5	3.5	3.5	3.25	3	3	3	3.3	3.4	3.5	3.6	3.7	4.6	5	5.3	5.5	4.2	4.5	4.1	4.1	4.1
8	3.1	3.5	3.5	3.25	3.25	3.25	3	3.75	3.5	3.25	3	3	3.4	3.5	3.6	3.6	3.6	4	4.2	4.4	4.4	4.7	4.7	4.4	4.2	4.2
9	3.1	3.25	3.25	3.25	3	3.25	3	3.75	3.5	3.5	3.25	3	3.5	3.5	3.6	3.5	3.6	3.8	3.9	4.1	4	4.2	4.4	4.4	4.2	4.2
10	3.1	3.25	3.25	3.25	3	3.25	3	3.75	3.5	3.5	3.25	3	3.6	3.5	3.6	3.6	3.6	3.7	3.8	3.9	3.9	4	4.1	4.2	4.1	4.1
11	3.25	3.2	3.25	3.25	3	3.25	3	3.5	3.5	3.5	3.25	3	3.6	3.5	3.6	3.6	3.6	3.8	3.7	3.8	3.8	3.8	3.9	4	3.9	3.9
12	3.25	3.1	3.25	3.25	3	3.25	3	3.5	3.5	3.25	3.25	3	3.6	3.5	3.6	3.6	3.6	3.7	3.7	3.8	3.7	3.7	3.9	3.9	3.8	3.8
13	3.25	3.2	3.25	3.25	3	3.25	3	3.5	3.5	3.25	3.25	3	3.6	3.5	3.6	3.6	3.6	3.7	3.7	3.8	3.7	3.7	3.9	3.8	3.7	3.8
14	3.25	3.25	3.25	3.25	3.1	3.25	3	3.5	3.5	3.25	3.25	3	3.6	3.5	3.6	3.6	3.6	3.7	3.7	3.7	3.7	3.7	3.9	3.8	3.7	3.7
15	3.25	3.25	3.25	3.25	3.1	3.25	3.1	3.5	3.5	3.25	3.25	3	3.6	3.5	3.6	3.6	3.6	3.7	3.7	3.7	3.7	3.6	3.9	3.8	3.7	3.7
16	3.5	3.25	3.25	3.25	3.1	3.25	3.25	3.5	3.5	3.25	3.25	3	3.6	3.5	3.6	3.6	3.6	3.7	3.7	3.7	3.6	3.7	3.9	3.8	3.7	3.7
17	3.5	3.25	3.25	3.25	3.25	3.25	3.25	3.5	3.5	3.25	3.25	3	3.6	3.5	3.6	3.6	3.6	3.7	3.7	3.7	3.6	3.6	3.9	3.8	3.7	3.7
18	3.5	3.5	3.5	3.25	3.25	3.25	3.25	3.5	3.5	3.25	3.25	3	3.6	3.5	3.6	3.6	3.6	3.7	3.7	3.7	3.6	3.7	3.8	3.8	3.7	3.7

Horneblende Lake Isopleth Data

Conductivity

Depth	05-Oct-99	09-Nov-99	07-Dec-99	06-Jan-00	02-Feb-00	08-Mar-00	10-Apr-00	10-May-00	17-May-00	24-May-00	31-May-00	07-Jun-00	12-Jul-00	09-Aug-00	13-Sep-00	17-Oct-00	28-Nov-00	03-Dec-00	17-Jan-01	05-Feb-01	14-Mar-01
0	105	100	35	15	10	30	25	19.2	20.8	21.6	25.5	26.4	30.6	29.6	32.4	6.4	23.7	25.6	6.2	14.5	13.8
1	105	100	95	15	10	55	25	19.1	20.2	23.1	25.7	26.9	30.2	29.6	27.9	29.1	34.1	32.3	6.3	16.7	13.6
2	105	100	100	17	10	60	30	18.3	21	23.2	25	26.1	30.1	30.1	32.4	28.7	32.9	32	38	40.6	46.7
3	105	100	100	20	10	65	30	18.5	20.3	23.2	23.4	29.4	28.5	30.8	31.6	29.6	32.8	32.5	38	41.4	46.1
4	105	100	100	25	10	80	30	18.3	20	22.6	22.8	26.3	27.3	30.8	31.9	29.4	32	32.5	38.2	40.9	45.9
5	105	105	100	75	10	90	30	18.3	20.5	21.2	22.3	23.2	26.3	28.2	31.6	28.7	32.8	32.3	39	40.9	45.6
6	108	105	100	97	20	95	30	18.3	19.8	19.8	21.6	21.7	26.3	27.3	29.7	29.1	31.6	32.5	39	39.2	45.6
7	110	105	100	97	103	95	33	18.5	19.7	19	19.9	20.4	25.5	25.8	28	29.3	31.8	32.5	39.2	42.1	45.4
8	110	105	100	100	103	95	35	18.7	19.4	19.9	19.8	20.5	23.2	25.6	28.4	29.3	32.4	32.6	38.3	42.7	51.2
9	115	105	100	100	103	97	85	19.4	19.9	20.6	20.6	21.1	31.6	30.2	35.9	29.4	32.4	32.9	38.7	41.9	44.7
10	150	105	100	100	103	97	100	20.8	21.5	24.7	23.9	26.5	41.9	47.6	56.9	42.9	32.4	33.5	39	42.5	45
11	172	105	102	102	103	100	100	24.1	33.9	34.7	41.8	39.7	60.3	64.8	71.5	66.6	33	34.2	39.4	42.2	45
12	213	105	102	102	103	100	103	34.9	38.4	57.4	80.3	61.8	78.5	74	77.7	79.2	33.3	34.8	39.2	42.7	46.2
13	220	110	107	105	110	100	110	83.9	54	83.9	100.1	91.3	86.8	81	83	83.3	34.2	35.9	40	43.3	46.7
14	220	230	180	150	190	140	140	171.1	113.8	121.9	122.3	118	96.2	89.3	86.3	83.7	39.7	39.2	42.5		52.1
15	220	235	240	235	233	230	235	212.4	183.4	170.5	140.4	135.2	98.8	92.5	85.4	84	83.8	81.8	80.8		82.2
16								213.8	194.8	172.9	144.6	137.9	112.8	92.6	87.5	84.3	87.2	87.2	89.5		89.3
17								216.9	196.1	177.2	147.9	138.3	102.1	93.1	87.5	84.4	90.2	90.2	90.1		91.2
18								218.2	197.4	178.3	149	138.9	102.5	93.9	87.5	90	91.4	98.9	90.8		

Dissolved Oxygen

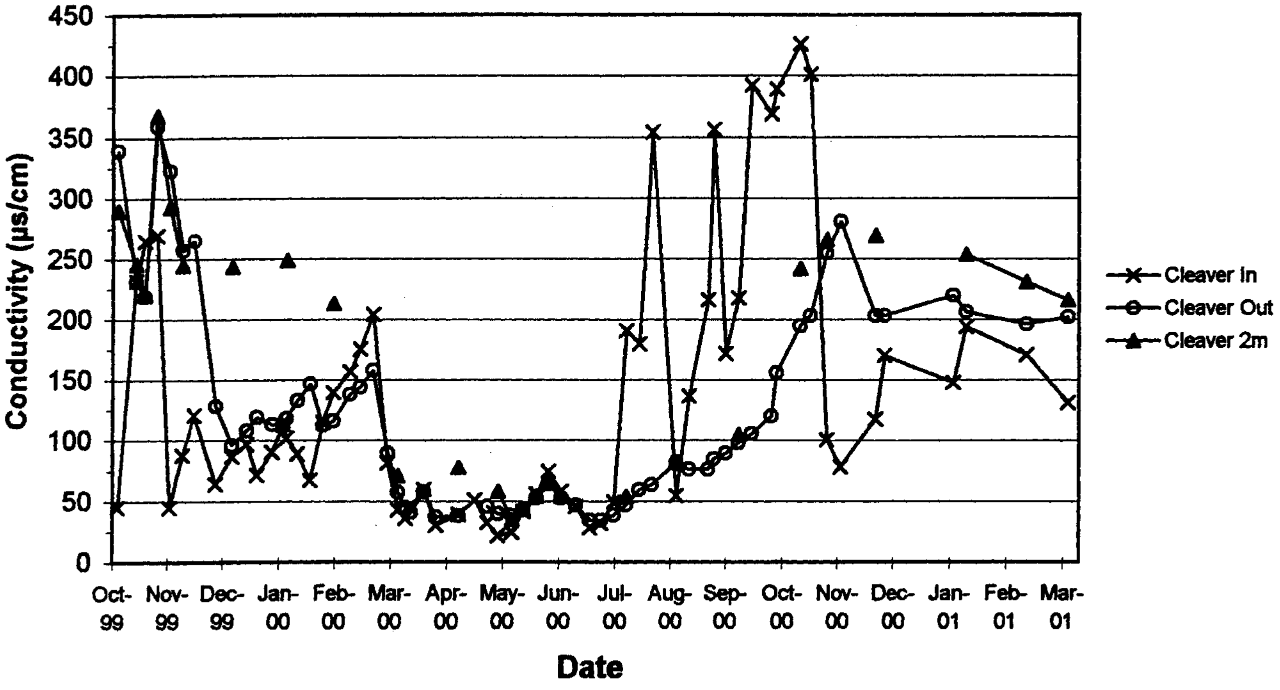
Depth	05-Oct-99	09-Nov-99	07-Dec-99	06-Jan-00	02-Feb-00	08-Mar-00	10-Apr-00	10-May-00	17-May-00	24-May-00	31-May-00	07-Jun-00	12-Jul-00	09-Aug-00	13-Sep-00	17-Oct-00	28-Nov-00	03-Dec-00	17-Jan-01	05-Feb-01	14-Mar-01
0	9.8	12.8	15.4	12.8	11.2	12.7	12.4	12	11.1	10.6	10.1	10.1	9.1	8.6	9.7	11.7	14	13	9.2	10.2	10.05
1	9.8	12.8	13.8	11.2	9.7	12.5	12.4	12	10.9	10.6	10.1	10.1	9.1	8.8	9.7	11.7	11.8	12	9.2	9.9	9.76
2	9.6	12.9	13.8	11	8.8	12.4	12.4	11.8	10.8	10.4	10.1	10.2	9	8.5	9.8	11.7	10.8	11	9.2	9.1	8.46
3	9.6	13	13.6	11	8.5	12.3	12.4	11.7	10.8	10.3	9.9	10.1	8.2	8.3	9.4	11.8	9.5	10.5	8.9	8.8	7.4
4	9.6	12.9	13.2	11	8	12.3	12.4	11.6	10.8	10.1	9.9	10	7.6	5.45	9.2	11.7	9.5	10.3	8.9	8.5	7.2
5	9.5	13	13	10.8	7.7	12	12.4	11.7	10.7	10.1	10	10	7.9	4.5	8.3	11.7	9.4	10	8.8	8.3	7.17
6	8.9	12.8	13	10.8	7.3	10.4	12.2	11.7	10.7	10.3	10	10	7.7	5.45	3.5	11.4	9.2	10	8.8	8.2	7.18
7	8.9	13	12.9	10.8	7.2	8.9	11.9	11.7	10.7	10.4	10.1	10	8	6.15	3.7	11.3	9	9.9	8.8	8.2	7.11
8	7.8	12.9	12.8	10.6	6.8	8.8	11.5	11.4	10.7	10.4	10.3	9.9	8.6	6.6	4.15	11.2	8.8	9.7	8.7	8.2	6.97
9	7.2	12.9	12.6	10.4	6.4	8.6	10.1	11.5	10.7	10.7	10.4	10.2	8.6	6.9	4.7	11.2	8.9	9.6	8.4	8.3	6.88
10	2.4	12.9	12.3	10.4	5.9	8.4	9	11.6	10	10.8	10.2	10.2	8	5.4	3	2.9	8.8	9.5	8.3	8.3	6.75
11	2.1	12.8	12	10.4	5.7	8	7.6	11.8	10	9.5	10.2	10.2	6.5	3.85	1.6	1.3	8.6	9.7	8.2	8.3	6.39
12	1.9	12.9	12	9.7	3.9	6.5	6	12	9.7	7.6	7.2	6.4	4.5	3.05	1	1.05	8.5	9.7	7.9	8.2	6.38
13	1.4	12.7	10.9	8.5	2.7	4.5	3.4	10.4	7.9	6	3.8	4.2	3.1	2.3	0.4	0.9	8.3	9.6	6.1	5.4	6.32
14	1	0.7	8.5	0.25	2.35	4.1	0.55	4.45	1.2	3.75	1.95	1.8	2.4	1.25	0.3	0.9	7.3	6.9	1.1		1.77
15	0.4	0.6	0.75	0.3	0	1.35	0.55	0.85	0.75	1.8	0.95	1	2.05	0.95	0.3	0.9	0.9	1.05	0		0.33
16	0.3	0.55	0.55	0.35	0.05	1.35	0.55	0.8	0.55	1.7	0.5	0.7	1.9	0.5	0.25	0.9	0.3	0.7	0		0.2
17	0.4	0.5	0.45	0.35	0.2	1.45	0.85	0.55	0.5	1.65	0.4	0.65	1.65	0.35	0.25	0.85	0.1	0.35	0		0.16
18	0.4	0.45	0.45	0.35	0.2	1.45	0.9	0.5	0.45	1.6	0.35	0.6	1.6	0.3	0.25	0.9	0.05	0.15	0		

Temperature

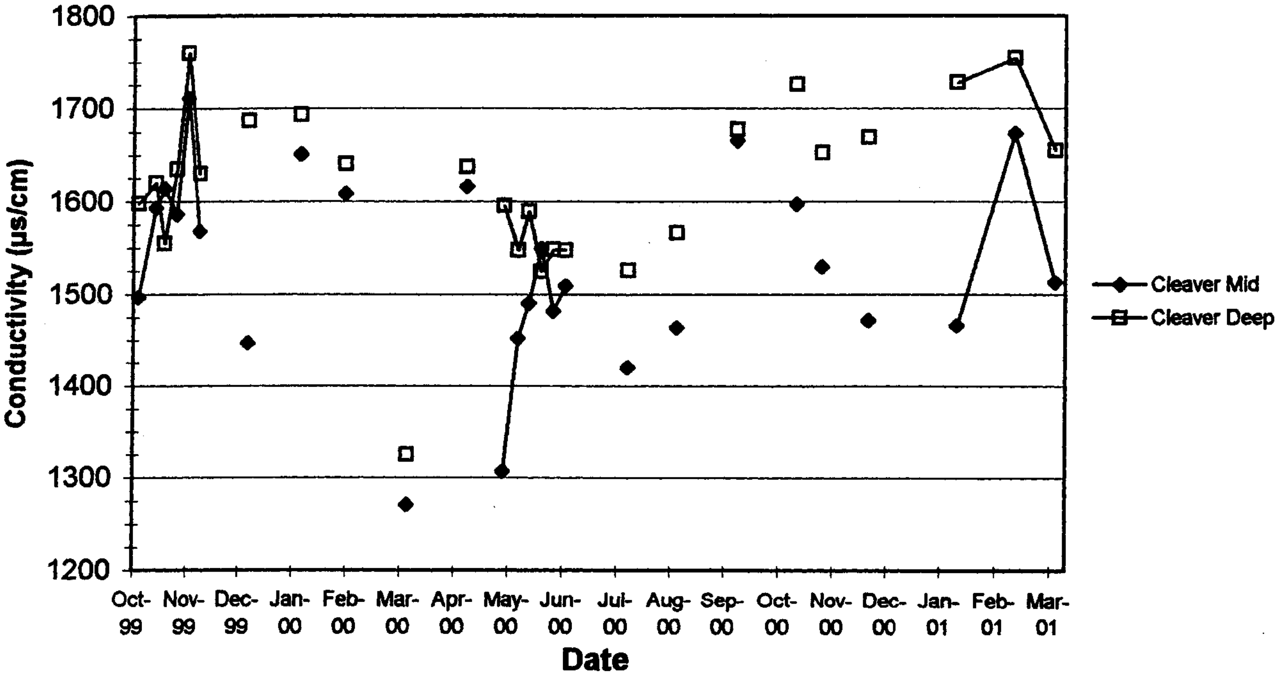
Depth	05-Oct-99	09-Nov-99	07-Dec-99	06-Jan-00	02-Feb-00	08-Mar-00	10-Apr-00	10-May-00	17-May-00	24-May-00	31-May-00	07-Jun-00	12-Jul-00	09-Aug-00	13-Sep-00	17-Oct-00	28-Nov-00	03-Dec-00	17-Jan-01	05-Feb-01	14-Mar-01
0	9	3	0.75	0	0	0	0	8.8	10.6	12.3	14.7	15.2	20.9	19.4	16.6	8.6	1	1.1	0.1	0.1	0.1
1	9	3	1.25	0.25	0	0.5	0	8.6	10.6	12.3	14.5	15	20.9	19.2	16.3	8.4	2.9	2.9	0.8	0.4	0.1
2	9	3	2	1.25	0	0.75	0.1	8.1	10.4	12.2	13.9	14.9	20.9	19.1	16.2	8.2	3.2	3.4	2.7	2.7	1.9
3	9	3	2.25	2	0	0.75	0.1	7.9	10.2	11.7	12.8	14.7	19	189	16.1	8.1	3.4	3.6	3.3	3.2	3
4	9	3	2.5	2.5	0.25	1	0.1	7.9	9.7	10.5	11.4	13.7	17.2	17.9	16	8.1	3.6	3.7	3.4	3.3	3.3
5	9	3	2.5	2.75	0.75	2	0.25	7.9	9.4	10.2	10.9	11.5	15	15.4	15.7	8	3.7	3.8	3.4	3.4	3.4
6	8.75	3	2.5	3	1	2.75	0.25	7.8	9.1	9.5	10.2	10.3	13.3	13.6	14	8	3.8	3.8	3.5	3.5	3.5
7	8.75	3	2.5	3	1.75	2.75	0.25	7.6	8.7	8.8	9	9.2	10.9	10.9	10.5	8	3.8	3.9	3.5	3.5	3.5
8	8.5	3	2.75	3	2	3	0.5	7.2	8.1	7.9	8	7.9	8.2	8.8	9	8	3.8	4	3.5	3.5	3.6
9	8.25	3	2.75	3	2	3	1.75	6.9	7.3	6.6	6.9	6.8	6.7	7.1	7.3	7.9	3.9	4	3.6	3.5	3.6
10	6	3.1	2.75	3	2.75	3	2.5	4.9	5.7	5.4	5.7	6	5.8	6.2	5.6	7.2	3.9	4	3.6	3.5	3.7
11	4.75	3.25	2.75	3	2.75	3	3	4.1	4.4	4.6	4.7	4.9	5.2	5.3	5.3	5.6	3.9	3.9	3.6	3.6	3.7
12	4	3.25	2.75	3	2.75	3	3	3.9	4.2	4.1	4.2	4.4	4.7	4.9	4.9	5	3.9	4	3.6	3.5	3.7
13	4	3.5	3	3	2.75	3	3	3.6	3.9	3.8	3.8	4	4.5	4.7	4.7	4.7	4	4	3.7	3.5	3.7
14	3.75	3.5	3.25	3.25	3	3	3	3.5	3.6	3.7	3.8	3.9	4.4	4.4	4.6	4.7	4.1	4.3	3.9		3.9
15	3.75	3.5	3.25	3.25	3	3	3	3.5	3.5	3.5	3.7	3.8	4.3	4.4	4.5	4.6	4.5	4.6	4.3		4.2
16	3.5	3.5	3.25	3.5	3	3	3	3.5	3.5	3.5	3.6	3.7	4.2	4.3	4.5	4.6	4.6	4.8	4.4		4.3
17	3.5	3.5	3.25	3.5	3	3	3	3.5	3.5	3.5	3.6	3.7	4.2	4.3	4.5	4.6	4.5	4.8	4.4		4.4
18	3.5	3.5	3.25	3.5	3	3	3	3.5	3.5	3.5	3.6	3.7	4.2	4.3	4.5	4.6	4.5	4.8	4.4		

