THE BIOGEOCHEMISTRY OF THE EQUITY SILVER MINE PIT LAKES.

By

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ABSTRACT

Between June 2001 and June 2003 a comprehensive two year study of the biological, geochemical and physical controls on trace metal behaviour in two mine pit lakes was undertaken at the Equity Silver Mine, British Columbia, Canada. Three major open pit developments occurred at this site generating the Main Zone, Waterline and Southern Tail pits. Mining operations at the Equity Silver Mine finished in 1994 and the Main Zone and Waterline pits have both since filled with water while the Southern Tail pit has been back filled with waste rock and is not considered in this study. Though located only metres apart, the two study lakes (Main Zone and Waterline) display considerably different physical and biogeochemical processes. The Main Zone pit lake (MZP) is polymictic, mesotrophic, well oxygenated year round and, for most of the year, contains relatively low concentrations of dissolved (< 0.45 \mu m) metals. The Waterline pit lake (WLP) on the other hand is meromictic, oligotrophic, anoxic at depths below 10 m (maximum lake depth is 40 m) and contains elevated concentrations of dissolved arsenic (2 ppm), iron (45 ppm), zinc (0.8 ppm) and manganese (4 ppm) in the hypolimnion.

The geochemical differences between the two pit lakes are driven largely by the deposition of acid rock drainage (ARD) treatment (lime neutralization) sludge into the MZP by PDC-Equity, the mine operators. The waste from an ARD treatment plant is deposited into the MZP, typically during the ice-free periods from May through to November. Due to a high suspended solids content (5 to 8 % by volume), the sludge creates a density current as it sinks through the water column. This imparts physical mixing energy to the pit lake as well as delivering dissolved oxygen to the bottom waters. Both of these factors promote a well oxygenated water column in the MZP with most metals either precipitating as, or co-precipitating with, oxyhydroxide solid phases. Unlike the majority of metals, dissolved Mn is introduced to the MZP through sludge deposition. This subsequently precipitates from the water column as a solid phase, likely MnO_x, during the sludge free periods.

As opposed to the MZP, the geochemistry of the Waterline pit lake is dominated by a permanent pycnocline at 4 to 10 m depth (varying seasonally) with significant mixing restricted to the epilimnion (mixolimnion). Sufficient biological / chemical oxygen demand coupled to the restricted transport of dissolved oxygen across the pycnocline, promotes reducing conditions below the epilimnion and elevated dissolved metal concentrations (particularly Fe) through the dissolution of oxyhydroxide solids. A combination of low rates of sulphate reduction and Fe-
Oxyhydroxide precipitation from the pycnocline operates to produce what appears to be a mixed pe system in the bottom waters / sediments of the WLP. Concentration profiles suggest that arsenic is predominantly controlled by adsorption to and dissolution from Fe-oxyhydroxide solid phases. Free dissolved sulphide was not detected in the water column but removal of Cu, Cd and Sb in the hypolimnion suggests their precipitation as sulphide minerals.

A series of limnocorral (in situ mesocosm) experiments were conducted in both the MZP and WLP to test biologically induced metal removal strategies. Only the WLP experiments are presented as part of this thesis. Algal growth and dissolved metal removal (through algal uptake / and / or adsorption) from epilimnetic waters of the WLP was induced with nutrient additions (N and P) to the corrals. Biological sulphate reduction and precipitation of insoluble sulphide mineral-forming metals (Cd, Zn, Sb, Co, Ni) was induced through ethanol additions to the hypolimnia of these corrals. Mn removal from the epilimnion was also induced though only after the algal growth period, possibly through bacterially catalyzed Mn oxidation.

The results have significant implications for the long-term management of pit lake water quality. In situ stimulation of phytoplankton growth has the potential to remove on a near-quantitative scale concentrations of zinc and other metals. The stimulation of sulphate reduction at depth in meromictic pit lakes offers a mechanism to sequester dissolved metals into underlying sediments, on a permanent basis if stable stratification can be guaranteed.
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1 Introduction

The tongue-in-cheek pro-mining slogan “if it’s not grown it’s mined” contains more than a grain of truth about the dependence of modern society on the products provided by the mining industry. The sometimes vast environmental impacts from resource extraction have spurred many environmental groups to call for a reduction of—or in some cases a complete halt to—mining activities around the world. Others have taken a slightly more forgiving attitude, but one that is often based on a “not in my backyard” sentiment. The fact is that the living standards sought by six billion people will continue to require products won from the ground. Mining is here to stay. This is not to say, however, that concerns over the environmental impacts of mining are misplaced. Indeed, such concerns have driven major improvements in mining practices over the last few decades together with, in many countries, considerably tighter legislation under which the industry operates.

The specific challenges faced by environmental management within the mining industry include the control of the quality of drainage, effluent, waste rock, tailings, soils, air, future land-use values and even aesthetics. In support of understanding and quantifying the impacts of mine operations on environmental values, a considerable number of research programs have been undertaken in recent years. These have ranged in focus from the downstream effects of metal-laden drainage from mine sites (Apte et al., 1995; Azcue and Nriagu, 1995; Sjoblom et al., 2004) (Bortnikova et al., 2001; Braungardt et al., 2003) to laboratory studies of specific causal mechanisms related to pollutant production and behaviour (Adler and Sibrell, 2003; Carlson et al., 2002; Fennemore et al., 1998; Monterroso et al., 1994). The development of remediation and control technologies has also garnered considerable scientific attention (Jong and Parry, 2003) (Frommichen et al., 2004; Romano et al., 2003; Runkel and Kimball, 2002).

Paramount among the impacts that mining has imposed on the environment in the past is acid rock drainage (ARD). As described below, exposure of sulphide minerals to oxygen and moisture at the Earth’s surface readily yields a metal-laden acid cocktail that may pose severe risks for surface water quality. However, techniques are evolving to avoid generation of ARD, and one of those includes submersion of sulphides under water. This approach has been shown to be very effective in limiting the production of ARD and the associated release of metals to aquatic systems (e.g. (Pedersen et al., 1998)). The filling of mined-out open pits with water to produce artificial lakes also shows promise in inhibiting or mitigating acid generation, and such
water bodies may have the additional benefit of serving as passive reactors within which dissolved metals can be sequestered into solid phases to be stored in a benign form essentially in perpetuity. To explore this possibility, the chemical evolution of two contrasting mine pit lakes in north central British Columbia has been studied intensively over the past three years in concert with manipulation experiments carried out in the lakes. This thesis describes the primary results obtained to date in this program, from an aquatic geochemical perspective. To establish the context for the study, this introduction offers in the following sections a brief overview of ARD generation, a short discussion on the potential utility of pit lakes as passive reactors, and a statement of project objectives.

1.1 Acid Rock Drainage

The thermodynamic conditions that most ore bodies were subjected to at the time of their formation were considerably different to those that exist at the surface of the earth. Through mining activities, rock minerals are fractured (typically by blasting with explosives) and exposed to atmospheric conditions. The minerals on the exposed surface planes of this rock (either as tailings, waste rock or pit walls) react with atmospheric constituents as they move towards thermodynamic equilibrium with the new environment. The products of these reactions can range considerably in their mobility, their toxicity, and their general geochemical impacts on the receiving environment (e.g. acidity and alkalinity).

The oxidation of sulphide minerals through reaction with oxygen and water can be particularly problematic. Such reactions produce protons, dissolved Fe and sulphate, in combination known as acid rock drainage (ARD). Of the environmental pollution issues facing the mining industry, ARD is the pollutant of greatest general concern.

The major sulphide mineral in crustal rock is pyrite or pyrrhotite (FeS$_2$ and Fe$_{1-x}$S respectively). While many other metal sulphide minerals oxidize, some more rapidly than pyrite, the following discussion shall use pyrite as representing the bulk of sulphide oxidation reactions. The initial reaction of pyrite with oxygen and water is represented in reaction 1.1 below, the products of which further react with oxygen to produce ferric iron (Fe$^{3+}$) as per reaction 1.2. This step occurs with the aide of iron oxidizing bacteria, typically members of the Thiobacillus and Leptospirillum genera (Edwards et al., 1999). Kinetically the pyrite oxidation process is controlled largely by the activity of ferric iron as the primary oxidant (reaction 1.3). The activity
of ferric iron is in turn largely controlled by the pH of the system and bacterially mediated ferrous iron oxidation (Wistotsky, 1995).

\[(1.1) \quad 2\text{FeS}_2 + 2\text{H}_2\text{O} + 7\text{O}_2 \rightarrow 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+\]

\[(1.2) \quad 4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}\]

\[(1.3) \quad \text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+\]

Other than the primary products of pyrite oxidation (sulphuric acid and dissolved Fe), the lowering of pH, often to below 2 and even into negative values (Nordstrom et al., 2000), can cause the further dissolution of other mineral phases in the host rock (Newbrough and Gammons, 2002; Plebow and Heinrichs, 2000; Rimstildt et al., 1994). Thus, acid rock drainage often contains elevated concentrations of multiple metals such as Al, Cu, Cd, As, Zn and Mn (Bortnikova et al., 2001; Gammons et al., 2003; Gray et al., 2003; Hammarstrom et al., 2003; PDC - Equity Division, 2003). The control and treatment of ARD waters is a major management issue for many mine sites including the site of this study (Equity Silver Mine, Houston, B.C., Canada).

### 1.2 Mine Pit Lakes

The decision to extract ore through underground or open pit mining often depends on the vicinity of the ore body to the surface, the spatial extent of the ore body and the grade of the ore. The increased capacity of modern mining equipment to move large volumes of rock, together with the increasing efficiency of milling practices in extracting the target metals from the ore, combine to make open pit mining more economic. This has had the effect of a vast increase in the number and size of open pit mines in recent decades (Castro and Moore, 2000; Eary, 1999; Shevenell et al., 1999). The majority of open pit mining operations extend below the local water table, requiring the continuous pumping (dewatering) of groundwater from the pit in order to keep the active mining surface dry. Upon closure of the mine and the cessation of dewatering, the mining voids (mine pits) naturally fill with water to a depth where hydrostatic equilibrium is reached with the local water table or the water decants into the local environment. These newly formed water bodies are generally referred to as mine pit-lakes (MPL).

The quality of water in mine pit lakes is often poor due to the presence of sulphide oxidation (ARD) in the pit lake catchment as well as the dissolution of minerals and weathering
products on the submerged pit walls (Morin and Hutt, 2001). Many pit lakes are of low pH (i.e. below pH 4) and have elevated concentrations of many metals (Blodau et al., 1998; Davis and Eary, 1997; Miller et al., 1996). The final water quality in these lakes impacts both the future use of the lakes (e.g. recreational, fishing, aquaculture, biological values) as well as that of their downstream receiving environments (Bowen, 2003; Kalin et al., 2001; Yokom et al., 1997). In environments with high evaporation rates and low rainfall mine pit lakes can often represent a significant proportion of the local open water (Johnson and Wright, 2003). These environments can also contain naturally hyper-saline groundwaters due to evapoconcentration of solutes where the water table nears the ground surface. These can fill the mine pit with water that contains elevated total dissolved solids (TDS). This is of particular concern in the central-western Australian desert, where several of the world's largest open pit mines operate. In Western Australia alone, for example, there are an estimated 1800 historic mining voids with 150 current mines operating below the water table (Johnson and Wright, 2003).