Appendix B

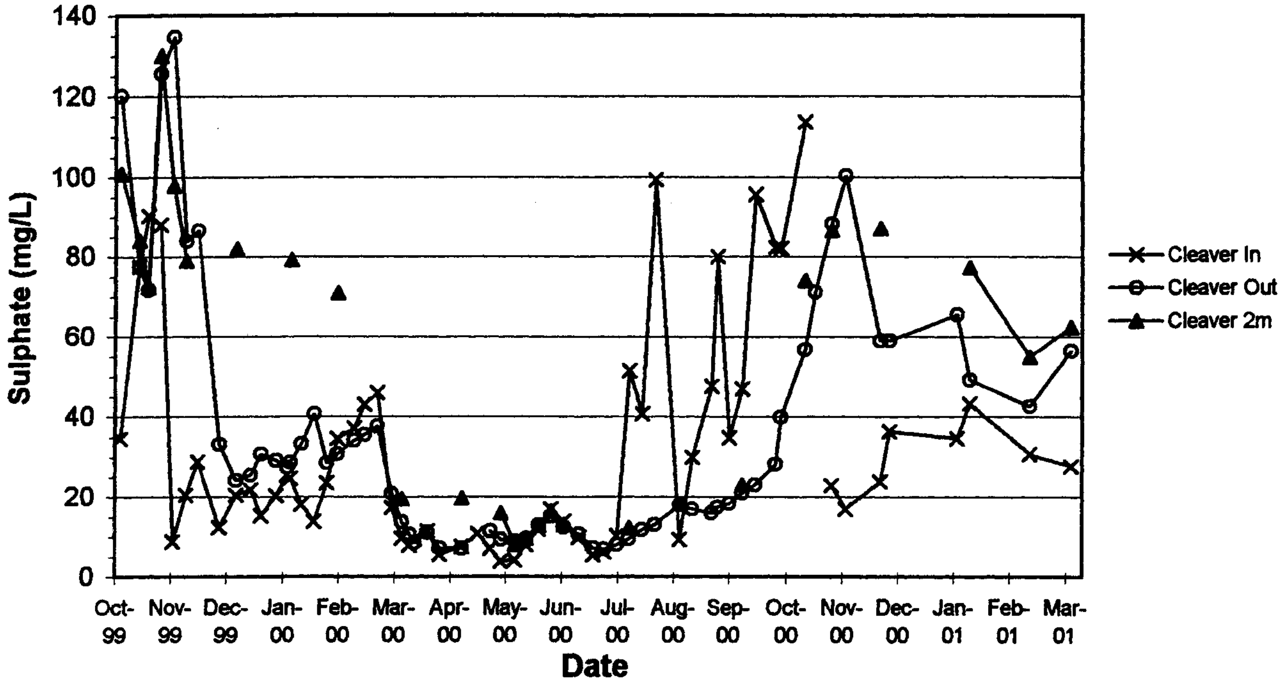
The following are plots of Cleaver Lake analytes in time. Each parameter is in mg/L except for conductivity (µs/cm) and pH.



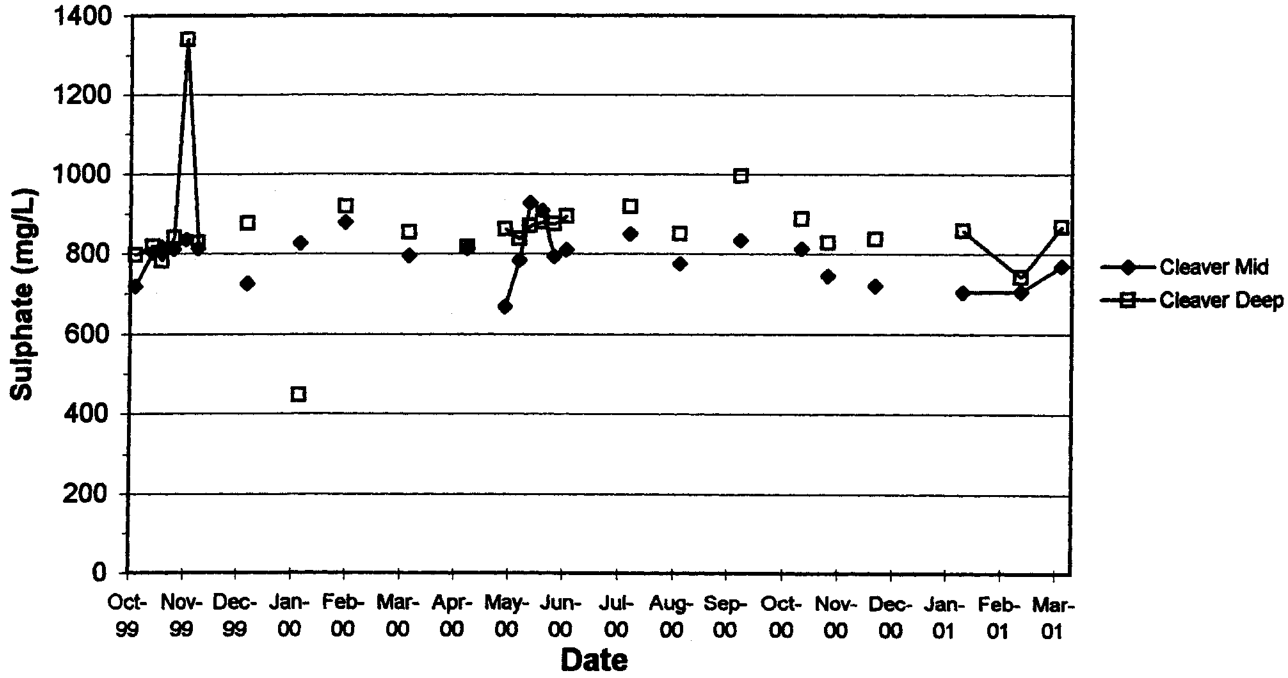
Conductivity on the Surface, Inflow and Outflow of Cleaver Lake



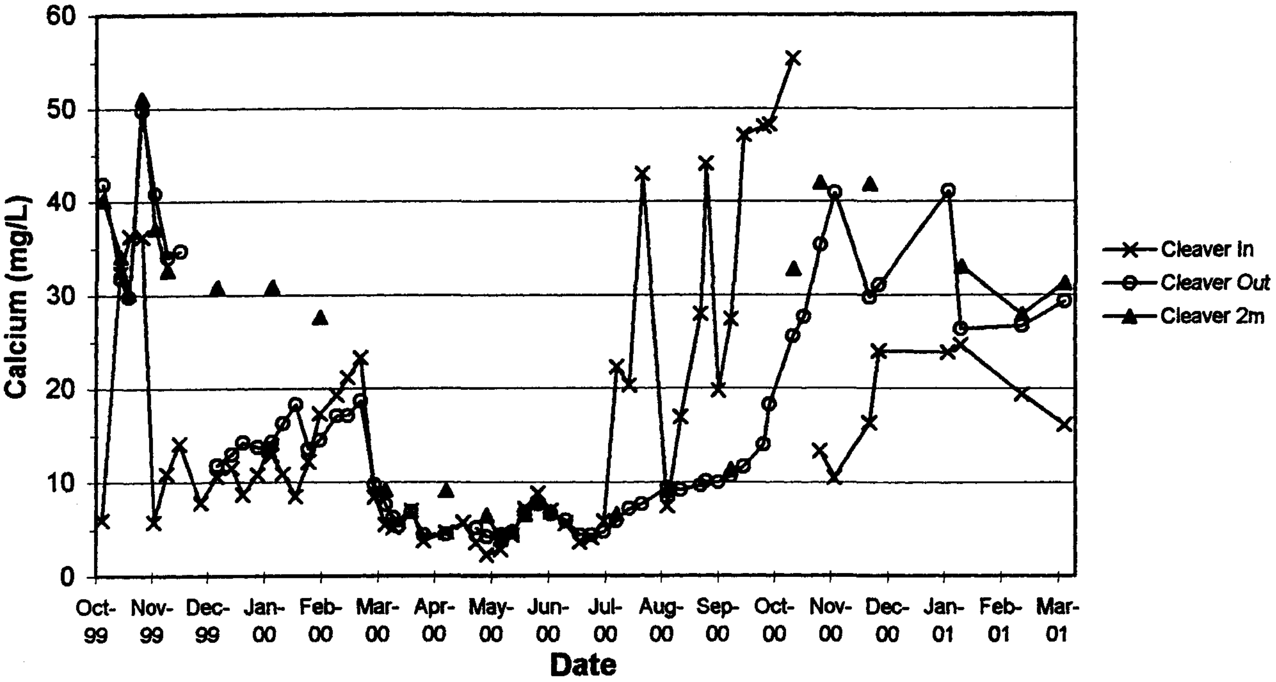
Conductivity of Cleaver Lake Mid and Deep Depths



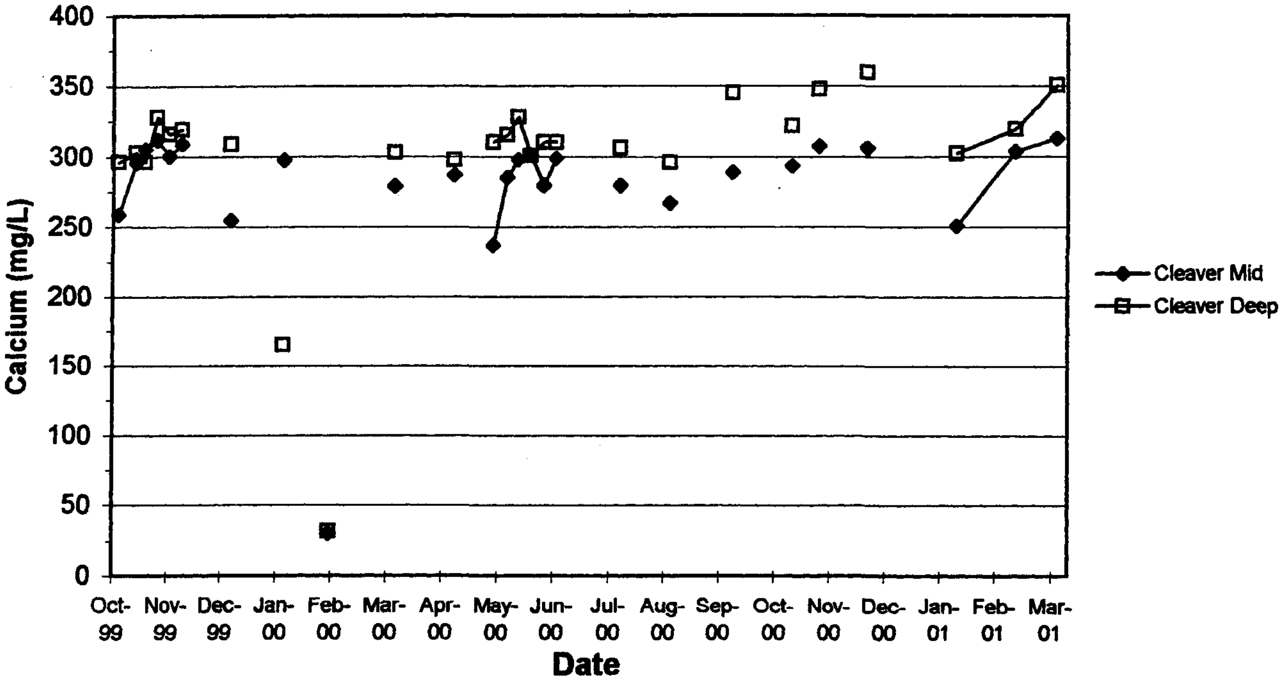
Sulphate on the Surface, Inflow and Outflow of Cleaver Lake



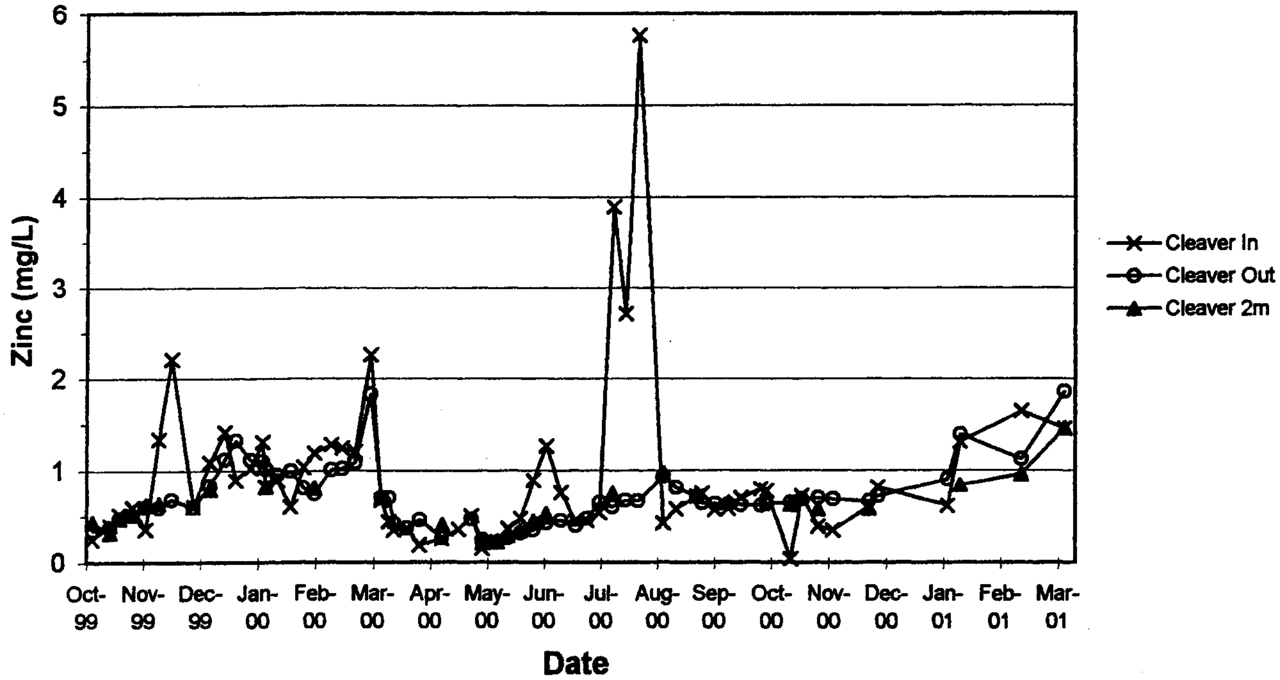
Sulphate of Cleaver Lake Mid and Deep Depths



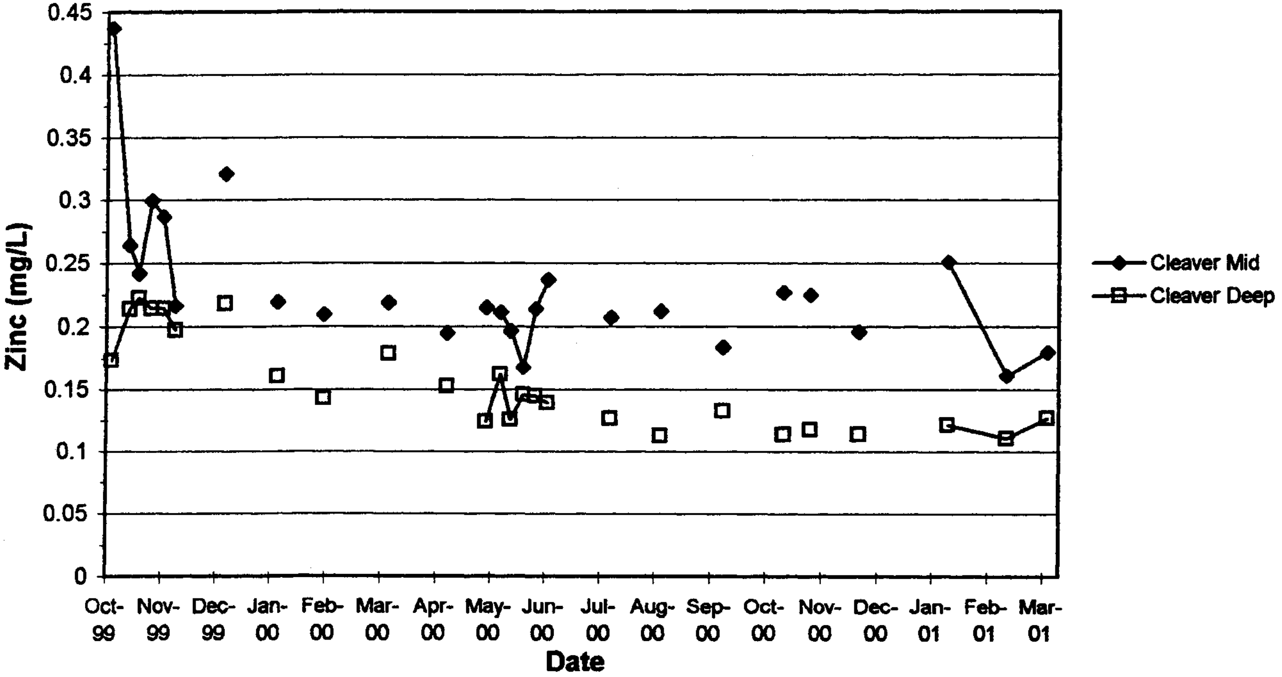
Calcium on the Surface, Inflow and Outflow of Cleaver Lake



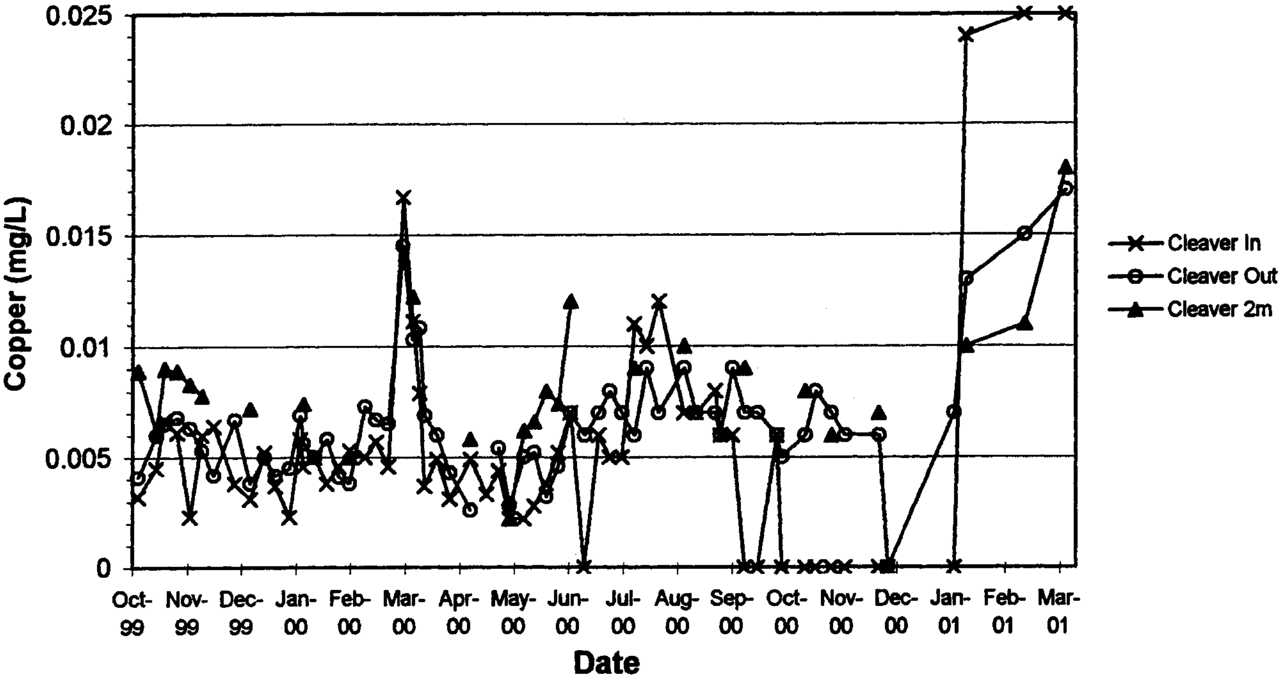
Calcium of Cleaver Lake Mid and Deep Depths



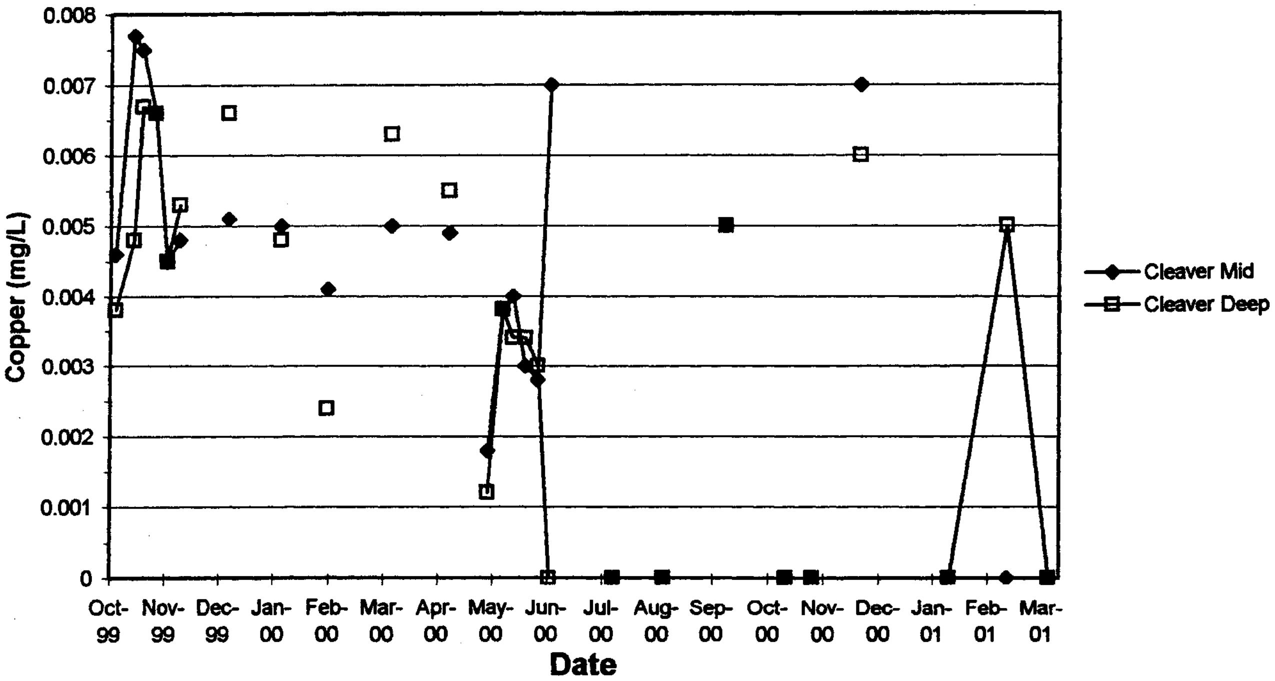
Zinc on the Surface, Inflow and Outflow of Cleaver Lake



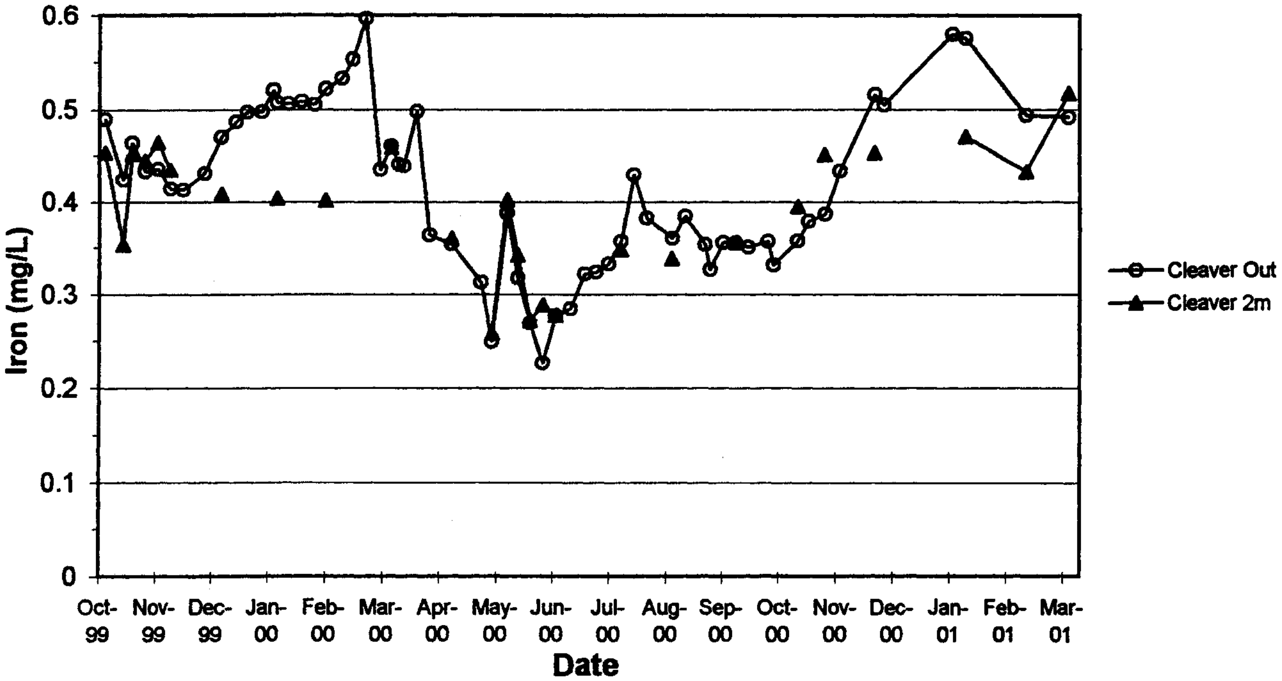
Zinc of Cleaver Lake Mid and Deep Depths



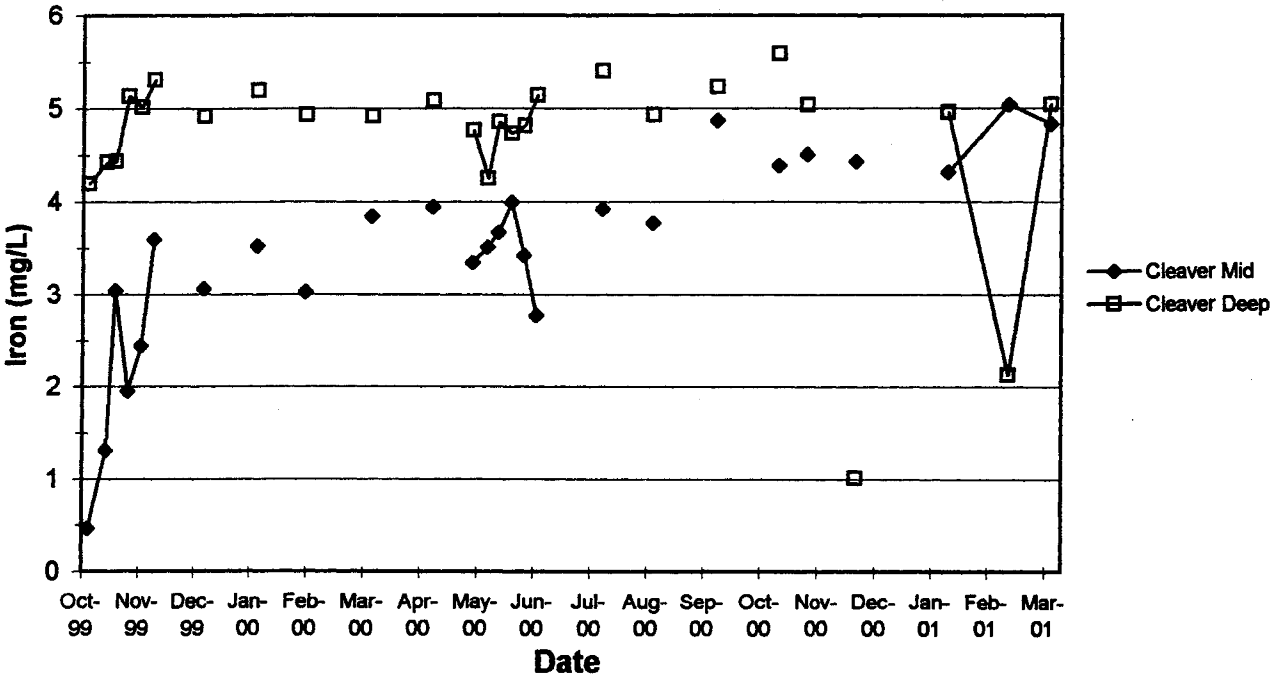
Copper on the Surface, Inflow and Outflow of Cleaver Lake



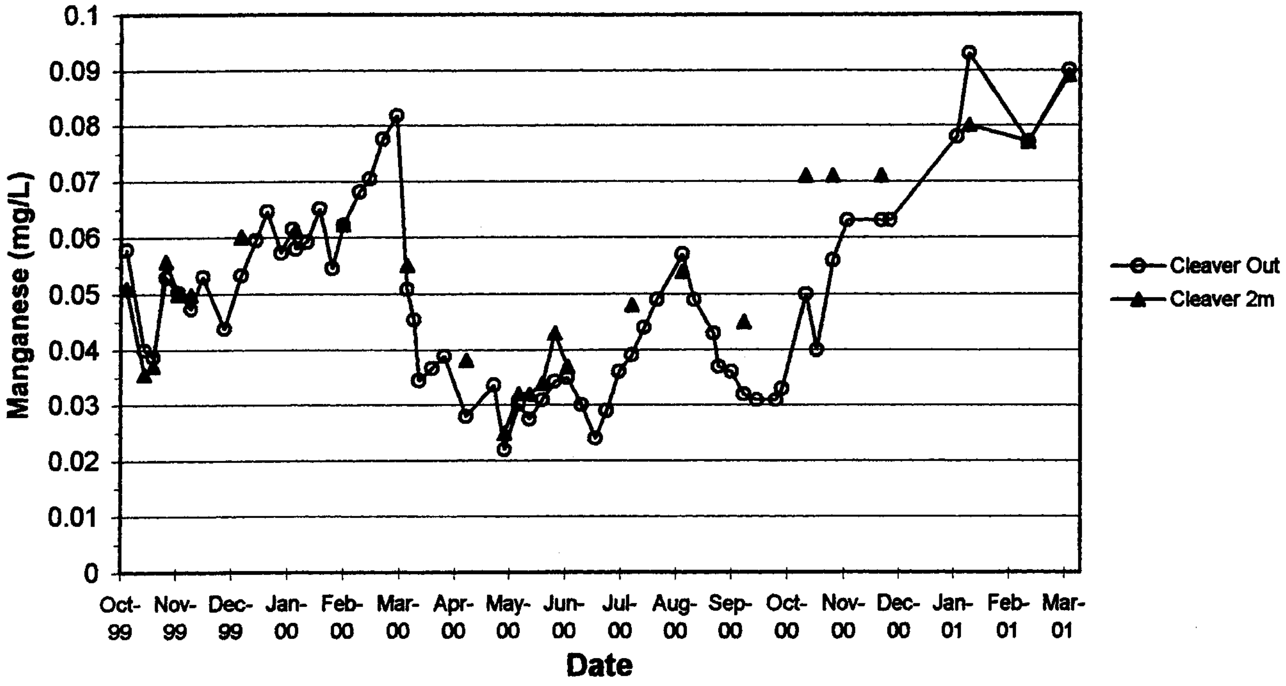
Copper of Cleaver Lake Mid and Deep Depths



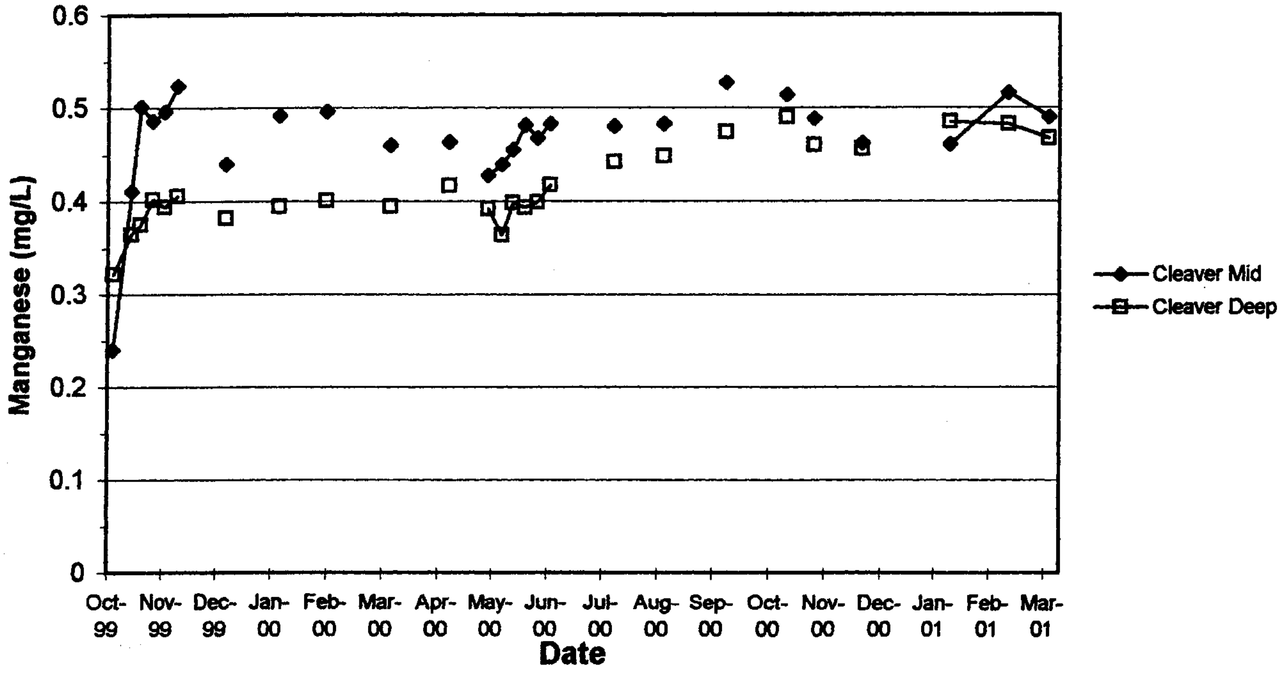
Iron on the Surface and Outflow of Cleaver Lake