In an effort to reduce the amount of waste rock removed from a mine pit during mining operations, the pit walls are kept as steep as is geotechnically safe. This leads to a final pit lake with a much higher depth to surface area ratio (relative depth) than is typical for natural lakes (Castro and Moore, 2000). The greater relative depth increases the likelihood of the final lake developing meromixis as the total mixing energy supplied to the lake through thermal variations and wind stress at the surface of the lake is reduced relative to the depth of the lake (Boland and Padovan, 2002; Stevens and Lawrence, 1998). As with natural lakes, meromictic mine pit lakes can form reducing environments in their hypolimnia due to the restricted transport of oxidants (primarily dissolved oxygen) to the deep water column imposed by the permanent stratification.

If the chemical and biological oxygen demand in the hypolimnion of the MPL is greater than that supplied by inputs from diffusion and turbulent mixing with oxygenated surface waters then anoxia can occur. This is most probable where significant concentrations of reduced species (primarily organic carbon) are present in, or exported to, the hypolimnion. Under anoxic conditions bacteria can utilize alternate oxidants in organic carbon mineralization (respiration) such as nitrate (Senn and Hemond, 2002), Mn and Fe-oxyhydroxides (Cummings et al., 2000; Taillefert et al., 2002), arsenate (Switzer-Blum et al., 1998) and particularly sulphate (Koschorreck et al., 2003; Riekkola-Vanhanen and Mustikkamaki, 1997). The use of sulphate as a terminal electron acceptor in the mineralization of organic matter has the effect of reversing the ARD process and removing the ARD products (protons, iron and sulphate) from the water.
column through the precipitation of sulphide minerals such as pyrite. This natural sulphate reduction process holds considerable potential for the remediation of mine pit lake water quality.

As outlined in the section 1.1, ARD is generated by the reaction of sulphide minerals with oxygen and water (and subsequently Fe$^{3+}$). It has been demonstrated in many laboratory and field investigations that the removal of either water or oxygen from the reaction severely impedes ARD generation (Fajtl et al., 2002; Newbrough and Gammons, 2002; Patterson, 1987; Pedersen et al., 1998). The placement of potentially acid producing rock under water has proven to be an effective long-term management strategy. Water, even when well oxygenated, contains four orders of magnitude less oxygen than the atmosphere. Decreased diffusion rates in water also serve to hinder the transport of dissolved oxygen to the sulphide mineral surface. Any alkalinity present in the water will also act to prevent a lowering of pH in the pore-waters and the formation of Fe$^{3+}$ (dissolved ion). All of these factors lead to mine pit lakes being potentially ideal final repositories for sulphide mineral bearing waste rock and tailings.

Paramount in the consideration of MPLs for waste rock disposal is the oxidation state of the mineral surfaces. If waste rock is left exposed to “atmospheric” conditions for several years (typically 1.5 to 5 years), the reaction products of ARD can build up on the mineral surfaces and within the interstices of the unconsolidated material. If waste rock of this nature is placed in the aqueous environment, the ARD products (such as acid jarosite, gypsum and various metal salts) can dissolve, reducing the ambient water quality and consuming alkalinity. Care must be taken with waste rock storage during pit operation to maximise the disposal options available.

While backfilling of mine pits with waste rock appears a logical and elegant engineering solution to the ARD problem, in reality this procedure is often prohibitively expensive (Johnson and Wright, 2003). The cost of hauling huge volumes of rock back to the pit after years, even decades, of excavation is likely to be comparable to that of the original excavation itself. Mine planning to optimise the retention of waste rock within the pit (i.e. continuous backfilling) may provide additional economies in this regard.

Understanding the physical and geochemical controls on the water quality of mine pit lakes is crucial in the development of both pit lake closure plans, remediation technologies and models for prediction of the evolution of pit lake water quality over time. As the environmental implications of the growing numbers of mine pit lakes becomes more apparent, mine planners and government regulating agencies will be increasingly required to manage these implications to maximize the environmental values of these new lakes.
1.3 Project Description and Thesis Objectives

This thesis represents a primary contribution to a larger multi-disciplinary, two year study of the physical and geochemical limnology of two mine pit lakes at the Equity Silver Mine, Houston, B.C., Canada (Figure 2.1). The over-all study involved the investigation of the chemical and physical controls on each pit lake (Main Zone and Waterline pit lakes) as well as the testing of several water quality remediation strategies through the use of limnocorrrals. These limnocoral experiments are described in greater detail in sections 3.3 and 4.3. The collection of physical data as well as the chemical sampling of both pit lakes was commenced in June 2001 and continued on a monthly or bi-monthly basis through to June 2003. In total 11 chemical profiles were taken in both the Main Zone and Waterline pit lakes. The main chemical parameters investigated were total and dissolved (< 0.45 μm) metals, major ions, chlorophyll and nutrients. Selected samples were also taken for dissolved sulphides, particulate and dissolved organic carbon, pH and alkalinity. The chemistry sampling was primarily conducted by the author, Dr. J. Crusius, Mr. D. Kramer, Dr. T. Pedersen (all of UBC), Mr. R. Goldblatt and Ms. S. Ames (of Lorax Environmental Services Ltd.).

The physical limnology of the pit lakes was primarily researched by the Environmental Fluid Mechanics group of the UBC Civil Engineering department, specifically by Dr. R. Pieters, Mr A. Leung and Dr. G.A. Lawrence. The data collection for the physical limnology program included profiles of conductivity, temperature, fluorescence, transmissivity and optical backscatter, obtained through casts of a CTD equipped with appropriate sensors, as well as temperature information collected through long-term deployment of thermistor chains, and weather data supplied via meteorological stations installed on each pit lake. Flow / stage height measurements were also collected. A total of 353 CTD casts were taken over the two-year period.

The primary objectives of the research reported in this thesis was to determine the major geochemical controls on the Main Zone and Waterline pit lakes as well as to evaluate the removal of metals from pit lake waters through the experimental induction of biological sulphide generation. The following chapters sequentially describe the results and offer an interpretation of the large volume of data collected in the study.
2 Site Description.

2.1 Location and History

The Equity Silver Mine (Equity) is located in central British Columbia, Canada at an altitude of between 1200 and 1400m. The site is approximately 35km southeast of the town of Houston and 575km by air north-northwest of Vancouver (see Figure 2.1). Geographically the mine site lies on a plateau between the Bulkley and Buck Creek drainage systems and as such drainage from the mine area has impacts on both these catchments. The ore body was discovered in 1968 and mine construction started in 1979. The Equity mine was predominantly an open pit operation with three main pit developments during operation from 1980 to 1994 (Southern Tail, Main Zone and Waterline Pits)(PDC - Equity Division, 2003). Limited underground mining was also undertaken from the northern face of the Waterline Pit (Figure 2.3).

A conventional floatation method for metal extraction (Ag, Cu) was employed with the consequent generation of considerable quantities of waste rock (66.3 million tons) and tailings (33.2 Mt). Additional Ag and Au were also extracted from tailings using a carbon-in-leach cyanide extraction technology. This cyanide was destroyed using SO2 prior to tailings disposal. As and Sb were also found to occur in elevated concentrations in the mill concentrate.

The majority of waste rock produced by mining operations contains significant sulphide mineral content and as such is potentially acid generating. The metal content of the ore tended to correlate with the degree of sulphide mineralization, generating tailings that have on average higher sulphide levels than the waste rock (Equity Silver Mines Ltd, 1991). Acid rock drainage (ARD) was first noted in leachate from waste rock dump in 1981 and is still a major environmental problem for Equity Silver Mines Ltd.

Although closed to mining operations, the mine site still operates an ARD monitoring, collection and treatment facility with a permanent staff of four. The collection and treatment of ARD at Equity is likely to be an ongoing necessity for at least several decades. ARD is treated by the introduction of slaked lime to neutralize the acid water and to precipitate major metal ions as oxyhydroxide phases. The precipitates are de-watered and pumped into the Main Zone Pit (refer to section 2.5.1.5) as a slurry containing between 5 and 10% solids on average. A new treatment plant is currently being built that will increase the solids content and improve the coagulation dynamics of the sludge.
Figure 2.1: Location of Equity Silver Mine, British Columbia, Canada.
Figure 2.2: Equity Silver Mine, Houston, B.C. Canada; Site map showing pit lake locations and basic hydrology.
Figure 2.3: Cross section of the Waterline and Main Zone Pit Lakes, Equity Silver Mine, Canada. Vertical exaggeration x 6.
2.2 Climate

Lying at between 54° and 55° North and 1200 m elevation, the Equity mine site has a cold temperate climate regime with mild summers (mean = 12°C) and cold winters (mean = -8°C). Typical snowfall during winter months reaches 250 mm (water equivalent) though can reach 450 mm in high snowfall years (Golder Associates, 1998). Snow melt (freshet) during the spring months accounts for approximately 80% of the annual mine site runoff. During the collection of field data for this project the property experienced both a near record snowfall season (winter 2002) and a very light snowfall season (winter 2003). The high snowfall events cause considerable strain on the ability of the mine site water management structures to contain and treat acid waters during the freshet. Due to accidental environmental discharges of acid water during the freshet of 2002, recent works at the mine site have been undertaken to improve the capacity of both the storage and treatment of acid waters.

Wet precipitation at Equity generally occurs from April to October with the months June to September averaging ~40 mm per month. March to May are the driest months averaging ~20 mm/month (Golder Associates, 1998). Total annual precipitation averages 670 mm (PDC - Equity Division, 2003). Although water infiltration to the waste rock dumps is greatly reduced during the winter months due to frozen ground and precipitation remaining as snow at the surface, the exothermic nature of the sulphide oxidation reaction and the acidic, high ionic strength leachate from the dumps inhibits freezing. For this reason subsurface flows of acid water still occur, though reduced, during winter months.

The period of this study (June 01 to June 03) encompassed two winter seasons of quite different precipitation and freshet regimes. Winter 01/02 was of average snowfall though the freshet occurred rapidly due to an intense rainfall event on a full snow-pack. This rapid snowmelt overwhelmed the mine site water management system and untreated ARD waters were accidentally released to the environment during May 02. Due to the contamination of previously treated water storage ponds by emergency ARD water diversion, a large volume of additional water was treated and released to the Main Zone Pit Lake during the summer / fall of 2002. In order to maintain the water balance of the MZP and increase emergency storage capacity the amount of water pumped from the MZP in to the environment was dramatically increased during 2002. Winter 02/03 was of light snowfall and, together with increased water management capacity saw the full collection and treatment of ARD effluents from the mine site.
Wind speeds on the mine site are, on average, relatively low for most of the year. Average wind speed on the mine pit lakes (at 10 m above surface) are 2.165 m/s (± 1.3995 s.d.) for the Waterline Pit Lake (WLP) and 1.88 m/s (± 1.16) for the Main Zone Pit Lake (MZP). Winds increase towards the late fall.