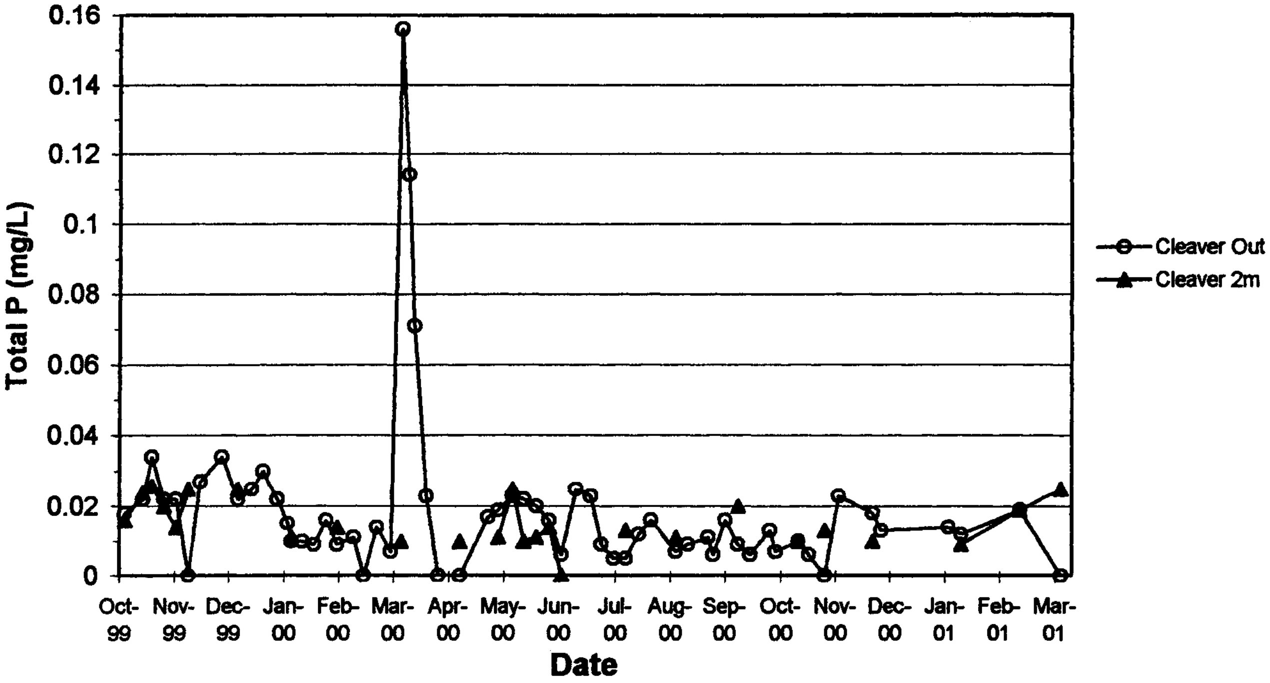
Iron of Cleaver Lake Mid and Deep Depths



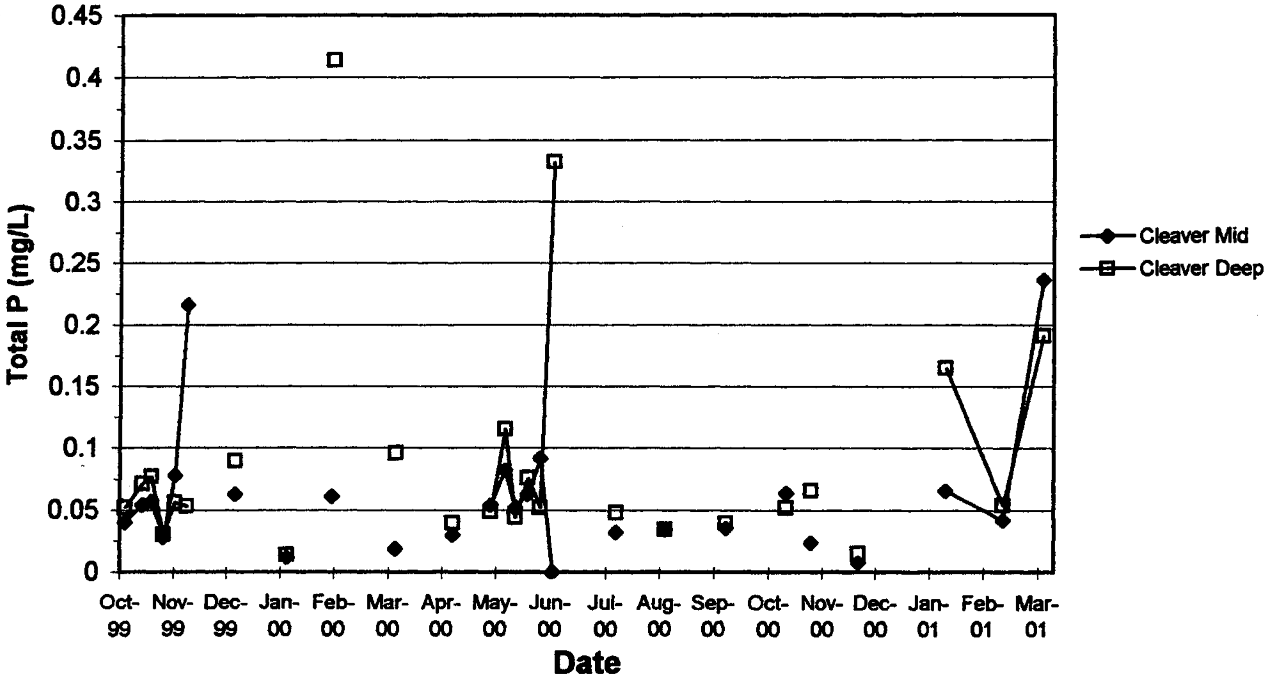
Manganese on the Surface and Outflow of Cleaver Lake



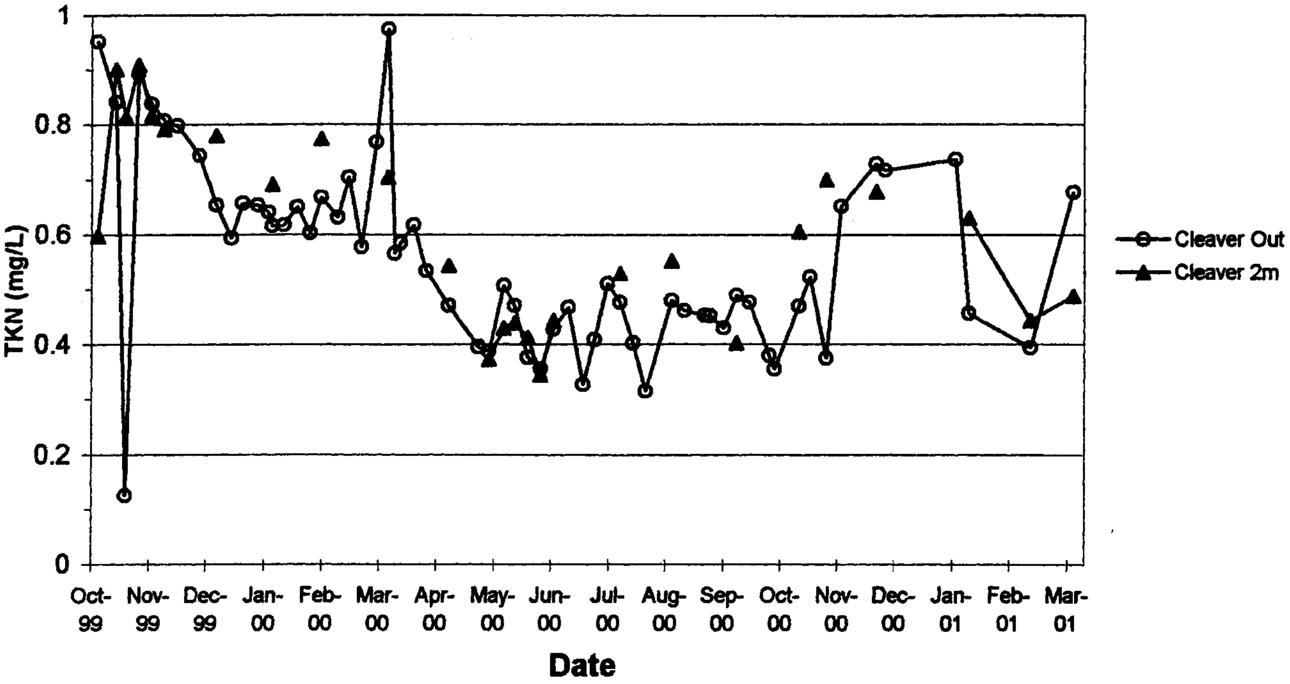
Manganese of Cleaver Lake Mid and Deep Depths



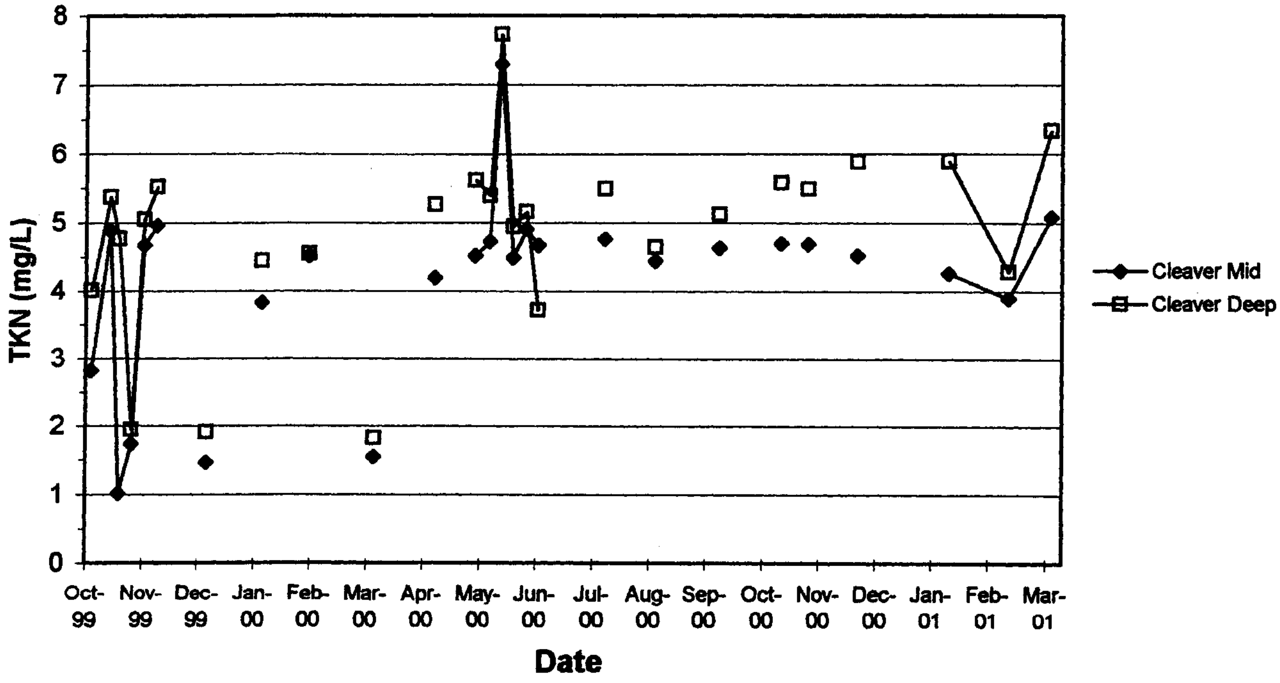
Total Phosphorus on the Surface and Outflow of Cleaver Lake



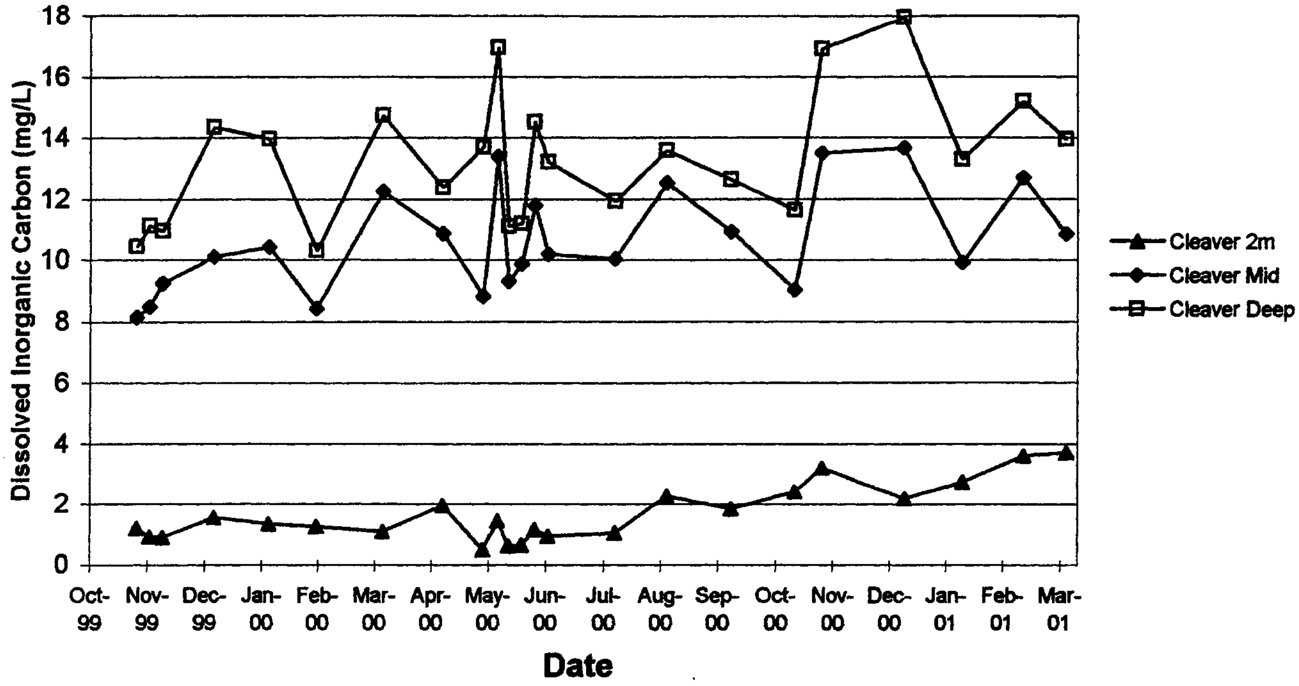
Total Phosphorus of Cleaver Lake Mid and Deep Depths



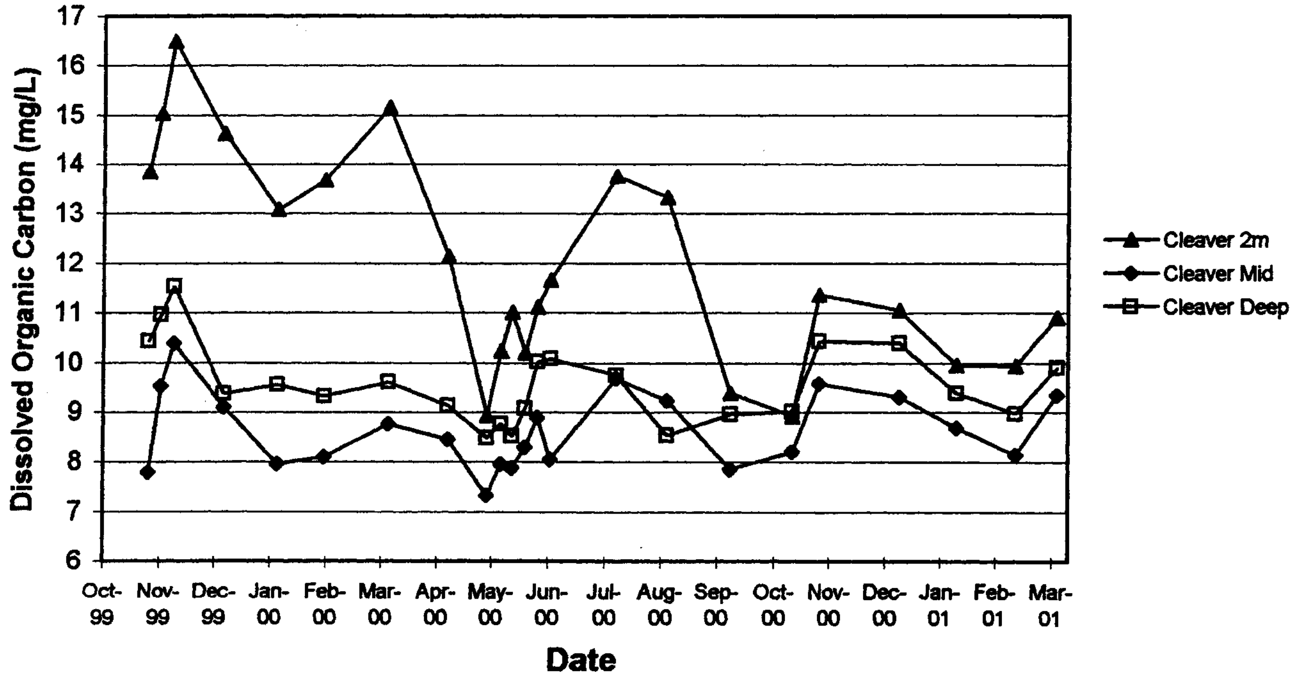
Total Kjeldahl Nitrogen on the Surface and Outflow of Cleaver Lake



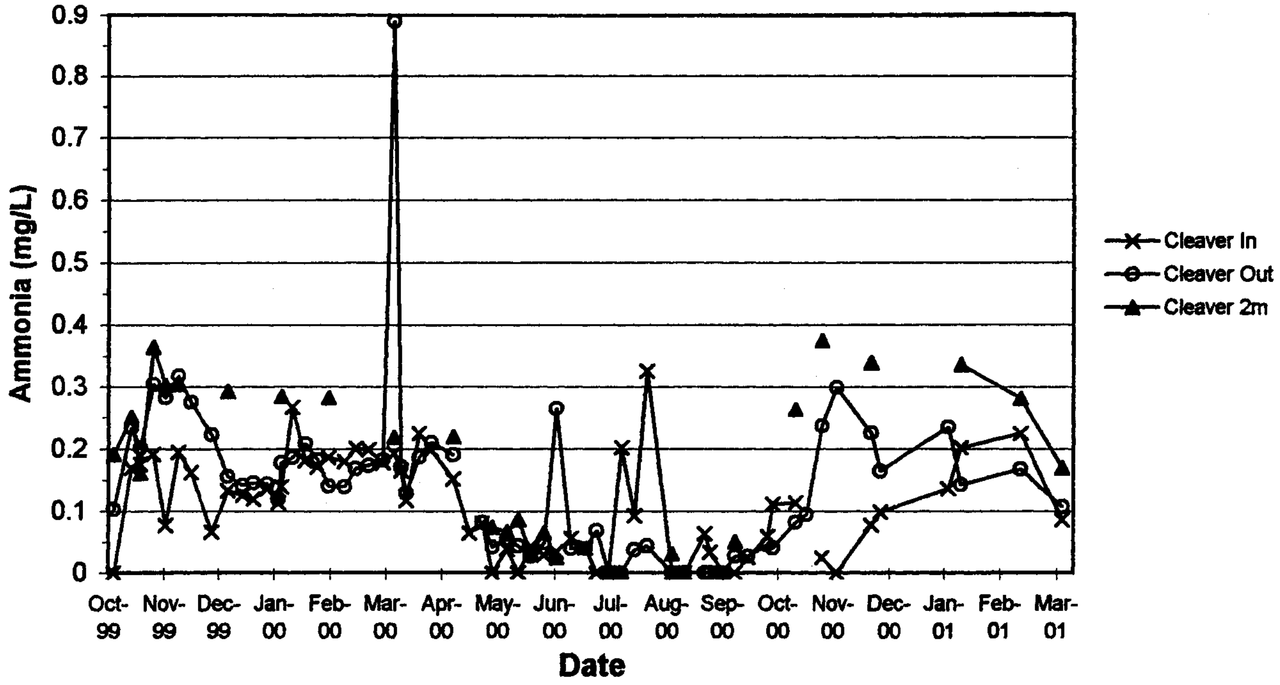
Total Kjeldahl Nitrogen of Cleaver Lake Mid and Deep Depths



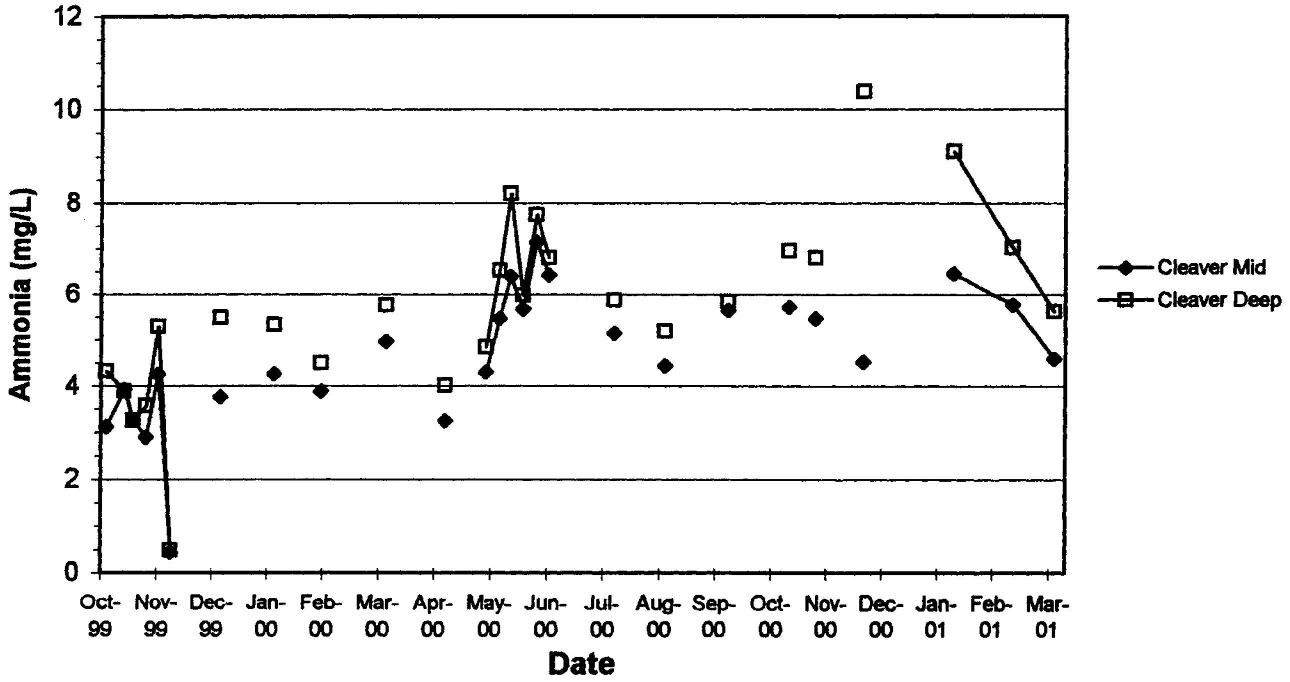
Dissolved inorganic carbon of Cleaver Lake



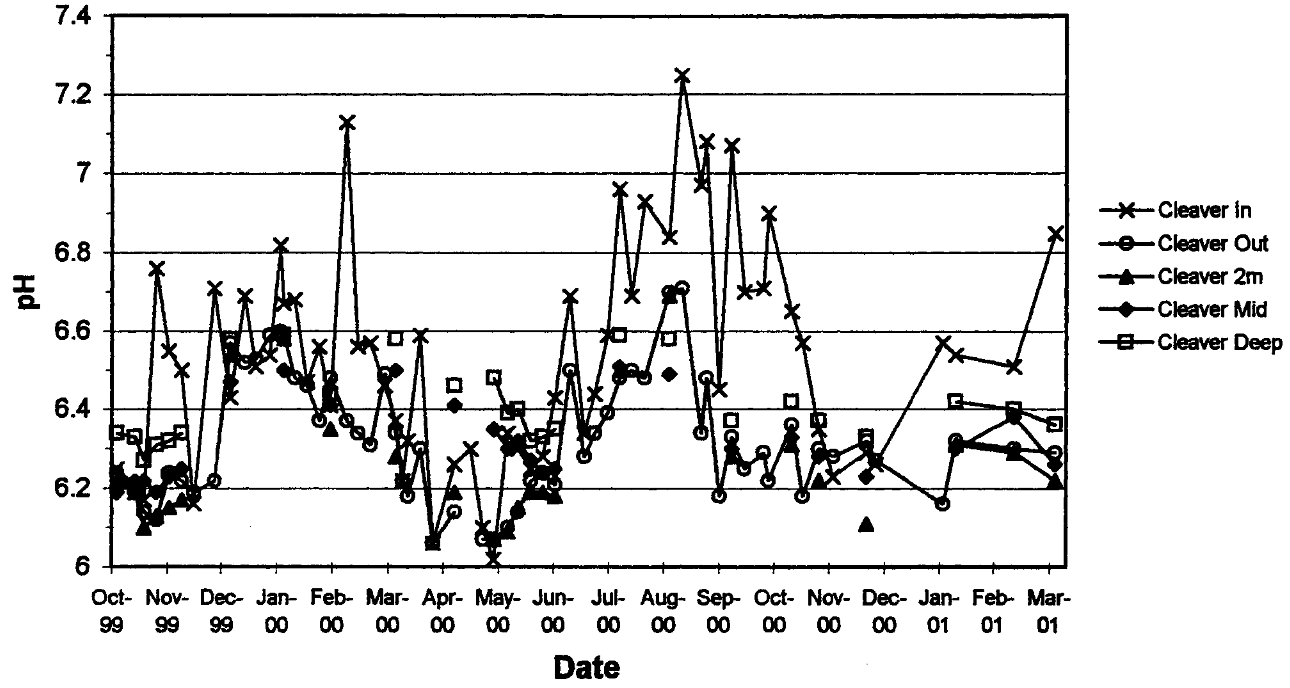
Dissolved organic carbon of Cleaver Lake



Ammonia on the Surface, Inflow and Outflow of Cleaver Lake



Ammonia of Cleaver Lake Mid and Deep Depths



pH of Cleaver Lake, Including Inflow and Outflow

Appendix C

The following are plots of Horneblende Lake analytes in time. Each parameter is in mg/L except for conductivity (µs/cm) and pH.