2.3 Geology

The Equity Silver Mine sits in a regional geological formation known as the Goosley sequence. This sequence consists of older Cretaceous sedimentary rocks inter-bedded with volcanic flows from the early Tertiary and sedimentary deposits from glacial scouring. The vast majority of the area is volcanic tuff and ash, consisting of silicate mineralogy (quartz-monzonite)(Figure 2.4). The prominent sulphide phase in the region is pyrite. Within the Main Zone Pit itself the major pit wall geology consists of gabbro (coarse-grained basic), andesite (sodic plagioclase, biotite, hornblende, pyroxene) and quartz latite (K-andesite) dykes, and lapilli tuff (pyroclastic fragments). Andesite is a very common rock in the Earths crust and is considered a good approximation of the average crustal composition (Krauskopf and Bird, 1995).

The productive ore deposits tended to occur as finer grained sulphide mineralizations within the pyroclastic beds. Silver, copper and gold were extracted economically from three zones, the Southern Tail, Main and Waterline Zones. Chalcopyrite, tetrahedrite and arsenopyrite were the principal ore minerals, the latter two providing the elevated concentrations of Sb and As in ore concentrates (Equity Silver Mines Ltd, 1991). These ore minerals are considered younger than the surrounding pyroclastic matrix though older than the gabbro-monzonite intrusions that form one limit of the ore body (Sperling, 1985).

The waste rock contains enough reduced sulphur that significant acid rock drainage occurs within the waste rock dumps. The general host rock of the Main Zone pit lake contains a net neutralizing capacity with the net acid producing sectors in the southern and western walls (Morin, 1990).
2.4 Biogeography

The Equity mine site sits within the Engelmann Spruce-Subalpine biogeographical unit. The waste rock dumps are deliberately kept treeless to inhibit destruction of the clay capping by root systems. Tree roots would create pathways for oxygen and water to infiltrate the dumps, thus enhancing acid rock drainage. The general region around the mine site is largely uninhabited and is primarily used for logging, recreational fishing, hunting and snowmobiling. Downstream recreational fisheries include salmon (Coho, Pink, Chinook and Sockeye), steelhead and rainbow trout (Equity Silver Mines Ltd, 1991).
2.5 Pit Lake Hydrography.

2.5.1 Main Zone Pit Lake Hydrography.

The excavation of the Main Zone pit began in March 1983 and was completed in mid 1991 at an elevation of approximately 1090 m (Figure 2.5.1) after the removal of more than half a million cubic meters of rock (Equity Silver Mines Ltd, 1991). During the mining operation, dewatering (pumping) kept the water table below the mining surface, allowing for dry mining conditions and reducing the groundwater pressure on the pit walls. Upon the cessation of mining and dewatering, the pit filled with groundwater, precipitation, surface run-off and waste water diversion. The water surface had risen to the final (artificially maintained) elevation of around 1260 m by July 2000 (Figure 2.5.2 A).

Figure 2.5.1: Main Zone pit excavation history and pit dewatering rates – 1984 to 1991. Data taken from (Klohn Leonoff Ltd, 1990) and (Klohn Leonoff Ltd, 1991). The pit floor elevation record is from the “South Interior” section of the pit.
Figure 2.5.2: (A) Elevation of water surface in Main Zone pit lake from start of sludge deposition (1993) to June 2003. (B) Cross section of Main Zone pit (north – south, vertically exaggerated). (C) Detail of water surface elevation in the Main Zone pit lake during the period of study (June 2001 to June 2003), open circles measured, solid circles interpolated.
2.5.1.1 Main Zone pit lake physical characteristics.

The MZP at water level is approximately 750 m long (north-south), 400 m wide (east-west), roughly oval in surface shape and has a maximum depth of 120 m. The surface area of the Main Zone pit lake at the current water elevation is approximately 20.5 to 22.2 ha (Leung, 2003)(R. Pieters, pers. com.), depending on how the mined topography is interpolated on available maps. The pit lake volume is approximately 10 million m$^3$ (Figure 2.5.3). The current depth of the pit lake (1140 m AMSL) has been reduced from the final excavation depth (1090 m AMSL) by backfill with waste rock and ARD treatment sludge deposition (Figure 2.5.2 B). 0.321 million tonnes of waste rock from the Waterline deposit were deposited in the MZP after pit decommissioning (Equity Silver Mines Ltd, 1991; PDC - Equity Division, 2003), occupying approximately 0.6 to 0.7 million m$^3$ or the bottom 25 m of the pit lake (using a specific gravity of 2 for waste rock). On top of this waste rock, ARD treatment sludge has been seasonally deposited into the lake since 1993 (Table 2.5.1 in section 2.5.1.2).

The MZP contains no natural overflow or decant point and such flow from the pit, under normal circumstances, would be over the top of a till core dam built on the western edge of the pit lake from 1270 m to 1288.5 m elevation. To prevent the water level reaching the base of the till core dam and to maintain emergency water storage capacity, water is pumped from a depth of 20 m from the Main Zone pit and discharged into the Getty Creek drainage system. The primary reasoning for keeping water levels below 1270 m elevation is to prevent water from the pit lake from seeping into the main waste rock dump over the top of a "divide" between undisturbed natural bed rock and the base of the till core dam. The dam itself does contain an engineered spillway that would feed the Getty Creek catchment if lake levels were allowed to rise to the overflow elevation. The rate of water discharge from the MZP over the summer of 2002 was sufficient to draw down the water level of the pit by 2 m despite a large volume of treated ARD water (1.4 Mm$^3$) being pumped into the pit at the same time (PDC - Equity Division, 2003). From October 2002 the storage capacity of the Tailings Pond was also enhanced by pumping decant water to the Main Zone pit lake.

For determination of physical and chemical parameters a CTD cast was taken with every chemical sampling session. Data collected by CTD included water temperature, conductivity, fluorescence, transmissivity and, in later casts (after June 02), optical backscatterance (Figures...
3.1.1 and 3.1.2). A thermistor chain was also deployed in the Main Zone pit lake from June 01 to June 03, providing a continuous record of water temperature at discrete depths. The physical limnology of the Main Zone pit lake has been discussed at length in the M.Sc. thesis of Mr Albert Leung (Leung, 2003). A summary of the physical structure and dynamics of the lake is given here with special reference to their relevance to the geochemical processes occurring in the pit lake.

2.5.1.2 Stratification and sludge inflow.

The Main Zone pit-lake (MZP) does not fit natural lake classifications based on turn-over rates (whole or partial lake mixing events). Although the surface layers of the lake behave much like a typical temperate climate lake (summer thermal stratification near the surface and ice cover during winter), the presence of elevated sulphate as well as sludge discharge alters the turn-over regime with respect to pure thermal forcing. A natural lake at the same latitude (54° 11.3’ N) as the MZP would be expected to undergo turn-over in spring due to penetrative convection driven by the warming of surface towards maximum density at ~4 °C and these sinking through the colder waters below. The elevated major ion concentrations (primarily sulphate) in the MZP inhibit this penetrative convection process through providing additional density to waters below the epilimnion such that they remain denser than the overlying epilimnion through out the spring.
Whole lake mixing was observed in October 2001, likely due to the cooling of surface waters (again towards ~4 °C) and the action of convective penetration. Unlike the spring, this mechanism is able to act in the late fall due to the much smaller difference in conductivity (as a proxy for dissolved ions) between the epilimnion and hypolimnion at this time. Similar mixing was seen in October 2002 though only to a depth of 40 m (discussed in section 2.5.1.3 below).

The input of sludge to the MZP also generates considerable mixing and oxygenation of the layer below thermocline / pycnocline with the "hypolimnion" acting more like a typical lake mixolimnion. Large amounts of sludge are deposited into the Main Zone pit, which is relatively dense and flows as a density current to the bottom of the pit lake. A considerable amount of pit lake water is entrained into the sludge density current such that a fraction of finer particulate material is distributed over the bottom 20 to 50 m of the water column during sludge deposition. The input of sludge to the bottom waters of the MZP pit impacts the circulation regime of the MZP such that the layer below the chemocline / theromocline is well mixed for most of the year.

At all times the sludge signature (as recorded through reductions in transmissivity and increases in optical backscatet) was predominantly below 50 m depth. Small amounts of sludge were detectable, through the particulate Fe concentrations, throughout the water column during sludge deposition periods. The sludge signature (particulate Fe) was two orders of magnitude lower above 50 m depth than that recorded in the deepest samples (100 m to 120 m depth). Visual inspection of the location where the sludge entered the surface waters of the MZP indicated that the sludge sank rapidly with the surface plume only visible for 5 m to 20 m from the outfall. The peak total suspended solids content of the sludge plume in the bottom waters of the MZP (at 110 m) was 105 mg/l. As a contribution to density this is less than 10% of that supplied by sulphate to the water column. The relative uniformity of sulphate distribution allows the additional sludge-supplied density to control deepwater density stratification during sludge deposition periods (e.g. Figures 3.1.1 and 3.1.2 (June 11, 03 at 115 m depth), pages 44 and 45).

Fresh water inflows and increasing temperature during the summer and fall generate a chemocline / pycnocline near the surface of the MZP at depths ranging from 1.25 m to 7 m in the early fall (e.g. Aug 26, 02). Figure 3.1.4 represents the (chlorophyll) fluorescence and CTD recorded thermocline / chemocline depths over the two-year study. Despite a much greater fetch, the MZP maintained a shallower epilimnion than the Waterline pit lake.

A more detailed history of the stratification and mixing regime of the MZP is given in section 2.5.1.3.
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<th>Diversion to Main Zone</th>
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Table 2.5.1: Pumping records for ARD treatment sludge and waters to the Main Zone Pit Lake (1986 to 2000). Courtesy of Mike Aziz, PDC – Equity Division.

2.5.1.3 Temperature

It can be seen from Figure 2.5.4, that at any given time the waters below 10 m were relatively uniform in temperature. The seasonal temperature variation for the bottom 100 m of the water column was a maximum of 3.6 deg C with the lowest temperatures being recorded in the late winter and the maximum temperatures in the late fall. A thermistor chain was deployed in the Main Zone pit lake from June 20, 2001 through to June 11, 2003. This chain contained 21 temperature-recording instruments (thermistors) at set depths throughout the water column. The sampling period for these instruments ranged from 1 min to 30 min. This continuous temperature record contains valuable information on temporal changes in the pit lake and gives a detailed response of water temperatures to the input of sludge (Leung, 2003). This information will only be touched upon here in relation to supporting chemical processes.

The thermistor data indicate that a surface thermocline existed in the top 5 m of the water column from June 20, 2001 (the first measurements made) through to the beginning of October
2001 where a brief period of reverse thermocline (lower surface temperatures) occurred before complete mixing of the water column in the second week of October. From mid October 2001 through to the first week of December the entire water column was well mixed and cooling at a relatively constant rate of 0.057 °C/day. The air temperature was decreasing at around 0.13 °C/day over the same time period. The uniform temperature profile of the Main Zone pit lake over this period was likely driven by mixing induced by the sinking of cooling surface waters. Upon reaching the temperature of maximum water density (3.6 °C, corrected for MZP salinity, (Pieters, 2004), pers. com.) reverse thermal stratification occurred down to depth of 20 m where temperatures graded from 3.54 °C at 20 m (and below) to 0 °C at the surface. The temperatures remained unchanged until the discharge of sludge was re-started in February 2002. 