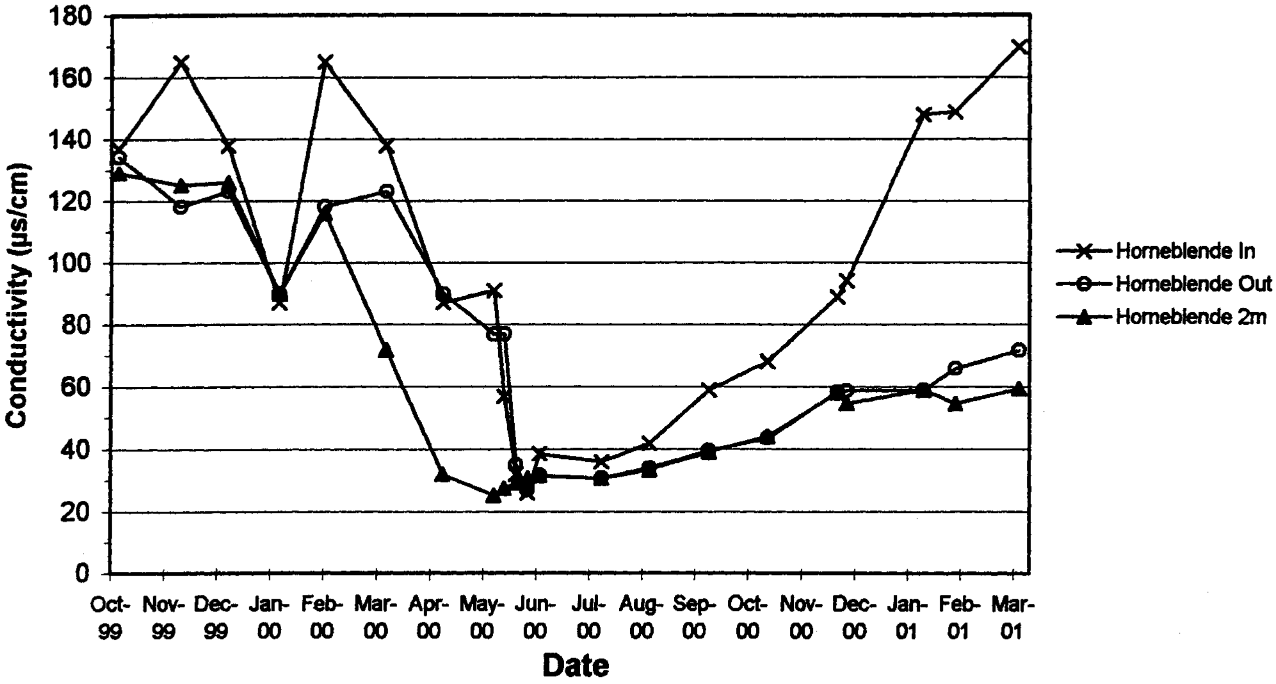


Figure: Conductivity on the Surface, Inflow and Outflow of Hornblende Lake

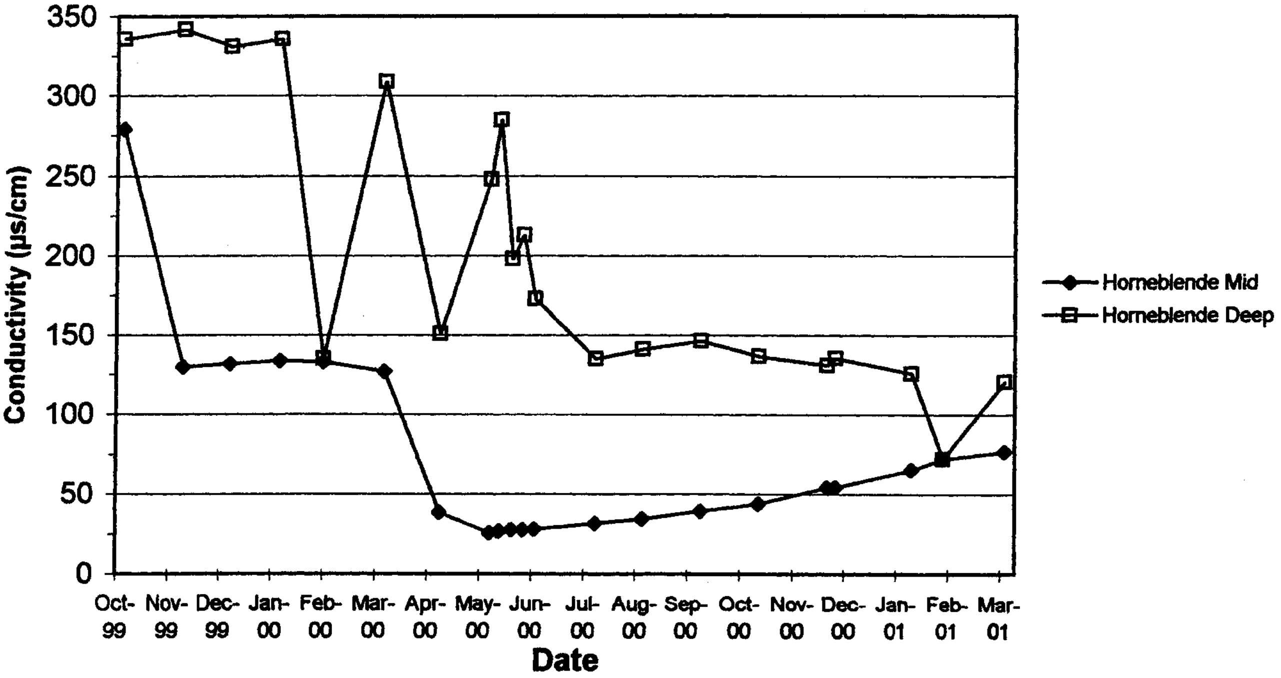


Figure: Conductivity of Horneblende Lake Mid and Deep Depths

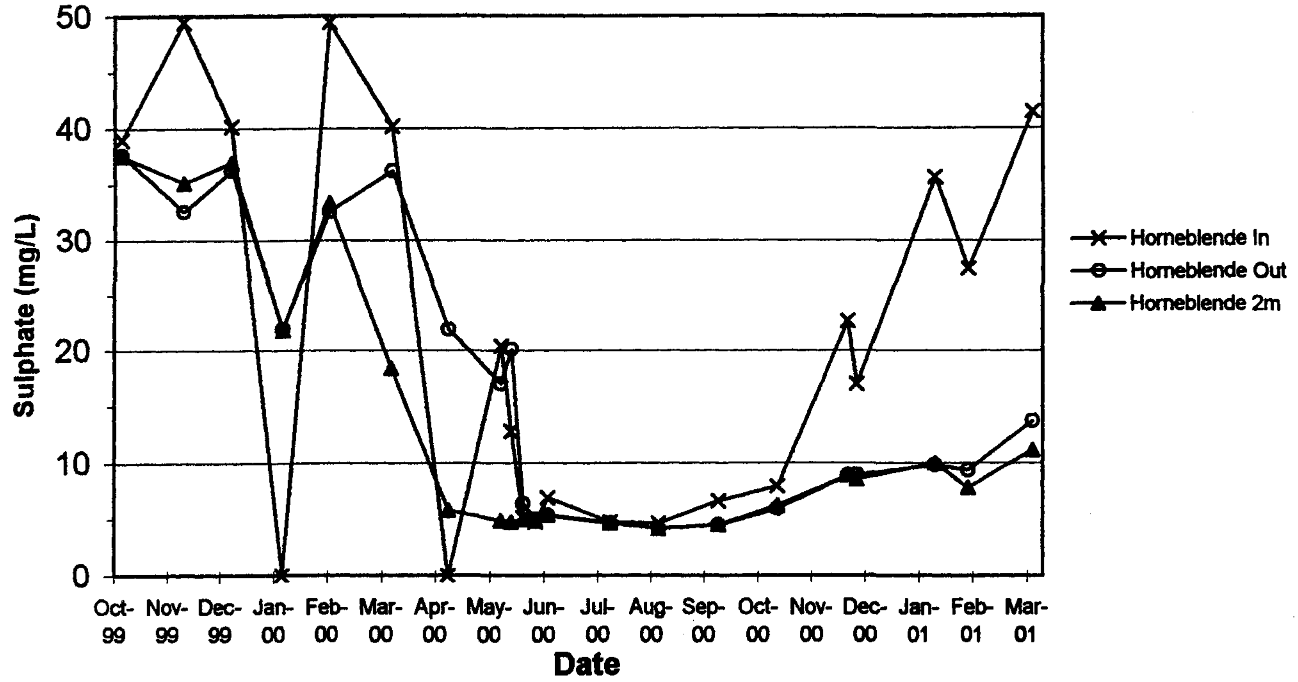


Figure: Sulphate on the Surface, Inflow and Outflow of Hornblende Lake

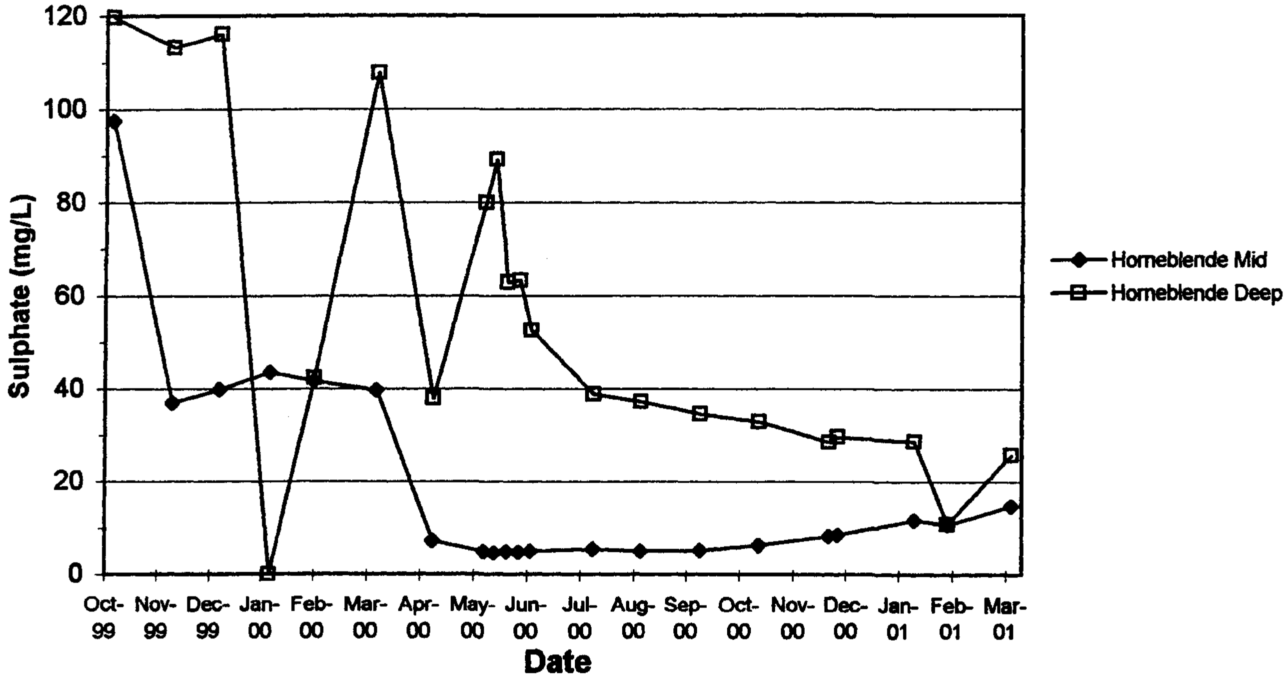


Figure: Sulphate of Horneblende Lake Mid and Deep Depths

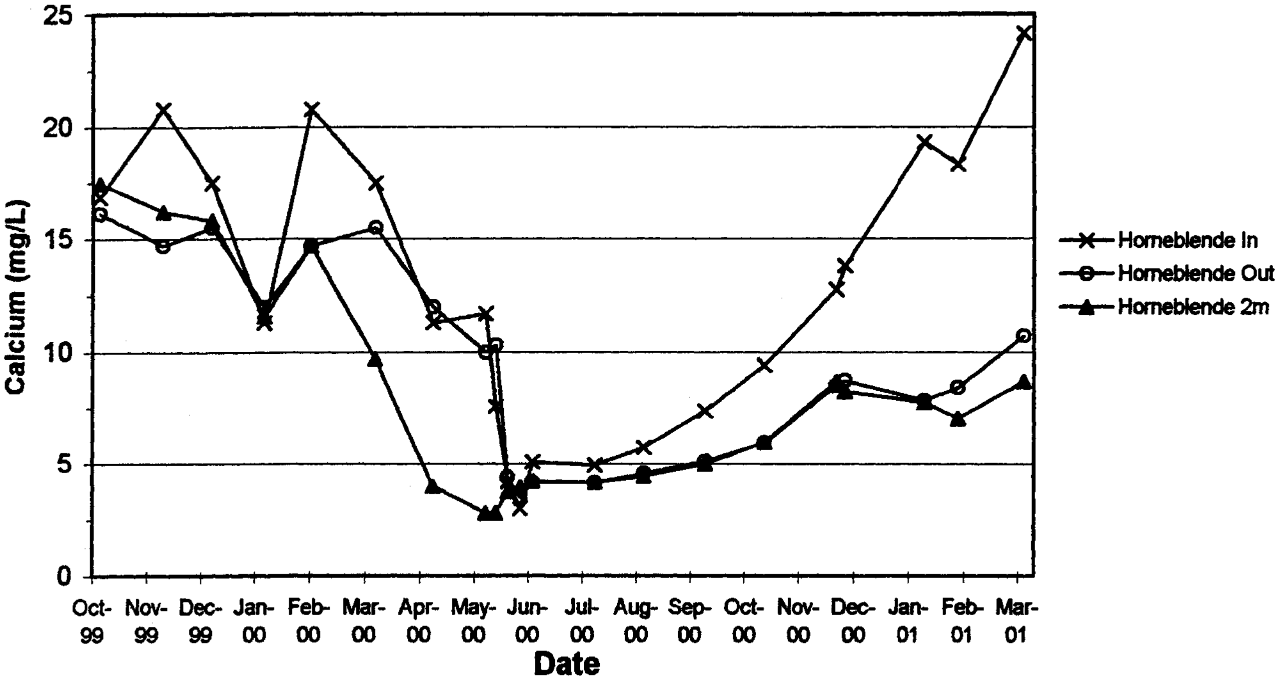


Figure: Calcium on the Surface, Inflow and Outflow of Hornblende Lake

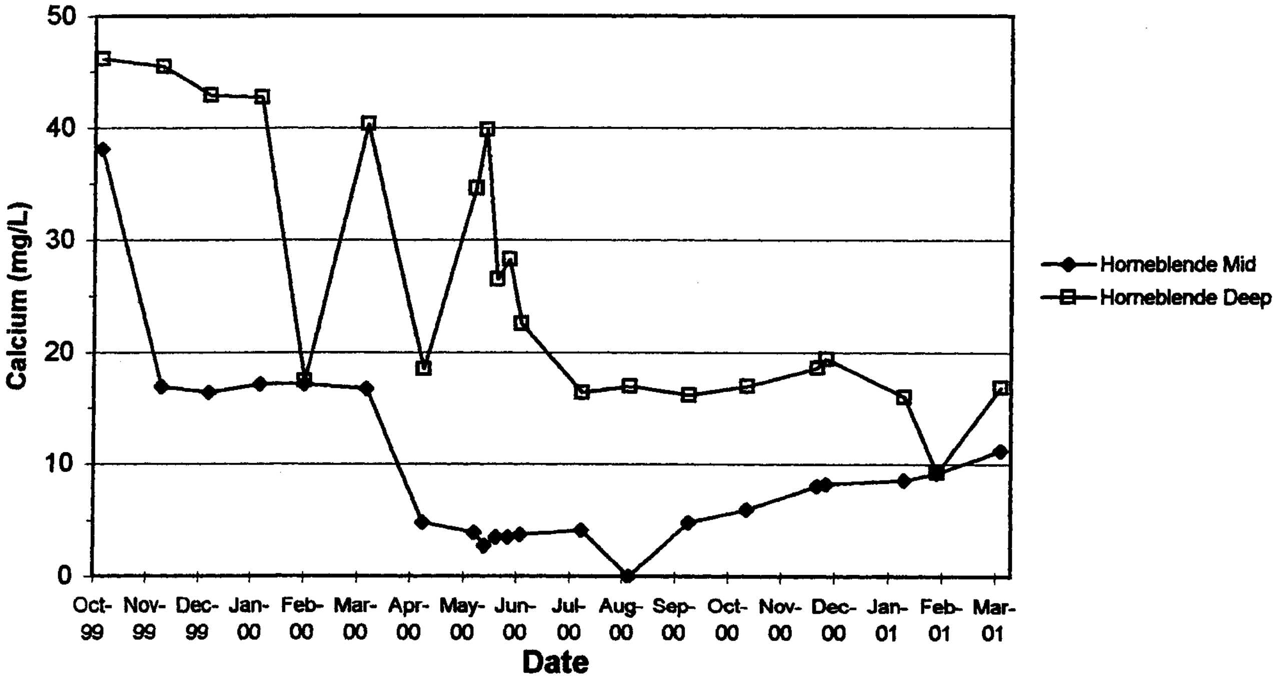


Figure: Calcium of Horneblende Lake Mid and Deep Depths

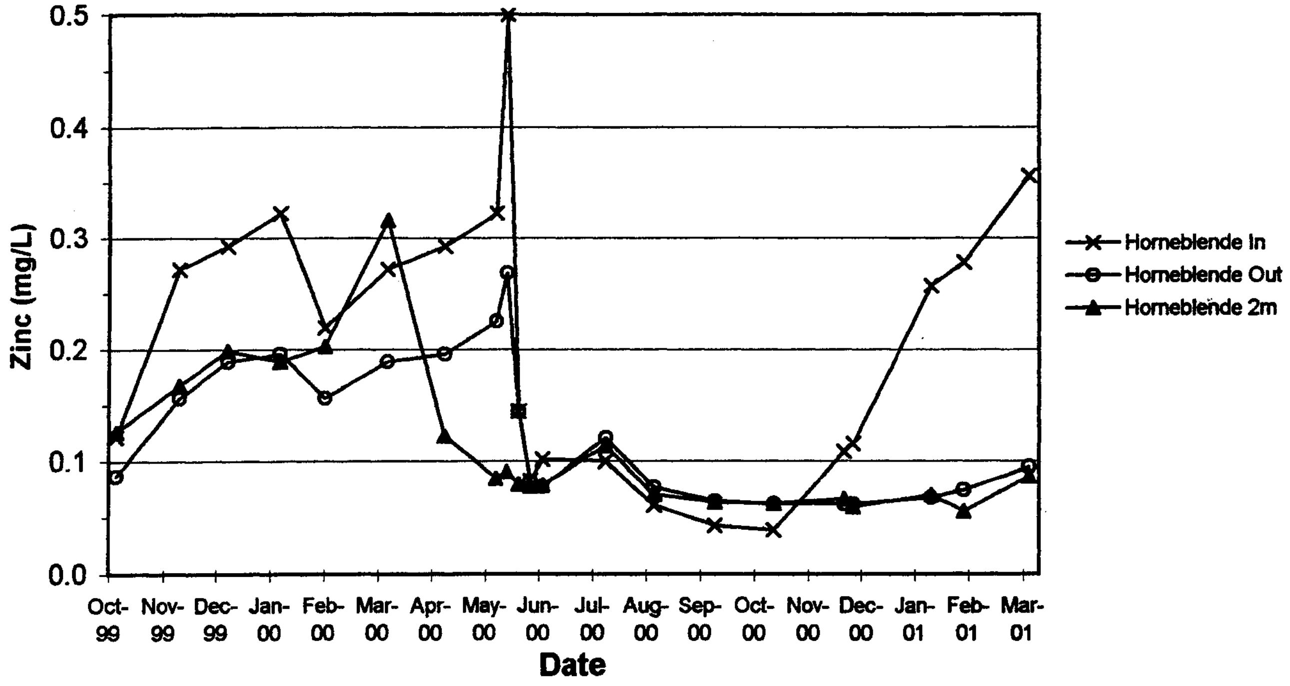


Figure: Zinc on the Surface, Inflow and Outflow of Hornblende Lake

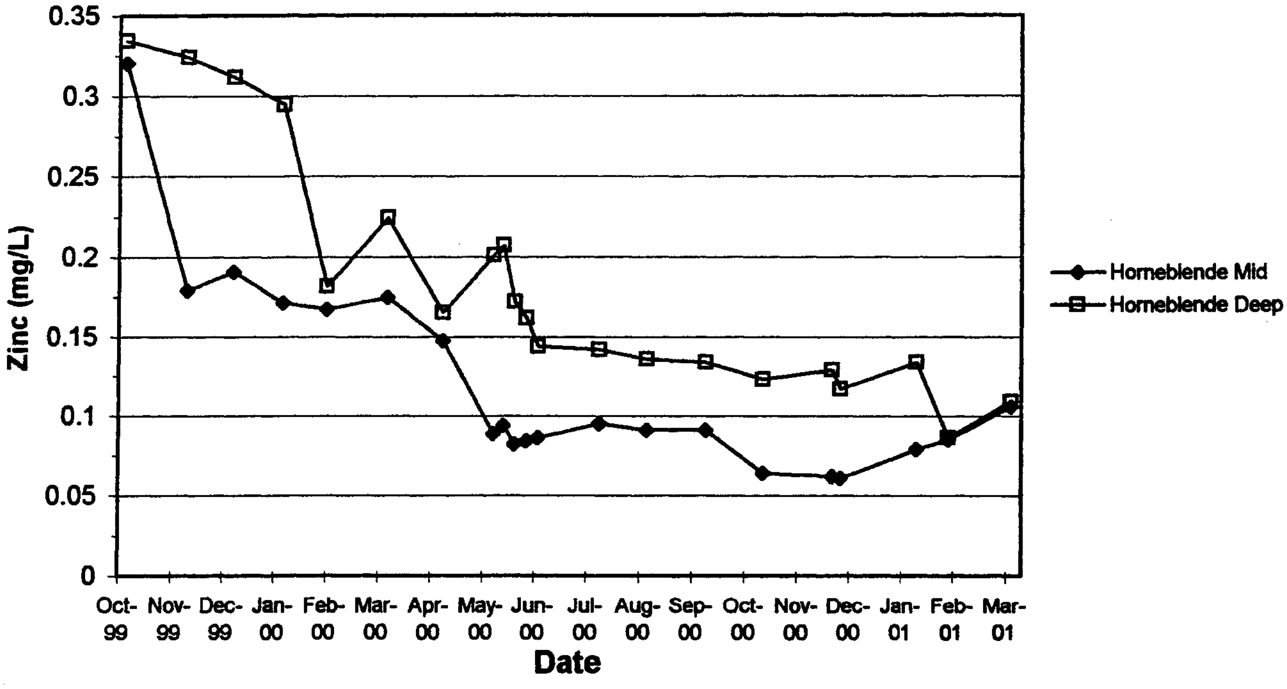


Figure: Zinc of Horneblende Lake Mid and Deep Depths

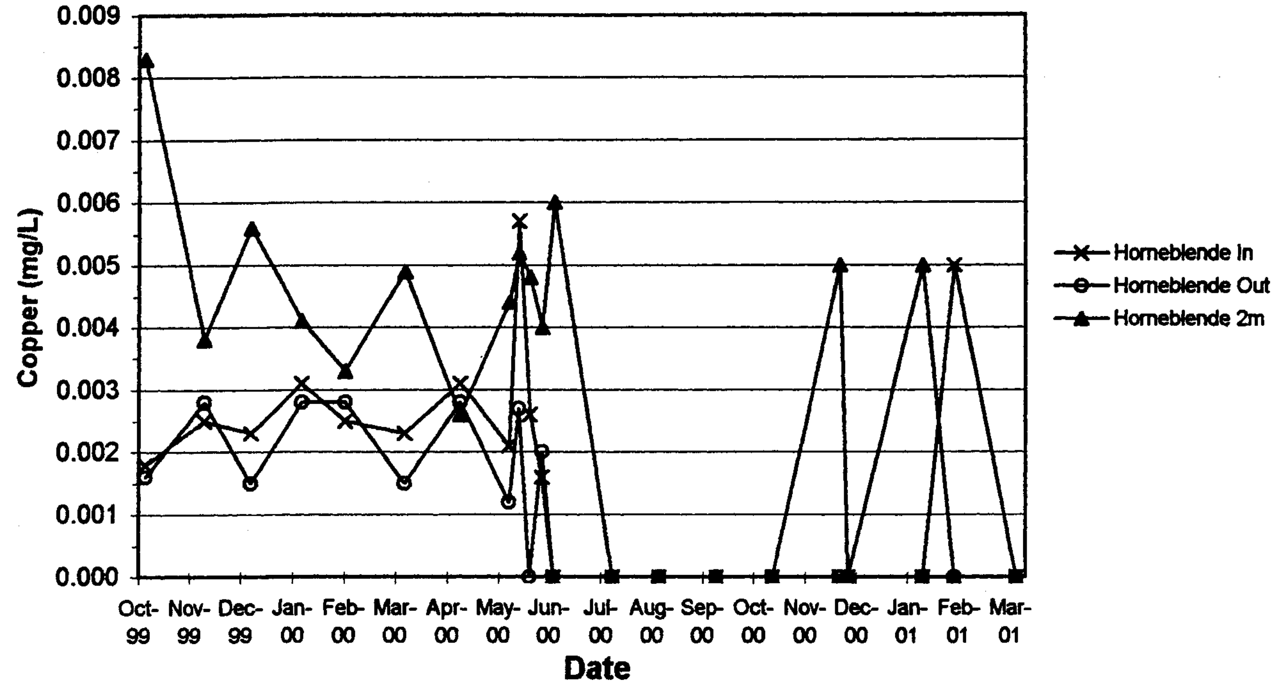


Figure: Copper on the Surface, Inflow and Outflow of Hornblende Lake

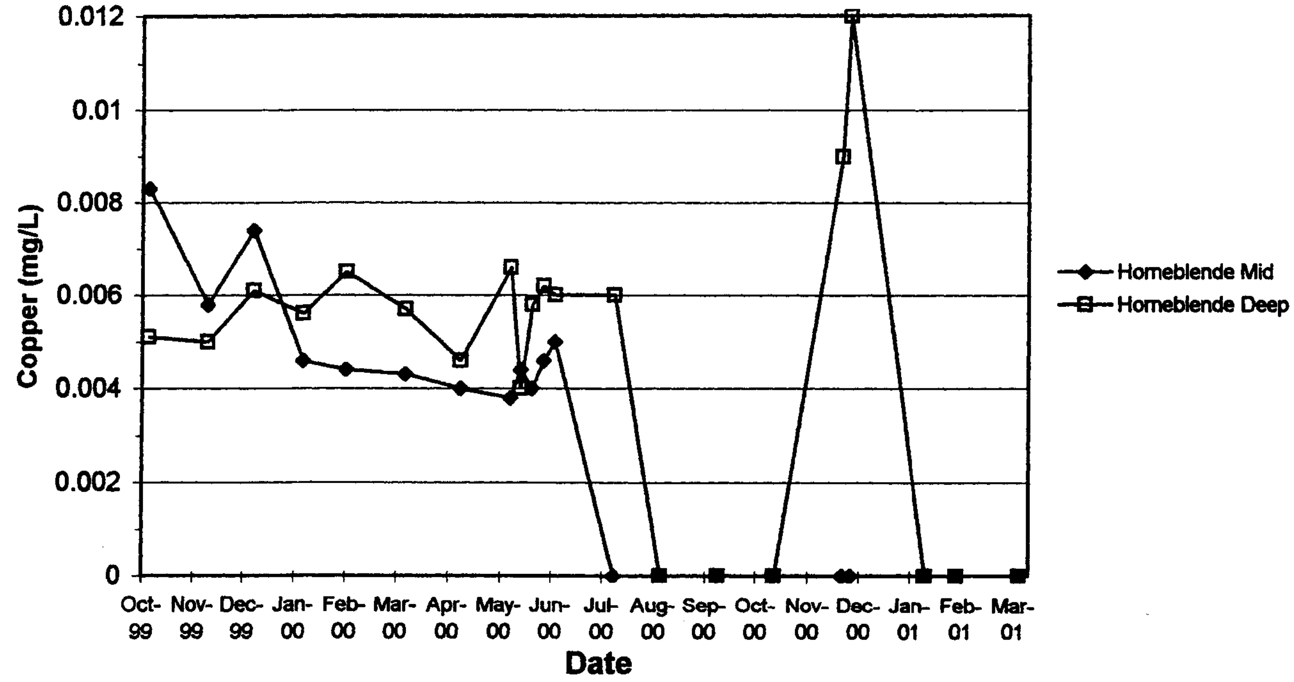


Figure: Copper of Horneblende Lake Mid and Deep Depths

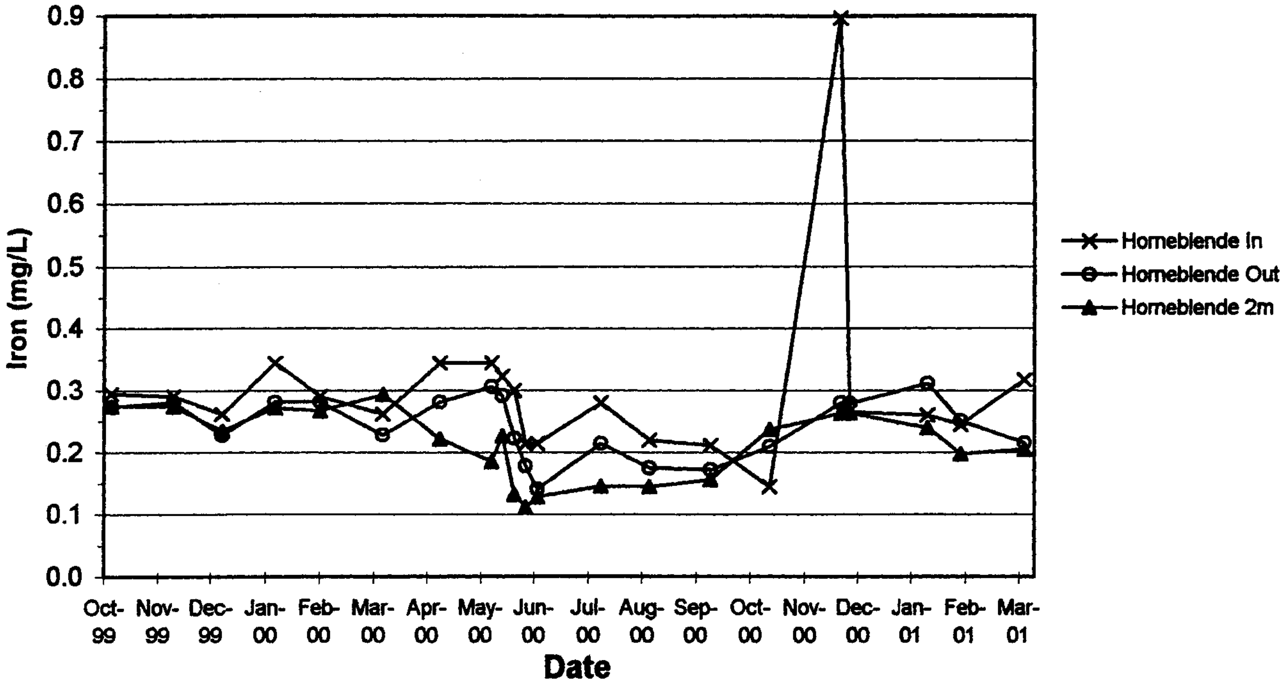


Figure: Iron on the Surface, Inflow and Outflow of Hornblende Lake

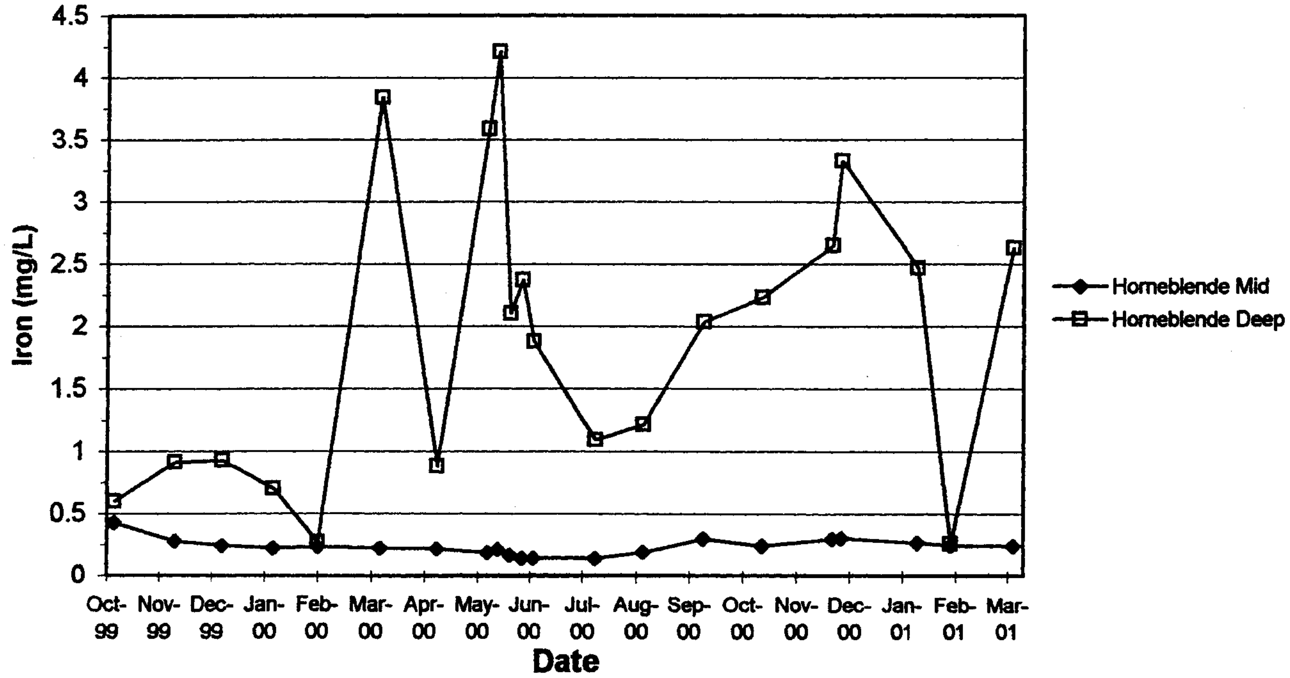


Figure: Iron of Horneblende Lake Mid and Deep Depths

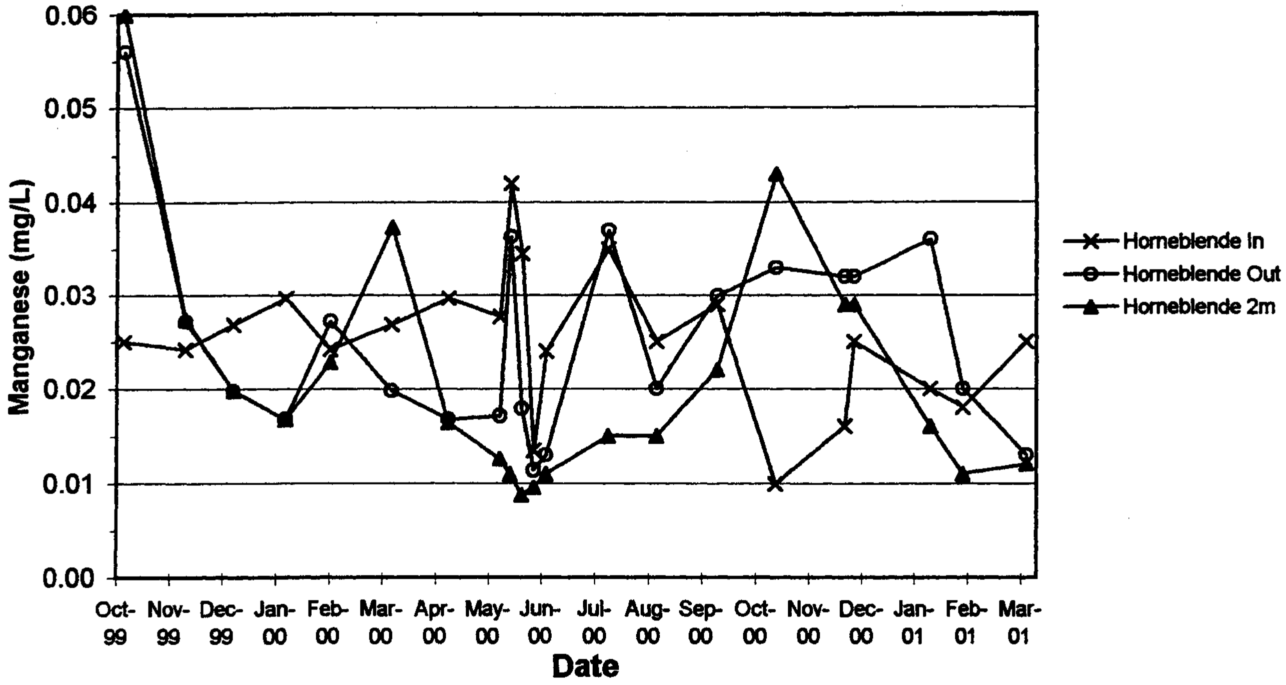


Figure: Manganese on the Surface, Inflow and Outflow of Hornblende Lake

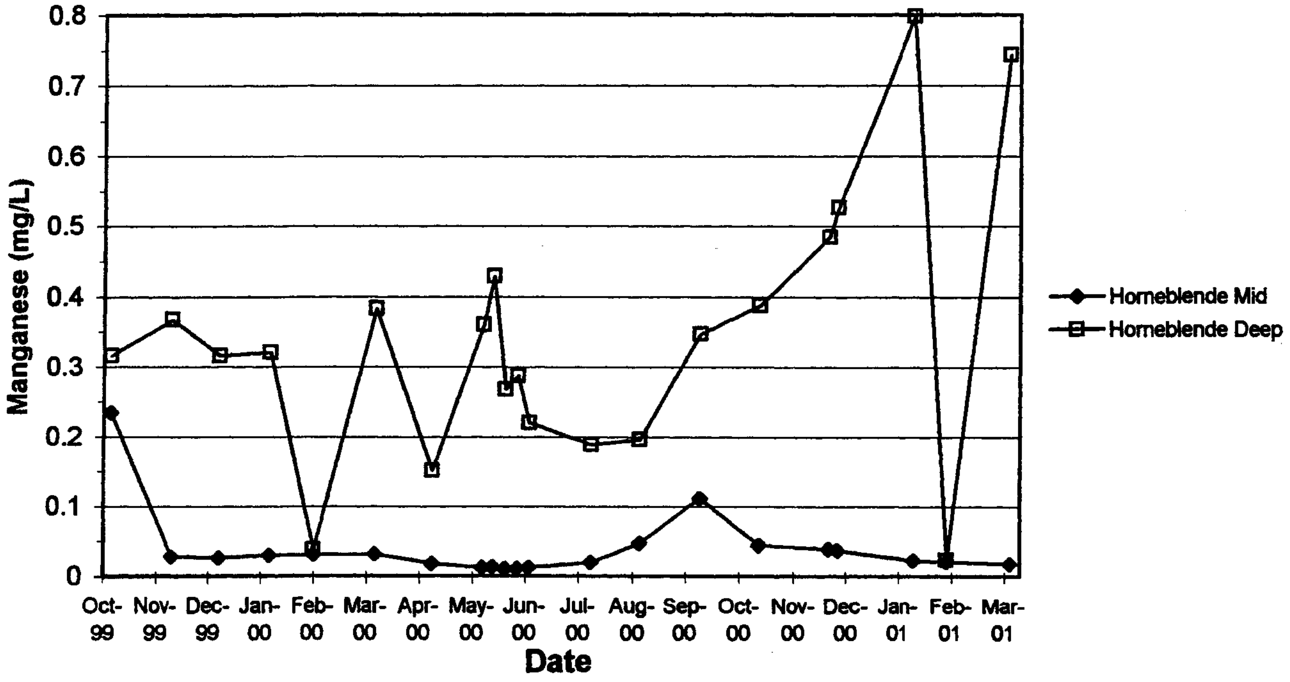


Figure: Manganese of Horneblende Lake Mid and Deep Depths

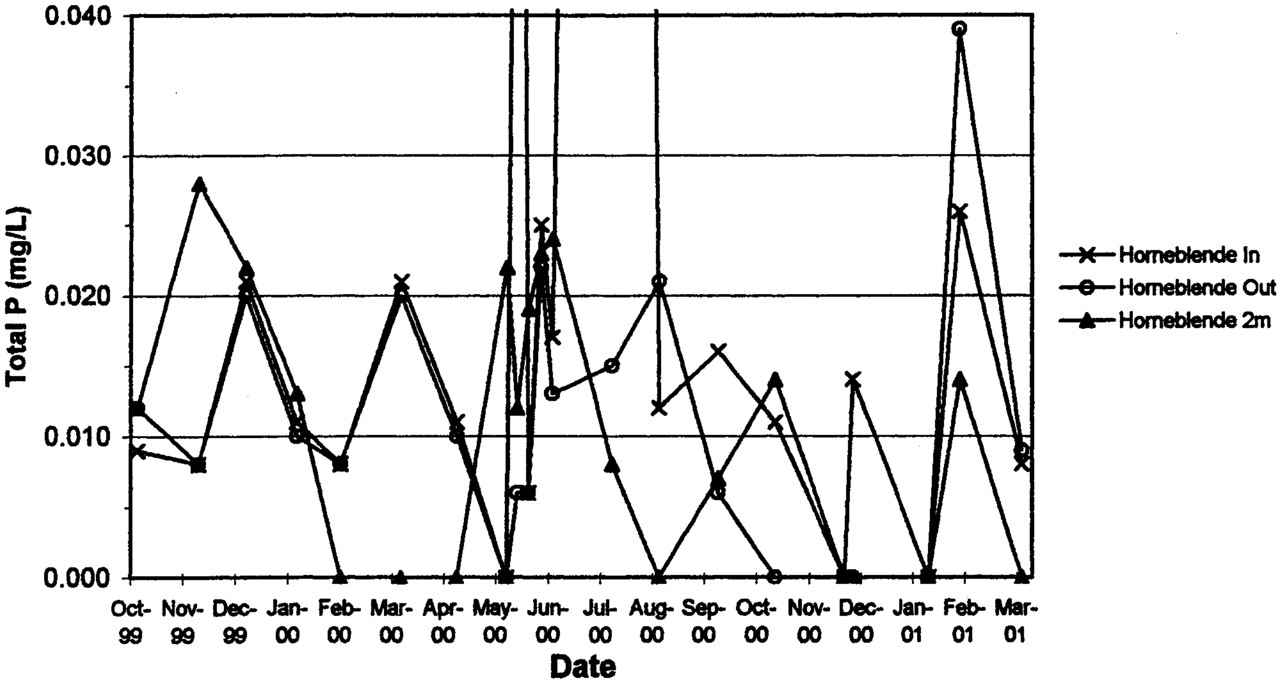


Figure: Total Phosphorus on the Surface, Inflow and Outflow of Hornblende Lake

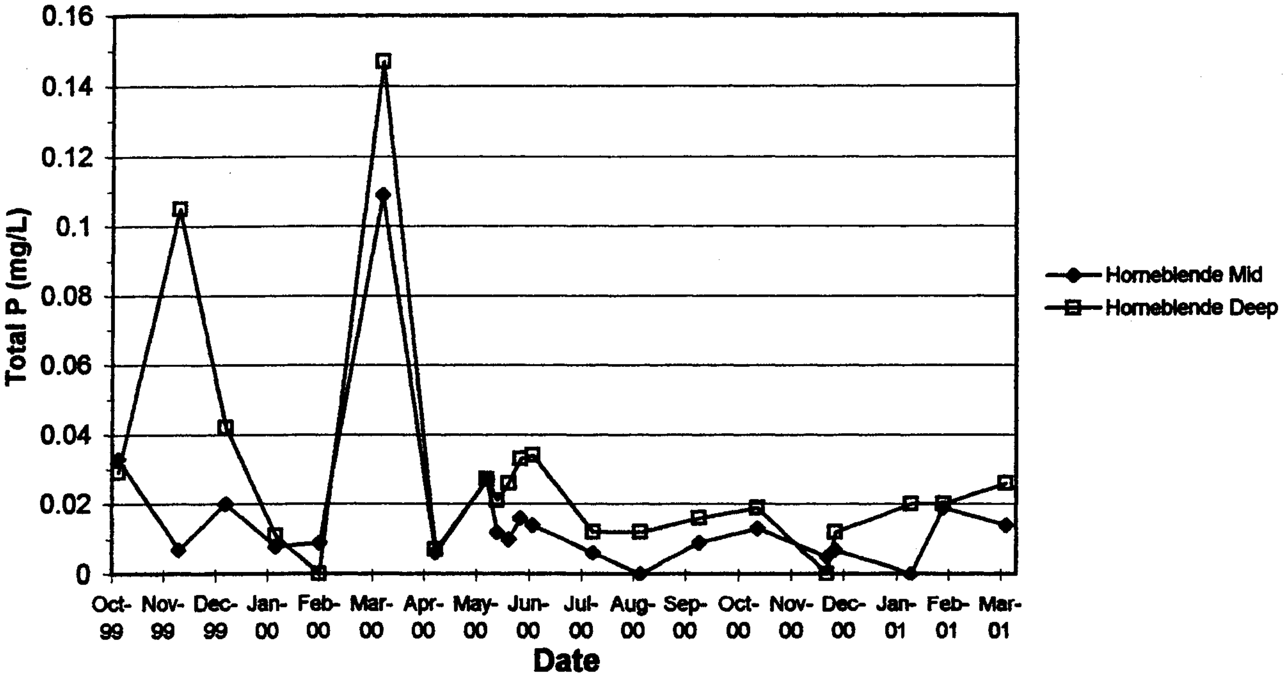


Figure: Total Phosphorus of Horneblende Lake Mid and Deep Depths

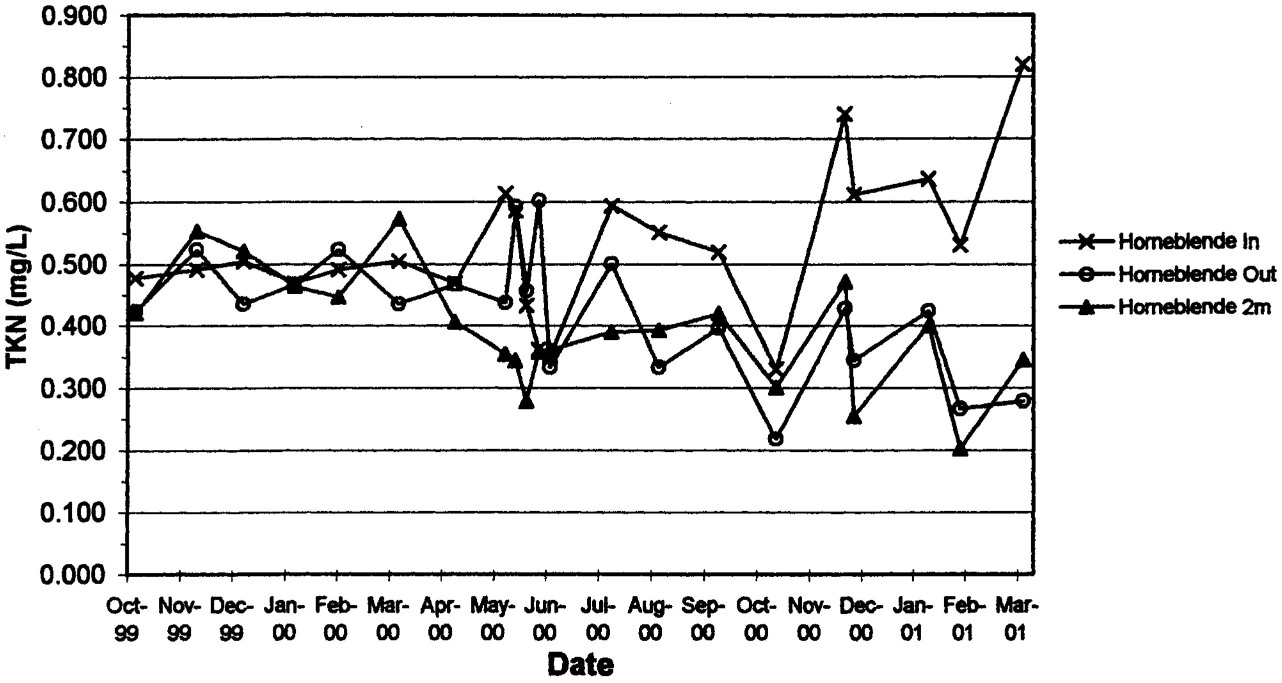


Figure: Total Kjeldahl Nitrogen on the Surface, Inflow and Outflow of Hornblende Lake