A brief period of sludge discharge was undertaken from February 21, to March 15, 2002 in order to increase the sludge storage capacity of the ARD treatment system in preparation for the spring freshet. This sludge deposition event had the effect of mixing much of the water column of the MZP, eroding the reverse stratification near the surface and resulting in the partial warming of the upper 20 m and slightly cooling the lower 100 m of the lake. A chemical sampling session was undertaken on March 19, 2002, four days after the cessation of sludge pumping to the pit lake. The water column remained reverse stratified in the upper 3 m for the duration of the winter / spring of 2002 until the freshet. At the end of May 2002 the water column began warming at the surface and normal thermal stratification was re-established (warmer surface waters) by the first week of June 2002. This event roughly coincided with the air temperatures increasing above an average of 5 °C.

Water temperatures rose throughout the water column through to October 2002 (to 6.8 °C) where, by Oct 7, 2002 the entire water column was mixed (no thermal stratification). By January 21, 2003 (a chemical sampling date) water temperatures had cooled throughout the entire water column to below 5.1 °C, though the pattern was different from the previous winter when whole lake mixing had occurred. Distinct thermal and chemical (dissolved solutes as conductivity) density stratification was present in the deep water column at ~ 40 m and 62 m depth on January 21, 02 (Figure 2.5.5). This was the only non-surface stratification seen in the MZP during the period of study. The pycnoclines were relatively weak (small density differences) in comparison to those found permanently in the Waterline pit lake with only a < 10 μS/cm change in conductivity and < 0.4 °C change in temperature. This resulted from the addition of tailings pond waters to the MZP (September 20 to November 15, 2002 Figure 2.5.2
C) altering the fall mixing regime of the pit lake with the hypolimnion not mixing completely to the surface of the pit lake.

Unlike the ocean, the dissolved solute component of the MZP density comes from sources that vary on short temporal and spatial scales (sludge pumping, freshet runoff, tailings pond water). A uniform "salinity" and thus density profile is only ensured by mixing of the water column on a scale greater than the propensity of the input waters to stratify. If the density difference between the pit waters and the input waters is too great then stratification will occur as a density equilibrium is reached before complete pit water entrainment (in the case of a density current).

The stratification event in January 03 was largely removed by the continuation of sludge disposal into the pit lake during the next spring. By March 11, 03 (after sludge pumping had resumed), the temperature profile was again uniform in the deep hypolimnion. A small stratification existed at around 20 m depth on this date with chemical and CTD profiles indicating that the water column had been mixed up from below, presumably by the sludge deposition (Figure 2.5.3). By June 13, 03 a typical summer pattern of surface thermal stratification had re-established itself in the top 6 m of the water column. Below this depth the water column was well mixed and moderately warmer (by 0.2 °C) than winter deep water temperatures.

2.5.1.4 Wind

The average wind strength on the Main Zone pit lake is around 15 % less than on the Waterline pit lake despite the much greater fetch and more exposed location of the Main Zone pit lake. During the period of study the average wind strength on the MZP was 1.9 m/s (± 1.2) (Pieters, 2004), pers. com.).
Figure 2.5.4: Temperature and conductivity evolution in the Main Zone Pit Lake, June 2002 to June 2003. Note that the 10 m, 50 m and 110 m values are essentially the same for most dates and the symbols overlap.
2.5.1.5 Currents

The water currents in the MZP were measured on selected dates using acoustic Doppler current meters (Aanderaa Instruments RCM 7, RCM 9). As would be expected, these measurements indicated that the currents were much stronger during periods of sludge deposition. Measurements taken at different depths tended to indicate the presence of a circulating current cell with water moving away from the point of sludge deposition (to the south) along the bottom of the pit lake and, at much slower speeds, moving west or north-west in the upper 100 m of the water column. The current speeds recorded at the bottom of the pit lake (123.5 m and 125 m) during sludge deposition were very high (up to 80 cm/s, August 14, 2001). This current speed appeared improbable as the reading was taken more than 400 m from the point of sludge deposition. Current measurements higher in the water column (at 20 m, 40 m, 60 m, 90 m and 115 m) were considerably slower, on average below 5 cm/s. Testing of the equipment in a water flume at UBC civil engineering indicated that the current speeds were relatively accurate. Communication with the manufacturer also indicated that there should be no adverse effects on the instrument accuracy from the high suspended solids content of the sludge.

The transmissivity measurements taken on August 14, 2001 at the same time as the current readings indicate that particulate matter from the sludge reached as high as 50 m in the water column. The pattern of current movement in the pit lake suggest that the suspended sludge particulates in the water column below 50 m (and above the density current at 120 m) may be from re-circulating waters rather than being entrained into the water column as the density current descends through the water column (Figure 2.5.6).
Figure 2.5.5: Main Zone pit lake conductivity and temperature profiles for January and March 2003 showing stratification in January 2003 at 40 m and 62 m depth.

Figure 2.5.6: Schematic representation of the water circulation patterns within the Main Zone pit lake during sludge deposition.
2.5.1.6 Surface inflows and seeps

The climatic conditions including the precipitation regime for the Equity site are given in section 2.2. The direct precipitation to the surface of the MZP is, at an average annual rainfall rate of 670 mm, approximately 150,000 m$^3$/yr. This is roughly similar to the input of overflow waters from the Waterline pit lake (~180,000 m$^3$/yr). The precipitation runoff from the pit walls is also likely to be of a similar order to that of direct precipitation to the surface of the pit lake. During this study several seeps into the MZP were sampled shortly after a rainfall event. The total flow associated with the visible seeps to the MZP is largely insignificant to the water balance of the pit lake although these seeps are of considerable importance geochemically. A total of five seeps were visible along the southern and western wall of the MZP directly after large rainfall events with an estimated flow of 1 L/s or less. A small degree of seepage comes from an “iron stain” high on the southern MZP pit wall and appears to be associated with the old southern tail pit and waste rock dump. The water quality of these seeps will be further discussed in sections 3.1 and 4.1.

Despite the diversion of the old Berzelius Creek away from the MZP, during the early part of the summer and after large rainfall events, water “leaks” from the diversion and follows the old Berzelius Creek channel into the MZP. Though this source of water has not been well quantified it appears relatively insignificant compared to the sludge and Waterline pit overflow. The overflow from the Waterline pit lake into the MZP is the only “permanent” inflow though this too ceases during the winter ice over of the pit lakes. As discussed in section 2.5.1.5, the discharge of wastewaters (sludge) from the mine site ARD treatment plant is a significant source of water to the MZP (see Table 2.5.1).

2.5.1.7 Groundwater

The groundwater hydrology of the Equity site has been extensively studied with respect to the contribution of groundwater to waste dump effluent streams (URS-Norecol Dames and Moore., 2000), slope stability (Sperling, 1985), pit dewatering (Marlow, 1987), pit inflows, outflows (Klohn Leonoff Ltd, 1990), pit lake chemistry (Morin, 1990) and environmental contaminant transport (Klohn Leonoff Ltd, 1991; KPA Engineering Ltd, 1993). With respect to the Main Zone pit lake, these studies indicate that the pit served as a localized sump for
groundwater during excavation. The pumping rate in 1987, while the pit floor elevation was at 1223 m (34 m below the current water surface elevation or 130 m above the final pit floor), was 1500 m$^3$/day (17 L/s) (Figure 2.5.1). This rate was calculated to be close to that of the theoretical inflow to the Main Zone pit using a groundwater model (Marlow, 1987).

The closure plan for the Equity mine site predicted that the pit lake would fill with water in 7 to 35 years depending on the drainage control measures taken. The original plans were for the pit lake to fill to the decant level at the top of the till core dam on the western side of the pit (1288 m). This would have joined the two pit lakes (Waterline and Main Zone) at the 1265 m elevation so that one lake would be formed (Equity Silver Mines Ltd, 1991). The water level was not allowed to reach this elevation due to further hydrological studies that indicated that water from the pit lake would infiltrate the main waste dump and increase ARD effluent flows (Klohn Leonoff Ltd, 1990). As the pit lake filled the difference in hydraulic head between the lake and the surrounding groundwater table would lessen, reducing the rate of groundwater inflow to the pit lake. 17 L/s then can be taken as a maximum value for groundwater input to the pit lake though the actual figure is likely to be considerably less. The maximum rate of 17 L/s is of a similar order to that from the Waterline pit over flow (during ice free periods). If groundwater flow is taken to be constant over the year then at the maximum flow rate of 17 L/s the total inflow (550,000 m$^3$) would be roughly equal to the sum of annual outflow from the Waterline pit, pit wall run-off and direct precipitation. A 1991 hydrological study of the mine site found that approximately twice the direct precipitation to the Main Zone pit was pumped out in order to keep the pit dry during mine operations (Klohn Leonoff Ltd, 1991).

An estimate of groundwater inflow can also be made from the average hydraulic conductivity of the geological units and the measured hydraulic head differences in the system. This method is very imprecise due the order of magnitude differences in hydraulic conductivity frequently observed between intact and weathered or fractured rock of the same basic mineral matrix (Klohn Leonoff Ltd, 1991).

It should be emphasised that the groundwater inputs to the MZP are not well constrained and inflows of groundwater mentioned in this thesis are estimates bounded by the likely maximum value of 17 L/s. The net groundwater balance for the pit is likely to be positive (more groundwater inflow than outflow) given the high eastern wall of the MZP and the positive head on the piezometer groundwater water elevations up gradient from the pit in relation to the pit lake surface (Klohn Leonoff Ltd, 1990).
2.5.1.8 Outflows

Other than possible groundwater discharge, the only direct outflows from the Main Zone pit lake are from pumping of water from 20 m depth by PDC-Equity and from evaporation. In July 2000 the water level of the Main Zone pit lake reached the desired operational elevation and this is maintained though pumping of water from the pit lake to the Getty Creek catchment. If the loss of MZP waters to groundwater and evaporation are assumed to be insignificant for the overall water balance (as is likely), then the pumping of water during the study period (June 2001 to June 2003) was by far the most significant outflow of water from the pit lake.

Figure 2.5.7 displays the monthly total discharge of water pumped from the Main Zone pit during the period of study. The residence time of pit water based on the yearly average pumping rate is on the order of 5 years, using the pit lake volume calculated by Leung (2003) of 9.7 Mm$^3$ and the average pumping rate of 1.9 Mm$^3$/yr for June 2001 to June 2003. A residence time based on inflow estimated by the same author gave a 4-year residence time (Leung, 2003). Within the inherent uncertainties of lake hydrology these estimates appear to agree reasonably well.

Evaporation is expected to be less significant in mine pit lakes in comparison to natural lakes due to the relatively high surface area to depth ratios (Shevenell, 2000). The high altitude and latitude of the Equity mine site will also have the effect of reducing evaporation rates.

![Figure 2.5.7: Monthly total volume of water pumped from the Main Zone pit lake – June 01 to June 03. Data courtesy of Mr. M. Aziz, PDC-Equity. No pumping was carried out where data points are absent.](image-url)
2.5.1.9 Pit walls

The MZP is located on a westerly sloping hillside, which was bisected by the Bessemer Creek channel. The upper portion of the Bessemer Creek is currently diverted both north and south across the top of the eastern pit wall and drains into both the Foxy Creek and Buck Creek drainage. The pit walls of the MZP extend above the lake surface by 30 to 100 m, decreasing in height from east to west (Figure 2.3). A “till-core” dam has been constructed in the center of the western wall to increase the wall height (by 18.8 m) and pit capacity (Equity Silver Mines Ltd, 1991). The current water elevation at 1255-1260 m is approximately 10 to 15 m below the original wall height and 30 m below the till dam crest.

Mine pit walls primarily influence the geochemistry of pit lakes in two ways (1) through the oxidation of sulphide minerals exposed to the atmosphere and, (2) through the supply of acid neutralizing capacity, primarily in the form of carbonate and silicate minerals. The acid neutralization / production capacity of the MZP mineralogy has been extensively studied in the later years of the mine operation and closure planning (Morin, 1990; Patterson, 1987). From these studies the eastern wall of the pit lake has been classified as largely acid neutralizing (net alkaline) with increasing net acidity from east to west. The upper portions of the western and southern walls contain the highest ratio of acid production to neutralization capacity, exceeding 50:1 in sections. Modeling of the Main Zone pit chemistry evolution based on groundwater input and pit wall interactions using the MINEWALL computer model predicted that the MZP waters would remain at a pH above 7 in the absence of significant “outside” acid water sources (Morin, 1990).

The mineralogy of the broad geological unit in which the MZP resides is given in section 2.3. With specific reference to the MZP, the eastern pit wall is comprised of andesic flows (andesite intrusions) and flow breccia. The central and western portions of the pit are composed of granitic material and volcanic “ash tuff” (Patterson, 1987).

As a general rule, the greater the exposed surface area of sulphide minerals the greater the rate of oxidation and ARD generation. Apart from the visible surface of the pit wall itself, the ARD generation capacity of pit walls can be increased through exposure of additional mineral surface area associated with rock fracturing during blasting and rubble that collects at the base of the benches. The rubble and crushed surface rock on pit wall benches can generate more ARD than the pit wall surfaces themselves (Morin, 1990; Norecol Environmental Consultants Ltd., 1991).
2.5.2 Waterline Pit Lake Hydrography

The Waterline pit lake was formed through the excavation of the Waterline ore body between 1988 and 1994 (PDC - Equity Division, 2003) with the ultimate water level being determined by a decant at 1265 m elevation into the Mainzone pit lake. The Waterline pit lake (WLP) is approximately 460 m long and on average 60 m wide, running roughly north-south with a total surface area of 2.6 ha (Leung, 2003). The average depth of the pit lake is approximately 18 m and its maximum depth is approximately 43 m, although this depth covers a small fraction of the pit lake area (Figure 2.3, page 10). The lake bottom is formed by a relatively shallow sloping ramp, extending northwards from the water surface at the southern end of the pit lake to approximately 2/3 the length of the lake, flattening out at 35 m depth. This ramp was used as access for ore extraction and underground mining during the pit operations. The northern, eastern and western walls of the pit lake are steep, representing the geotechnical limits of stability for the host rock type (with safety margins)(Sperling, 1985). The Waterline pit was not used as a repository for waste rock or ARD treatment sludge as is the case for the Mainzone pit lake.

A CTD cast was taken with every chemical sampling session including temperature, conductivity, fluorescence, transmissivity and, in later casts (after June 02), optical backscatter. A thermistor chain was added to the Waterline pit lake in June 02 and removed in June 03, providing a continuous record of water temperature at discrete depths. The physical limnology of the Waterline pit lake has been discussed at length in the M.Sc. thesis of Mr Albert Leung (Leung, 2003). A summary of the physical structure and dynamics of the lake is given here with special reference to their relevance to the geochemical processes at work in the pit lake.

2.5.2.1 Stratification

No overturn of the Waterline pit lake was observed during the two-year study period with the maximum depth of the oxic epilimnion reaching 8.5 m. The WLP is stratified due the changes in the concentrations of solutes rather than temperature or particulates. The major solutes contributing to the density changes in the WLP are sulphate, calcium, magnesium and sodium. Although several metals are elevated in concentration relative to natural lakes (e.g. Fe and Mn), these make only a minor contribution to density differences. The largest stratification (largest
density difference) is present between the epilimnion and the hypolimnion, referred to in this thesis as the “chemocline”.

The chemocline varies in depth between 4.5 m in at the start of the summer, deepening through the late fall to a maximum depth of 8.5 m. Over the course of the fall season the chemocline is eroded downwards by a combination of wind stress and penetrative convection, entraining the more “saline” hypolimnetic waters into the epilimnion, thereby increasing the conductivity of the epilimnion. Wind stress at the surface of a lake transfers energy to the surface waters and drives turbulent mixing, surface sloping, internal seiching (Stevens and Lawrence, 1997) and upwelling (Brown et al., 2001). This turbulent mixing is constrained by the density difference at the chemocline where considerably less energy is required to push uniform density water (epilimnion) horizontally than to overcome the inertia of the denser waters below the chemocline.

Up to six separate density layers can be identified in the WLP as the conductivity profile shows a stepped structure through the hypolimnion. The deeper layers (> 10 m) are relatively stable in comparison to the seasonal changes occurring in the epilimnion and at the chemocline although small variations in the hypolimnetic conductivity and metal profiles were seen over the two-year study. The following layers have been identified for formal discussion and reference in this thesis (Figure 2.5.8, page 40):

**Layer 1** – (Surface to 4.5 - 8.5 m) The epilimnion; well mixed; oxic; undergoes the greatest temperature changes over the year (from 1 to 17 degrees) and has the shortest residence time (Leung, 2003). The depth of this layer increases in the fall and decreases over the winter / spring (Figure 2.5.9). The temperature of the epilimnion is greatly influenced by the ambient air temperature and degree of insolation, reaching up to 15 °C in the summer and 0 °C (directly beneath the ice) in winter.

**Layer 2** – (4.5 – 8.5 m to 17 m) The upper part of this layer is part of the mixolimnion while the deeper part is part of the hypolimnion, as it has remained sub-oxic to anoxic during the period of study. This layer contains a relatively uniform conductivity profile with seasonally changing temperature. The conductivity of this layer was remarkably stable considering the seasonal changes in the volume of the layer (as bounded by the chemocline depth) (Figure 2.5.10). Conductivity does increase slightly from June to October, decreasing again over the winter months although is much less variable than other layers. The top of this layer is confined by the less saline and oxic epilimnion with
a turbidity layer consisting primarily of Fe-oxyhydroxide particulates. The bottom of Layer 2 is confined by an increase (cline) in conductivity (a proxy for density) and a decline in the concentration of most metals and metalloids. Despite the relatively uniform conductivity profile, the concentration profiles of several metals (e.g. As and Cd) vary within the layer, suggesting that mixing is not complete within the time frame of some geochemical processes.  

Layer 3 – (17 m to 20.5 m) A relatively thin layer that may be formed through intrusion of a density current or groundwater. Possibly oxic source waters although likely to be anoxic in situ. The conductivity of the lower portion of this layer varies seasonally with the top of the layer remaining relatively stable. The conductivity of this layer increases from top to bottom by up to 240 µS/cm in the early summer (June). Over the course of the summer and into the winter months the conductivity decreases in the lower portion of the layer, possibly indicating the reduced input of intrusive ground waters. The intrusion of groundwater into this layer in spring / early summer is consistent with the freshet and the likely supply of runoff waters.  

Underground mine workings adjacent to the WLP are connected to the pit itself via two adits, Adit 1 at 15 to 20 m and Adit 2 at 33 to 37 m. The roof of these underground workings collapsed several years after mine closure and the holes exposed at the surface were backfilled with waste rock. It is likely that the hydraulic conductivity of the underground workings was increased due to the unconsolidated nature of the waste rock cap. Snow melt, direct precipitation and intercepted local groundwater are all likely to be hydraulically connected to the hypolimnion of the WLP via the old underground mine workings.  

Layer 4 – (20.5 m to 28 m). Layer 4 is assumed to be anoxic although dissolved oxygen measurements were not taken. The conductivity (density) of this layer increases nearly linearly from top to bottom by ~ 170 µS/cm. As with Layer 3, conductivity varied seasonally with an increase at the base of the layer in the early summer and a decrease over the fall / winter. The top of the layer remained relatively constant with respect to conductivity. This layer is characterised by and increase in most metals relative to Layer 3. Temperature throughout the layer remained very constant over the two-year study at 5.2 to 5.4 °C.  

Layer 5 – (28 m to 30.5 m). Layer 5 is also assumed to be anoxic although dissolved oxygen measurements were not taken. The presence of this layer was most obvious in the
January and March 02 sampling sessions. During this period Layer 5 was marked by relatively gently increasing conductivity and moderate haloclines at the top and bottom. Between March 02 and June 02 the conductivity increased most markedly in this layer although an increase was observed through the entire hypolimnion below 20 m. From June 02 through to June 03 the conductivity at the base of this layer decreased steadily although still remained higher than that pre-June 02.

**Layer 6** – (30.5 m to 45m). Layer 5 is also assumed to be anoxic although dissolved oxygen measurements were not taken. This layer represents the deepest portion of the pit lake and has the highest dissolved Fe and As concentrations. As with Layers 4 and 5, the temperature remained constant over the two-year study at 5.4 to 5.6 °C. The conductivity increased with depth most rapidly in the top half of the layer with a more uniform conductivity profile towards the bottom of the pit lake. The lower boundary of Layer 6 is marked by the sediment-water interface.

### 2.5.2.2 Temperature

Spatial and temporal changes in temperature have implications for the density, stratification, chemical kinetics, biological activity and chemical speciation of lake waters (Karr et al., 2003; Stumm and Morgan, 1981). In natural freshwaters, where the concentration of solutes is relatively low (low ionic strength) and conservative with depth, temperature can often determine the stratification of the lake through the development of a thermocline, where a rapid drop in temperature with depth provides enough of a density change to inhibit mixing with surface waters. The depth of the thermocline is dependent on the depth of the lake, the degree of perturbation by wind stress and the variation in temperature on a daily and seasonal basis (Boland and Padovan, 2002; Rodrigo et al., 2001; Schernewski, 2003).

The greatest temperature changes in the WLP occur in the epilimnion with a seasonal variation from close to 0 °C at the surface in winter to up to 16 °C in the summer. Temperature profiles taken within 24 hours of each other during the summer months showed as much as 1 °C change in epilimnnetic waters. Layer 2, directly beneath the chemocline, showed moderate temperature variation from 4.3 to 5.0 °C from mid winter to late fall. Temperatures in this layer also increased over the spring / summer / fall, cooling again through the winter. Below the first chemocline, significant seasonal temperature changes are only observable to a depth of 20 m or
the base of Layer 3 (figure 3.5.3). The coupling of changes in the water column temperature with changes the seasonal atmospheric temperature was only observable to the base of layer 2 (16 m). The warming of the base of layer 2 between January and March (for 2002 and 2003 winter seasons) is likely to be a function groundwater intrusion. The relatively constant conductivity in this layer indicates that the intrusion depth was salinity rather than temperature controlled.