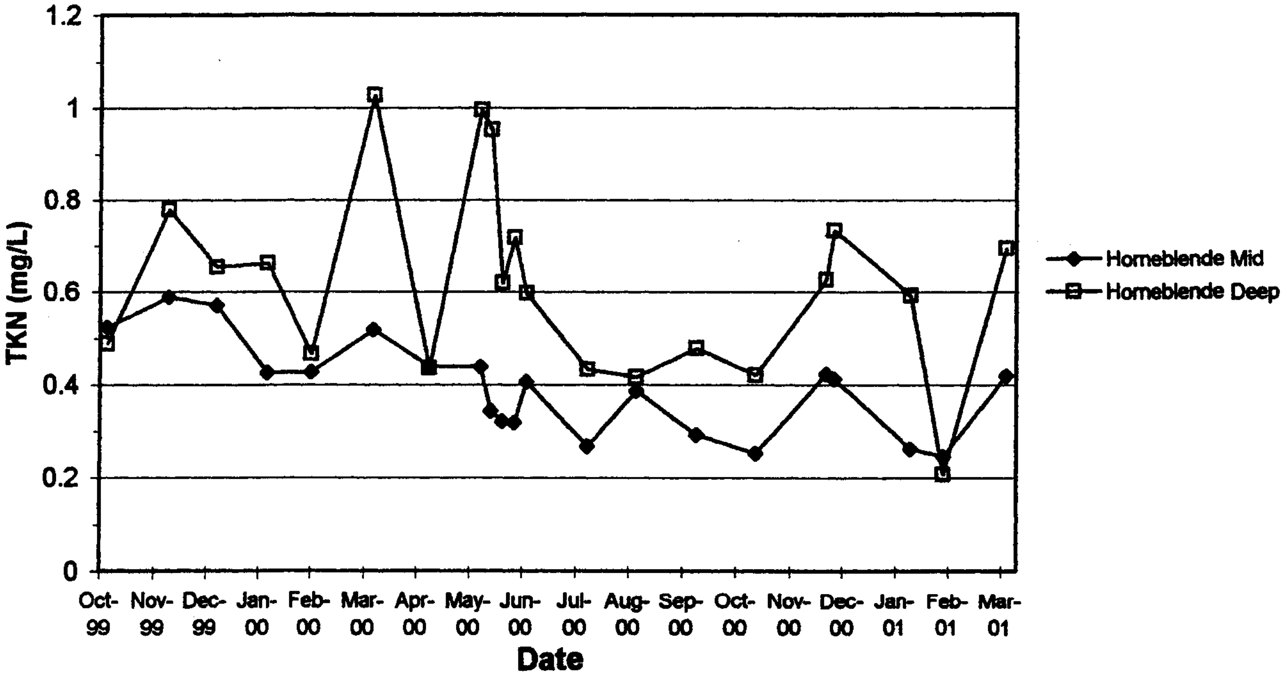


Figure: Total Kjeldahl Nitrogen of Horneblende Lake Mid and Deep Depths

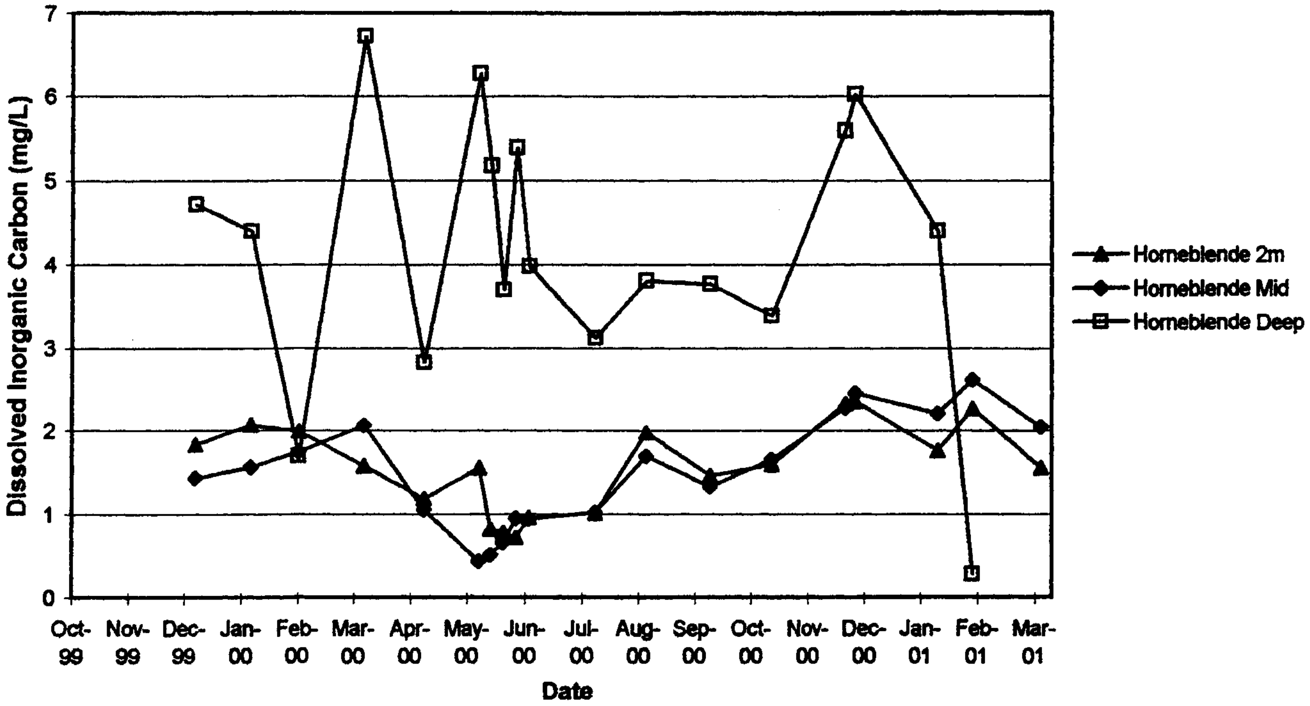


Figure: Dissolved Inorganic Carbon in Horneblende Lake

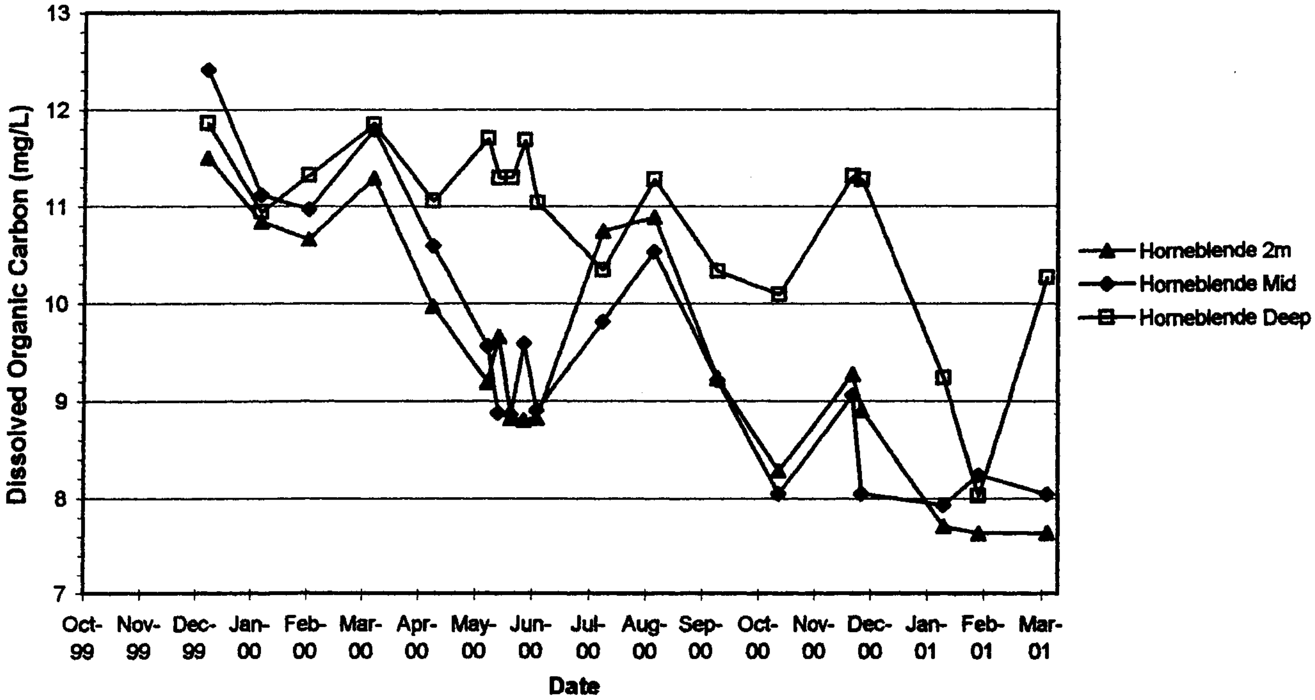


Figure: Dissolved Organic Carbon in Horneblende Lake

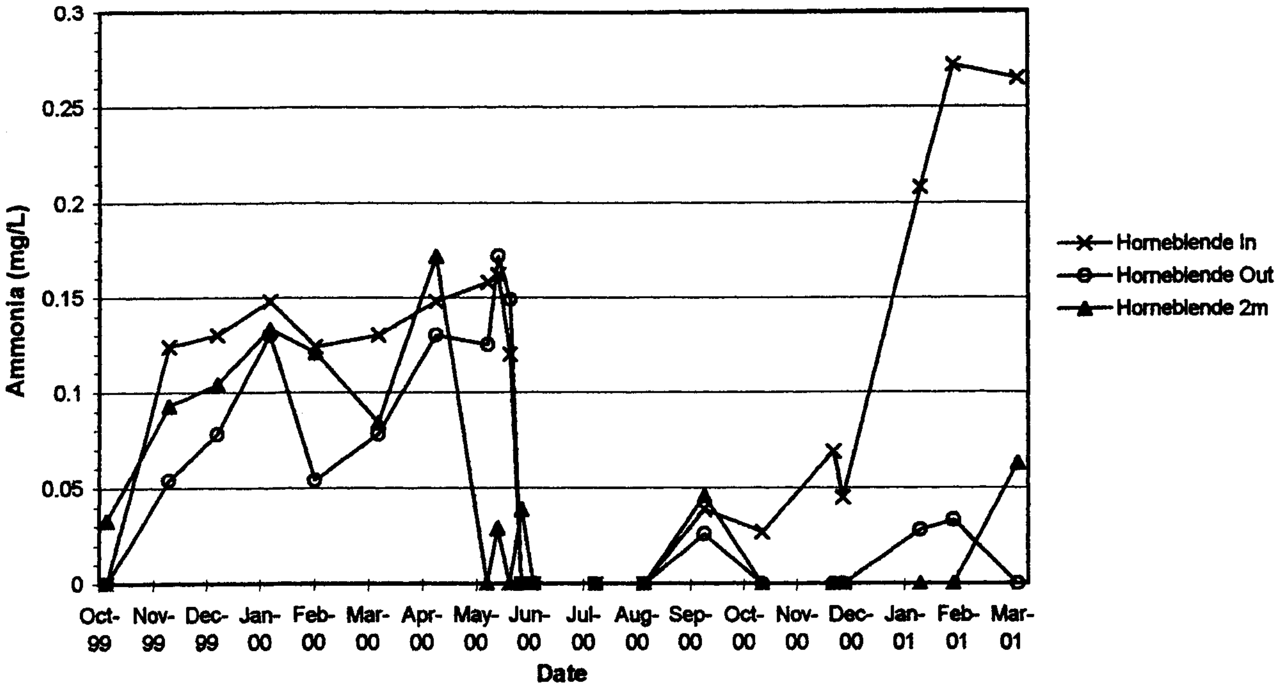


Figure: Ammonia on the Surface, Inflow and Outflow of Hornblende Lake

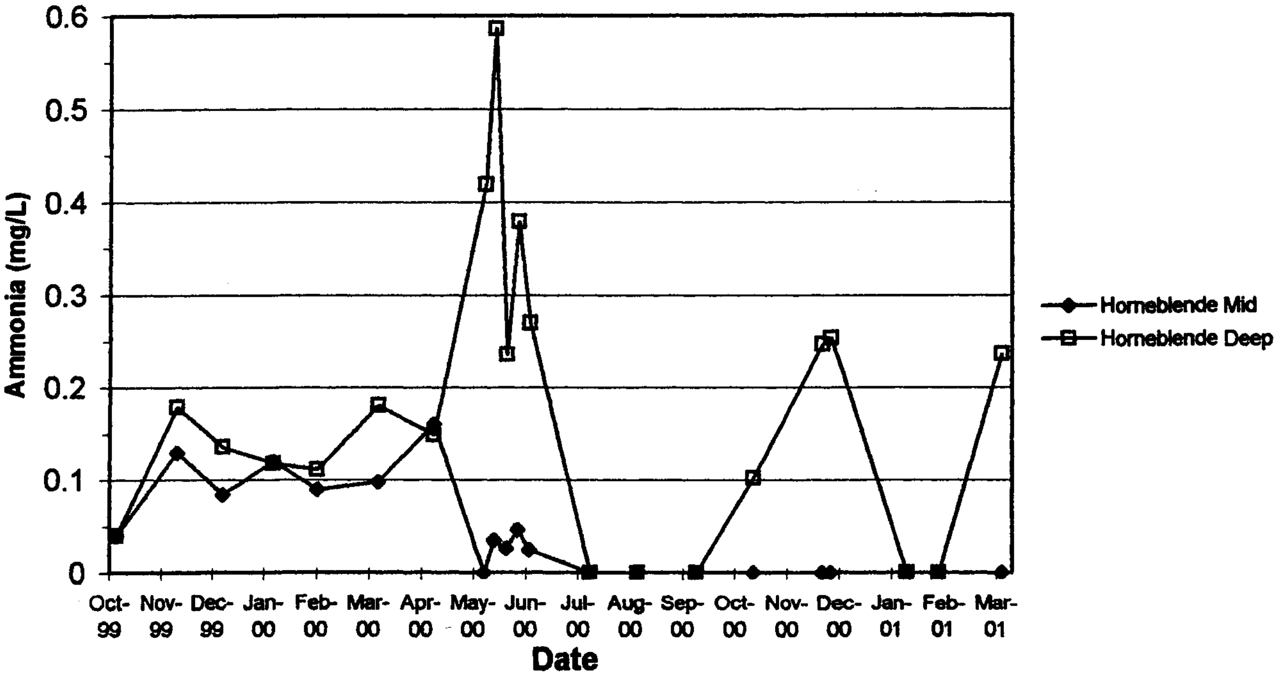


Figure: Ammonia of Horneblende Lake Mid and Deep Depths

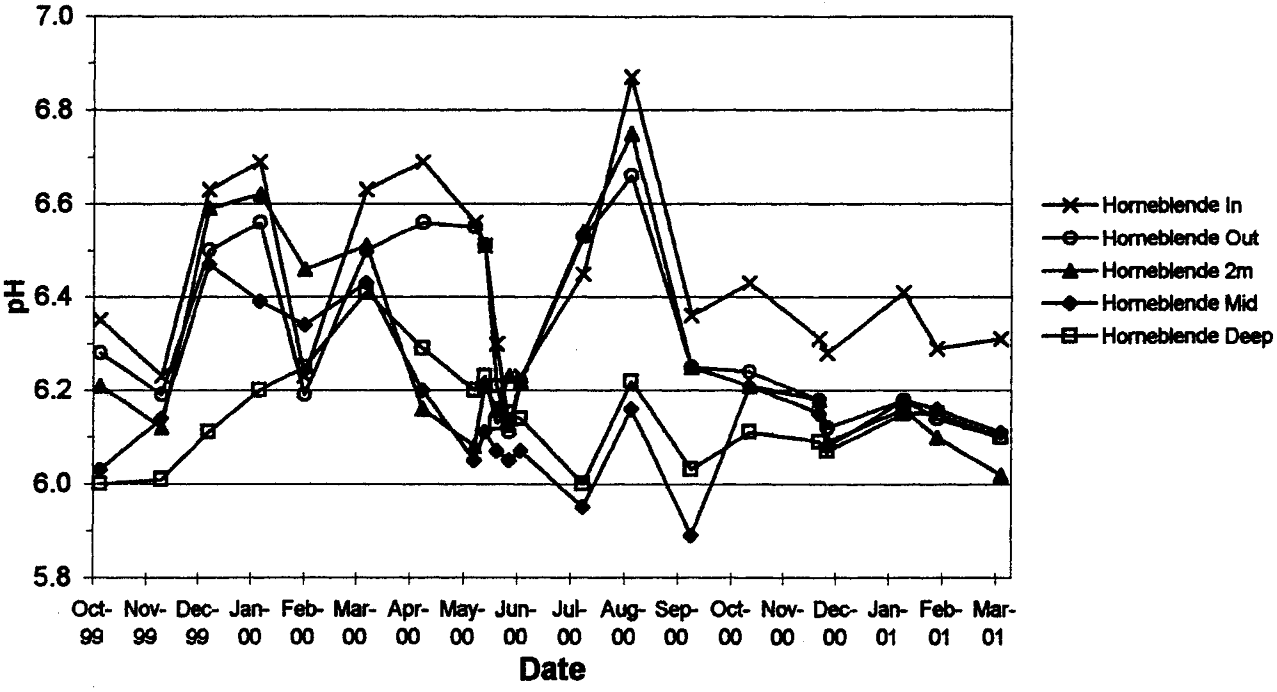


Figure: pH of Horneblende Lake, Including Inflow and Outflow