No significant temperature change was observed below 20 m depth in the WLP over the two-year study. Although relatively constant with time at any given depth below 20 m, the temperature increased with depth from 5.2 °C at 20 m to 5.5 °C at 35 m. The underground workings adjacent to the WLP seem to be the most likely non-geothermal source of heat at depth. The process of sulphide oxidation in these mine workings would produce both the heat and sulphate salts required to produce the temperature and conductivity gradient in the WLP hypolimnion.

During the summer / fall of 2002 a series of CTD casts were taken in both the northern (normal chemistry sampling point) and southern (limnocorral experiment location) regions of the WLP. A horizontal gradient in the temperature of the hypolimnion at approximately 8 m was noticed with the southern location being consistently 0.2 to 0.5 °C higher in comparison to the northern region. The heat transfer to this layer from the epilimnion would be distributed over a greater vertical distance in the deeper northern region of the WLP, leading to less temperature gain per unit volume during the summer. It is important to underline that the north-south horizontal temperature difference mentioned here is trivial compared to the temporal and vertical temperature differences in this layer.

2.5.2.3 Intrusions.

The most active intrusion in the WLP appears to be between 15 to 20 m depth (layer 3). As discussed in section 2.5.2.2, an intrusion of warm water enters between these depths and is most notable during the winter months as the water temperature above 15 m cools. Evidence for this intrusion is found in the seasonal increase in conductivity in layer 3, the spring increase in volume in layer 2 and a small increase in conductivity in layer 2 over the summer (section 4.2.5; Figure 4.2.12). The most likely candidate for the source of the intrusive waters is the upper adit (Adit 1) between 15 and 20 m depth (Figure 2.5.8).

Turbidity was seen to increase in layer 2 in the early summer, possibly in response to oxygenation and Fe-oxyhydroxide formation although settling of the same phase from the epilimnion could produce a similar signature. Oxygen was detected at very low levels (< 0.02
mg/L) below the first chemocline to a depth of 10 m on June 21, 2002. It is not clear if this oxygen entered this layer with the intrusive waters or was mixed down from the epilimnion.

The increase in conductivity throughout the hypolimnion, particularly at 19 to 20 m and at 30 m, between March and June 02 (spring/freshet 2002) suggests water intrusion from both adits. The change in conductivity is somewhat hard to explain in the absence of any changes to temperature. Either the source water for the additional conductivity was at thermal equilibrium with the WLP hypolimnetic waters or was of small enough volume not to perturb the temperature. A factor in the lack of a temperature change in the intrusive waters is that temperature has a faster effective diffusion rate than salts and may dissipate through the water column faster than the salinity signal (Pieters, 2004) pers. com. (Stevens and Lawrence, 1998).

The WLP conductivity appears to be primarily due to sulphate. It is interesting that, although the sulphate concentration of the WLP hypolimnetic waters is much greater than natural lake or groundwater, it is relatively low with regards to ARD leachates. The neutral pH and moderate sulphate concentration of the WLP hypolimnetic waters indicate that the vast majority of the water mass is derived from non-ARD impacted meteoric waters. The ARD drainage from the Equity waste rock dumps averages around 15 g/L sulphate (PDC - Equity Division, 2003), three orders of magnitude higher than that in the WLP. It is possible that the additional conductivity came from a small input of high sulphate ARD water near the surface of the pit lake and was entrained into the various layers of the hypolimnion as it sank. No increase in hypolimnetic conductivity or turbidity was seen for the March-June 03 period.

The accidental sludge discharge into the WLP (28th July 02) occurred between the CTD casts taken on 23rd of July 02 and the 1st of August 02. The only definitive change to physical parameters in response to this sludge discharge appears to be a slight warming of layer 3 (17 m). Two distinct layers of turbidity, peaking at 11 and 16 m, also appeared between July 23rd and August 1st although these may be attributable to settling of particles present in the water column prior to the sludge discharge (Figure 2.5.11).

2.5.2.4 Inflows

The major inflow into the WLP is seepage from Berzelius Creek at the northeastern corner of the pit lake. The annual inflow of Berzelius Creek water into the WLP is estimated from the pit outflow rate as between 10 to 20 L/s. The Berzelius Creek is a natural waterway that bisected the present location of the WLP, crossing east-west. During mining and the subsequent mine closure this creek has been diverted around the northern perimeter of the WLP so as to
reduce the input of natural runoff into the pit and so the volume of "mine impacted" water. Base-
flow permeates the diversion channel levy as it passes the northeast corner of the WLP, causing
seepage from the Berzelius Creek flow to enter the WLP. The catchment of the Berzelius Creek
upstream of the WLP is largely un-impacted by mining and the creek waters are fresh and
contain low metal concentrations. The conductivity and major ion content (and hence density) of
the creek waters is much lower than that of the epilimnion of the WLP. In the absence of mixing
the creek waters would be expected to form a fresh cap over the top of the WLP waters. The
absence of a freshwater cap on the WLP can be attributed to mixing of the Berzelius Creek
inflow waters with the WLP epilimnion waters and with pit wall run off. The epilimnion of the
WLP is at its freshest during the early summer suggesting that the stronger flows during the
freshet contribute a higher percentage of the epilimnion at this time.

2.5.2.5 Precipitation

The surface area of the WLP is approximately 2.6 ha at the current water level (1265 m
elevation) which, at an annual precipitation rate of ~ 670 mm, gives a direct precipitation volume
of 0.017 Mm$^3$/yr. Direct precipitation is almost an order of magnitude less than the estimated
inflow from the Berzelius Creek. The contribution of run-off from the pit walls to the WLP
inflows is likely to be on the same order as that for direct precipitation. Estimates of the total
catchment area (0.078 km$^2$) taken from contour maps gives a total precipitation run-off to the pit
of 0.052 Mm$^3$/yr, assuming no loss to groundwater or evaporation.

2.5.2.6 Wind

A meteorological station was installed on a raft in the northern end of the WLP from June 02 to
June 03, recording wind speed and direction. Average recorded wind speed, corrected to 10 m
above ground, was 2.2 m/s ($\pm$ 1.4 s.d.), approximately 15% greater than the average wind speed
on the adjacent Mainzone Pit Lake (R. Pieters, pers. comm.). The wind direction was
predominantly from the south, particularly during stronger winds. The higher wind speed can be
attributed to the channelling effect of the narrow, north-south aligned pit contours.

2.5.2.7 Seeps

The pit walls above water level did not appear to contain any permanent groundwater seeps of
significant flow. Free flowing seeps only appeared after heavy rains and would stop flowing
within two to three days after the cessation of precipitation. After a major rainfall in late June 02,
several seeps were sampled from the eastern wall of the pit lake. No seeps major seeps were observed on the western pit wall, possibly indicating the hydraulic gradient in the vicinity of the pit runs from east to west. The eastern pit wall is comprised of largely non-sulphide material (visual inspection only) and does not contain significant sulphide bearing overburden or waste rock in its direct catchment zone. The estimated flow rate of the post-rainfall seeps was trivial in comparison to that of the Berzelius Creek overflow (the major tributary to the WLP) or the outflow of the WLP into the Mainzone pit lake. The flow rate of WLP seeps were not accurately determined due to the lack of access and subsequent safety concerns.

2.5.2.8 Groundwater

The contribution of groundwater to the WLP is unknown although it is suspected that one or possibly two groundwater intrusions are active in the hypolimnion (see section 3.2.2). No accurate filling rate records are available for the WLP after mine closure to judge the contribution of ground waters. Pit filling rates are also likely to over estimate the contribution of groundwater to the filled pit lake as the difference in hydraulic head between the groundwater and the pit void is reduced or even reversed upon filling. The topography of the surrounding catchment area and several hydrological investigations would suggest that the hydraulic gradient is from east to west with the upstream recharge area being relatively small (< 1 km²). The low flow rate and temporary nature of the visible seeps into the WLP (see section 3.2.6) indicate that the seeps represent discharge from a relatively small catchment, possibly only the fractured pit wall face (where blasting during mining increased the hydraulic conductivity of the bedrock adjacent to the blast surface).

The study of hydraulic conductivity in the local geological structures has been largely confined to the area adjacent to the Mainzone Pit although the close proximity of the Waterline Pit to the Mainzone would suggest that these are probably relevant to both pit lakes. The hydraulic conductivity values determined by Sperling (1985) were found to be dependent on the geological unit (e.g. gabbro, lapilli tuff, dust tuff) and the alteration status (e.g. weathered or intact). The major geological unit in the vicinity of the WLP is composed of lapilli tuff, having one of the higher hydraulic conductivities at $10^{-5}$ to $10^{-6}$ m/s (Sperling, 1985). A significant portion of the eastern wall of the WLP is composed of gabbroic monzonite, having a bulk hydraulic conductivity of between $9.6 \times 10^{-6}$ to $1.2 \times 10^{-9}$ m/s, considerably less than that of the dominant lapilli tuff.
The actual hydraulic conductivities adjacent to the pit walls are likely to be considerably different to those of the bulk geological unit due to increased local fracturing caused by blasting during mine operation as well as the targeted nature of the ore extraction. The silver / copper ore was found predominantly in the form of discrete massive and disseminated sulphide mineralizations within local pyroclastic material (lapilli tuff). The lower portions of the pit lake walls are likely to be bounded by the local alteration structures hosting the sulphide mineralizations rather than material typical of the wider geological unit.

2.5.2.9 Pit Walls

The composition of the WLP walls is discussed above in 3.5.1.8 (Groundwater) in relation to hydraulic conductivity and in section 5.2.1 in relation to their contribution to sulphate in the WLP waters. The pit walls of the WLP have not been closely studied in relation to their acid neutralization capacity or net acid generation capacity. The effects of ARD are usually visually apparent in the form of “yellowish” and unconsolidated rock material. The only obvious ARD generating rock in the WLP walls was present in the top two benches of the western wall and in a thin layer of possibly oxidized material at the surface of the north-east corner of the pit. This sulphide bearing rock is estimated to make up less than 20% of the total pit wall area.

The WLP is located within tapilli tuff (pyroclastic material) with the eastern wall bounded by a gabbroic monzonite (siliceous material) intrusion. A study of the net neutralization capacity of the lithologies in the Mainzone pit lake found that the lapilli tuff is likely to be net acid producing while the gabbro material is likely to be acid neutralizing (Morin, 1990).
2.5.2.10 Outflows

The only directly observable outflow from the Waterline Pit Lake (WLP) is an overflow channel (decant at 1265 m elevation) at the southern end, flowing directly into the Mainzone Pit Lake (MZP). The flow rate at the Waterline Outflow (WLO) is approximately 5-20 L/s for the duration of the summer and fall. This flow rate is likely to be much greater during the spring freshet although this has not been well confined. A pressure sensor was located in the WLP for the duration of the 2003 freshet although the flow / stage curve could not be calibrated due to the lack of data points during the highest stage and the irregular nature of the outflow channel. The water quality at the outflow is representative of the top 20 cm of the WLP epilimnion only and does not introduce elevated Fe or As into the MZP.

The calculation of epilimnion residence times is difficult due to the largely unknown flows during the freshet. Outflow rates recorded during the course of the summer indicate that residence times for the epilimnion are on the order of 100 days. The residence time for the whole lake could not be calculated due to unknown contributions from adits and groundwaters.
Figure 2.5.8: Waterline Pit Lake density structure (using conductivity as a proxy for density). March 21, 02.

Figure 2.5.9: Waterline Pit Lake – Development of the epilimnion over summer / fall 2002.
**Figure 2.5.10:** Waterline Pit Lake Temperature and Conductivity Evolution – 21 June 01 to 13 June 03. Note: 0 m and 2 m temperature timeline not shown for simplicity (temp varies with daily temps). Accidental ARD treatment sludge discharge on 28th July 02 shown.
Figure 2.5.11: Waterline Pit Lake conductivity, temperature and optical backscatter (OBS) profiles for the period June 21, to August 1, 02 (Accidental sludge discharge July 28, 02).
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3 Results

3.1 Main Zone Pit Lake Biogeochemistry.

3.1.1 Main Zone Pit Lake – Aqueous biogeochemistry

The Main Zone pit lake (MZP) does not represent a typical mining void lake in that this waterbody is significantly influenced by the input of ARD treatment sludge by the mine operators. The sludge discharge has both geochemical and physical implications. Particulate phases of metals in the water column can also be almost entirely attributed to the presence of very fine-grained particles of sludge that are dispersed throughout the water column. Despite variability in the volume and timing of sludge inputs, the concentrations at depth (below ~10 m) of the dissolved metals did not change significantly over the two-year study. However, a seasonal enrichment of several metals, most notably Fe$_{\text{part}}$, Cu$_{\text{diss}}$, Zn$_{\text{diss}}$ and Ba$_{\text{diss}}$ occurred in the epilimnion of the lake during the early spring / summer. This surface “plume” of metal enriched waters appeared unrelated to the sludge and disappeared at depth due to mixing (dilution) with hypolimnion water. The remainder of this section and the following discussion focus on the sources and geochemical dynamics of the surface enrichment of metals and the influence of sludge addition to the lake. The formal discussion of the sludge composition is given in the Main Zone Sediments section (3.1.2). The mining history, physical dimensions, temperature, conductivity, sludge deposition history and water balance of the MZP are discussed in section 2.5.1. Sampling locations are shown in Figure 2.2 (section 2.0). Profiles of conductivity and temperature collected on dates when samples for chemistry were retrieved are shown in Figure 3.1.1, along with profiles of fluorescence (chlorophyll), transmissivity (light transmission), and optical backscatter (OBS) (Figure 3.1.2). Transmissivity and OBS profiles were used as the primary source for detecting the extent of the sludge plume in the MZP during sampling sessions. It is useful to refer to Figure 3.1.2 when interpreting the dissolved and particulate metal profiles (Figures 3.1.10 to 3.1.20).
Figure 3.1.1: Main Zone pit temperature and conductivity profiles - June 01 to June 03
Figure 3.1.2: Mainzone Pit fluorescence, transmissivity and, optical backscatter (OBS) profiles - June 01 to June 03.
3.1.1.1 Major element chemistry

The major anion in the Main Zone pit lake is sulphate with dissolved sulphate concentrations being almost double that of the neighboring Waterline pit lake. Only two major ion determinations were carried out on the Main Zone pit waters, both in June 2001. These returned sulphate concentrations of 18 at the surface and 23 mM at 40 m depth. The conjugate cations are comprised primarily of Ca (9.4 and 11.9 mM) and Mg (3.67 and 5.5 mM) with lesser concentrations of Na (0.5 and 0.65 mM), Sr (70 and 80 µM) and K (40 and 50 µM). The charge balance was not well constrained from these determinations with only 74 and 77 % of the charge attributable to dissolved sulphate balanced by the measured cations. Dissolved metals contribute a negligible cationic charge in comparison to the major ions listed.

The sludge deposited into the MZP can contain dissolved cations at much higher concentrations than those listed above. During the late freshet period of 2002, partially treated ARD waters were discharged to the MZP. These contained up to 30 mM Ca and 39 mM Mg. The impact of sludge disposal on major ions was unfortunately not assessed in this study.

The alkalinity of the MZP was assessed on two dates, March 19, 02 and June 11, 03. On both dates the profile of alkalinity was reasonably uniform throughout the pit lake with an average value of 40.1 mg/L and 27.3 mg/L, respectively (CaCO₃ equiv.). These values are only 15 to 40 % of the alkalinity of the Waterline pit waters on the same dates. Measurements of the sludge alkalinity during 2002 averaged 17 mg/L (s.d. = 8.5, n = 42). Historic sludge alkalinity is recorded as 30 to 40 mg/L (CaCO₃ equiv.) (Norecol Environmental Consultants Ltd., 1991).

The pH of the MZP ranged from 6.7 through to 8.09, with values toward the lower end of this range consistently characterizing the epilimnion during the winter sampling sessions. The pH meters available had stability problems and despite regular calibration during analysis they still displayed some variance (up to 0.2 pH units) in repeat samples. The lowest average water column pH (6.75) was recorded on the last sampling session in June 2003. The frequency of pH sampling in this study was insufficient to ascertain seasonal changes though PDC-Equity regularly took pH samples from 15 to 20 m depth (depth of pump intake for discharging MZP waters to the environment). These samples displayed a gradual increase in pH over the summer of 2002 from pH 7.0 on June 13, to pH 8.6 on Sept, 12, 02. The well mixed nature of the MZP during periods of sludge deposition (as was the case between the above dates) would suggest that the pH at 15 to 20 m depth would be representative of that in the pit as a whole.
**Dissolved Oxygen.** The dissolved oxygen (D.O.) concentration and % saturation profiles (calculated as a function of water temperature) are shown in Figure 3.1.3. While a slight increase in D.O. could be observed in the vicinity of the sludge plume, the overall water column D.O. concentrations and oxygen saturation state did not display any distinct pattern between sludge-deposition and non-sludge-deposition periods. The upper 5 to 10 m of the water column were near to, or in excess of, saturation with respect to D.O. for all sampling dates apart from January and March 2003. The saturation state of the water column below 10 m depth ranged from 68 % (March 2003) to 100 % (summer / fall 2002). Winter oxygen demand could not be calculated as sludge was deposited into the pit lake between all sampling dates and this discharge almost certainly entrained oxygen into the pit waters.

During the summer and fall of 2001 most of the water column remained <80 % D.O. saturation despite near continuous sludge deposition over this time period. D.O. concentrations and % saturation increased between the fall and winter of 2001/2002 to reach ~90 % saturation throughout the water column by March 2002. With continued sludge deposition, the water column reached ~100 % saturation by the late summer/fall 2002. There was evidence of a slight stratification of the water column October 2002 and a stronger stratification observed on January 21, 2003. This stratification coincided with a lowering of D.O. concentrations in winter 2003 to below 70 % saturation (Figure 2.5.6). The water column remained at below 75 % saturation over the following six months to June 13, 2003 despite three months of sludge deposition during that period.
Figure 3.1.3: Main Zone pit dissolved oxygen and % oxygen saturation profiles - Oct 01 to June 03.
3.1.1.2 Nutrients and biology

The productivity of phytoplankton in the MZP was measured semi-quantitatively through the measurement of chlorophyll fluorescence with a fluorometer attached to a Seabird SBE 19 CTD (see Methods section in Appendix A.). On the majority of ice-free sampling dates a distinct peak in fluorescence was measured in the top 10 m of the water column. The depth and breadth of the fluorescence peak is shown by sample date in Figure 4.1.4, together with thermocline and chemocline depths. To confirm the presence of phytoplankton chlorophyll samples were also taken for particulate chlorophyll using glass fiber filters (GFF). These were analyzed via acetone digestion (90%) and lab-based fluorometry. Figure 3.1.4 shows a fluorescence profile calibrated to chlorophyll measured in discrete GFF samples together with dissolved phosphate. It can be seen that the peak in chlorophyll corresponds to a decline in dissolved phosphate concentrations. The chlorophyll peak is close the bottom edge of the phosphate depleted zone suggesting that the phytoplankton bloom may be balanced between light availability and phosphate availability.

Phytoplankton blooms were detected beneath the ice during the January and March 02 and to a lesser extent in January and March 03 (Figure 3.1.2). Chlorophyll values measured in the top 2 m of the water column in March 02 (average = 3.9 ug/L) were of a similar order to those found at the height of the previous summer (Aug 14, 2001, average = 3.17 ug/L). This suggests that the phytoplankton blooms may be phosphate limited rather than light limited during the summer months. This was confirmed by the generation of large phytoplankton blooms upon the addition of phosphate during the Main Zone pit limnocorral experiments. The largest integrated fluorescence peak was measured under the ice on Jan 22, 02 and coincided with the highest dissolved phosphate concentrations recorded in the top 8 m of the water column (average = 0.06 umol). The fact that dissolved phosphate concentrations were positively correlated to fluorescence on Jan 22, 02 may indicate that on this date the phytoplankton were light rather than phosphate limited.

Figure 3.1.7 shows the distribution of dissolved phosphate, nitrate and silicate with depth during sludge deposition to the MZP on Aug 14, 2001. While nitrate and silicate follow similar distribution patterns, no direct correlation could be made to the presence of sludge (as defined in Figure 3.1.7 by a reduction in transmissivity). Nitrate concentrations typically ranged from 20 to 40 umol with the lowest concentrations being recorded in Oct 01. Dissolved silicate concentrations were typically highest in the upper 10 m of the water column, reaching a peak of 51 uM in the surface waters of the MZP on Jan 22, 02. On this same date the total water column
inventory of dissolved silicate was almost double that of the previous summer. Silicate levels dropped considerably over the next two months to March 19, 02 to a third of that present in January. Despite the well-documented affinity of phosphate for adsorption to Fe-oxyhydroxides (Ding et al., 2000; Ler and Stanforth, 2003), the highest dissolved phosphate concentrations were recorded during sludge deposition into the MZP and at the same depths as the sludge particulate plume.

As would be expected, particulate organic carbon concentrations were highest in the upper 10 m of the water column at the location of the summer phytoplankton blooms (Figure 3.1.6). Unfortunately chlorophyll and POC samples were not taken congruently in the MZP and as such a ratio of one to the other could not be ascertained. The fluorescence values were calibrated to chlorophyll on dates where chlorophyll was sampled and then this calibrated “fluorescence - chlorophyll” relationship was used to estimate chlorophyll from fluorescence on dates where POC was sampled. The calculations estimated the ratio of POC to chlorophyll to be 200:1 to 300:1. This is on the lower end of the typical range of growing phytoplankton (typically between 50:1 and 150:1) (Cloern et al., 1995). Lower carbon to chlorophyll ratios tend to be associated with lower growth rates in phytoplankton as well a nutrient rather than light limitation.

POC concentrations in the water column of the MZP were lower over the winter period, ranging from 100 to 400 mg C/L.

Dissolved organic carbon (DOC) was not measured during the phytoplankton blooms. DOC concentrations during the winter of 2003 were relatively stable and uniform throughout the water column at 0.7 to 0.8 mg C/L.
**Figure 3.1.4:** Timeline of Fluorescence peak depth, thermocline and chemocline depth in the Main Zone pit lake – June 01 to June 03.

Notes: The total chlorophyll values in the lower graph are relative only and are calculated from CTD fluorescence measurements, not field samples. Values for field chlorophyll concentrations tended to be lower than those for CTD fluorescence by a factor of two-thirds or more. CTD fluorescence “chlorophyll” units are calculated based on the manufacturers generic calibration values.
Figure 3.1.5: Profiles of dissolved phosphate and fluorescence (Chl. a) in the Main Zone pit lake – Aug 14, 2002. Note: fluorometer chlorophyll values calibrated from GFF (field sample) chlorophyll values. Fluorometer depth also corrected for pumping lag (fluorometer aligned to sample depths).

Figure 3.1.6: Profile of Particulate Organic Carbon (POC) and fluorescence (calibrated to chlorophyll a.) in the Main Zone pit surface waters – Aug 26, 2002. Note: CTD pump lag has not been corrected for in fluorescence data. Fluorescence peak would become slightly broader upon correction.
Figure 3.1.7: Main Zone pit lake dissolved phosphate, dissolved nitrate, dissolved silicate and transmissivity profiles – Aug 14, 02. Note: sludge deposition occurring at time of sampling.
3.1.1.3 Metals (biogeochemistry and distribution)

The particulate fraction of most metals (e.g. Fe, Ni, Cu, Zn, Cd and U) in the MZP could be directly attributable to the disposal of ARD treatment sludge into the pit lake (Figure 3.1.8). Dissolved concentrations of most metals did not vary greatly over the course of the two-year study period with the exception of Mn and possibly Co. For the sake of brevity, only the key metals (present in large concentrations in the Equity ARD) of Mn, Fe, Cu and Zn are presented in detail. Other metals are discussed in support of likely physical and geochemical processes involving these key elements. While As is also present in elevated concentrations in the Equity ARD, this element is near or below detection limit in dissolved form in the MZP waters.

The dissolved and total concentration profiles for each element on each sampling date are presented in Figures 3.1.10 through to 3.1.20. To aid in the interpretation of metal concentration profiles, the conductivity and temperature profiles are given in Figure 3.1.1 and the optical backscatter, transmissivity and fluorescence profiles in Figure 3.1.2. Dissolved oxygen profiles (mg/L and % saturation) are given in Figure 3.1.3. A full set of dissolved and particulate metal profiles for Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Cd, Sb, Ba and U are given in Figures 3.1.10 through to 3.1.20.

**Manganese.** The MZP dissolved and total concentration profiles for Mn are shown by date in Figure 3.1.10. The record of Mn concentrations in the MZP is not as comprehensive as those for most other metals as this element was only added to the analytical suite mid-way through the project. Of the dissolved metals analyzed, Mn was present in by far the largest concentrations with peak values of 2200 ppb in the surface waters on June 13, 2003. A peak in dissolved Mn was seen in the surface waters during the winter period (under ice) and in the early summer, suggesting a surface source of dissolved Mn not associated with sludge deposition.

The lowest water column inventory of total Mn (predominantly dissolved Mn) was recorded in January 2002 in the absence of sludge deposition. Sludge deposition from February to March 2002 appeared to increase the concentrations of dissolved Mn in the entire water column. Between January 22, and October 8, 2002 the concentration of dissolved Mn in the MZP increased markedly from less than 100 ppb to more than 2100 ppb. Apart from a small fractionation to a particulate phase (~30%) below 80 m depth observed on June 19, dissolved Mn accounted for more than 95 % of the total Mn pool over this period.
Between Oct 8, 02 and Jan 23, 03 the fractionation of Mn to a particulate phase occurred with total Mn remaining at October 02 levels (in the water column above 40 m depth), although dissolved Mn concentrations declined by approximately 15%. By March 11, 2003, dissolved Mn was below detection limit (5 ppb) in the water column above 20 m depth. Below this depth dissolved Mn concentrations increased up to 325 ppb due to the resumption of sludge deposition into the MZP in early March 03. This decrease in dissolved Mn concentrations in the upper 20 m of the water column from 2100 ppb to below 5 ppb over the period of 5 months indicates that a strong Mn removal mechanism operates in the MZP during the winter months. Particulate Mn had decreased by 1800 ppb over the same time period indicating precipitation of Mn from the water column had occurred. This mechanism may operate during the sludge deposition periods as well, although is masked by the continual input of dissolved Mn with the sludge.

By June 11, 2003 Mn was again almost entirely in the dissolved fraction and had increased to concentrations similar to those present in the water column in the previous June (2002) (average below 10 m depth = 950 ppb). As with June 2002 and March 2003, a distinct peak in dissolved Mn was present in the surface waters (top 5 m) on June 11, 03, reaching concentrations of 2200 ppb.

Iron. The MZP dissolved and total concentration profiles for Fe are shown by date in Figure 3.1.11. A surface peak in particulate Fe was seen in the top 10 to 15 m of the water column during most of the summer and fall period. No dissolved Fe was detected within this peak. The dissolved Fe concentrations in the MZP were typically below detection limit (5 to 10 ppb) throughout the water column. The only dissolved Fe detected over the two year study period occurred in the upper 10 m of the water column during the winter ice over and once in the deep water column (40 to 80 m depth) in March 2002, during sludge deposition. The highest dissolved Fe concentration in the MZP (52 ppb) was at 5 m depth in January 2002. The dissolved Fe in the deep water column in March 2002 was detected largely above the sludge plume and was not detected in the bulk of the sludge plume (as measured by optical backscatter). Fe occurred entirely in the dissolved fraction at 40 m depth on this date (44 ppb), following an increase in dissolved Mn with depth and coinciding with an increase in transmissivity (clearer water).

It can be seen from Figure 3.1.8 and a comparison of water turbidity data with particulate Fe concentrations (Figures 3.1.2 and 3.1.11), that the particulate Fe concentrations were closely associated with the sludge deposition. The highest concentrations of particulate Fe were recorded on June 19, 02 with up to 10 mg/L Fe in the peak of the sludge plume (120 m depth). The total
suspended solids (TSS) measured at the same depth was 125 mg/L, Fe therefore comprised 8 %
of the TSS, roughly the same percentage Fe as in the freeze cored sediments of the pit lake
sludge (average = 8.2 %). Fe comprised 12 % of the solids deposited in the 50 m sediment trap
over the period from March 20 to July 8, 2002 (encompassing the June 19 sampling session)
suggesting that the winter sludge deposition (Feb-March 02) or early freshet discharge may have
contained a slightly higher percentage of Fe. This hypothesis is confirmed by Figure 3.1.9
showing average monthly metal loadings in ARD flows during 2002 together with the ratio of
Fe/Cu and Fe/Zn. It can be seen from this figure that the ratio of Fe to both Zn and Cu in the
ARD decreases over the course of the freshet / summer period with the greatest loading of ARD
being Fe enriched. This ARD is the foundation for the metal content in the ARD treatment
sludge and as such the sludge can be expected to follow the same pattern.

Copper. Cu is abundant in the ARD treatment sludge, forming up to 5 % by weight of
the trace metal concentration in the sludge. The changing ratio of Fe:Zn:Cu in the ARD (and
hence sludge) over the 2002 season is presented in Figure 3.1.9. The total and dissolved Cu
concentration profiles for the MZP are shown in Figure 3.1.14. A significant dissolved and
particulate fraction of Cu existed in the water column of the MZP throughout the year. The
highest dissolved Cu concentrations were observed during the early summer on June 25, 2001
and June 19, 2002 (19 and 47 ppb respectively) in the top 2 m of the water column. This pattern
is similar to the distributions of dissolved Zn, Cd, Ni and Mn. Dissolved Cu concentrations
typically ranged from 1 to 3 ppb with both the lowest surface water and highest deep water
concentrations being recorded in March 2003 (0.5 and 4.4 ppb respectively). In general the
dissolved concentration profile did not follow that of the particulate Cu profile during periods of
sludge deposition suggesting that the sludge contained little dissolved Cu or that the dissolved
fraction was distributed more widely than the particulate sludge fraction. The exception to this
rule was the March 2003 profile in which moderate concentrations of dissolved Cu did appear to
be introduced to the pit lake through the deposition of sludge.

Particulate Cu was predominantly associated with the deposition of sludge into the MZP
and during these periods reached up to three orders of magnitude greater concentrations (2450
ppb) than the dissolved phase (2 ppb). In the absence of sludge deposition (during the winter
months) particulate Cu still constituted around 50 % of the Cu pool. This is in contrast to Ni, Zn
and Cd where the particulate phase was at or near detection limit in the winter (January)
samples.
**Zinc.** The dissolved Zn distribution appeared similar to that for Cu in that an early summer surface maximum was observed with a late fall minimum though, unlike Cu, the Zn surface peak began to re-establish itself during the winter months. The deep water-column concentrations of dissolved Zn ranged from 3 ppb (October, 2001) to ~140 ppb (March 2003). Other than a summer / fall mixing down and dilution of elevated Zn in the surface waters, no seasonal pattern could be observed for dissolved Zn concentrations. Particulate Zn was sourced predominantly from the sludge and was below detection limit in the water column in January 2002 in the absence of active sludge deposition. A small particulate Zn fraction was present in January 2003 though this also coincided with a significant Mn particulate fraction at this time.

**Other trace metals.** The ratios of Ni, Cd and U in suspended particulate matter in the MZP to sludge are shown in Figure 3.1.8. From this figure it can be seen that, during sludge deposition, the particulate distribution of these metals is dominated by sludge particles. Moderate surface maxima of Mo and Sb were present during the spring / summer.
Figure 3.1.8: Ratio of metals in ARD treatment sludge to particulate metals in the water column of the Main Zone pit lake, during sludge deposition (Aug 26, 02). Total particulate concentration in the water column is represented by a decrease in light transmissivity (thick black line). Sludge sample taken on Aug 30, 02 at the outfall into the MZP. Sludge digestion by concentrated nitric acid.
Figure 3.1.9: Average ARD metal loadings for Fe, Cu and Zn and; Fe/Zn and Fe/Cu ratios in the ARD stream for 2002. This ARD is fed into the lime neutralization plant and forms the basis of the sludge deposited to the Main Zone pit lake (Sourced from (PDC - Equity Division, 2003)).
Figure 3.1.10: Main Zone pit lake total and dissolved manganese profiles – Jan 02 to June 03.
Figure 3.1.11: Main Zone pit lake total and dissolved iron profiles – Jan 02 to June 03.
Figure 3.1.12: Main Zone pit lake total and dissolved cobalt profiles – Oct 01 to June 03.
Figure 3.1.13: Main Zone pit lake total and dissolved nickel profiles – June 01 to June 03.
Figure 3.1.14: Main Zone pit lake total and dissolved copper profiles – June 01 to June 03.
Figure 3.1.15: Main Zone pit lake total and dissolved zinc profiles – June 01 to June 03.
Figure 3.1.16: Main Zone pit lake total and dissolved cadmium profiles – June 01 to June 03.
3.1.2 Main Zone Pit Lake - Sediments

**Background.** As outlined in section 2.5.1 and 3.1.1, the sediments of the Main Zone Pit are dominated by ARD treatment sludge pumped into the pit for final disposal. A freeze core was taken in March 02 in an attempt to characterize the sediment-water interface. This core penetrated past the interface and so did not achieve this primary objective. Although the absolute depth of the core material in relation to the sediment-water interface is not known, the core still contains useful information on the general density and composition of the sediment solid phase. This core, together with other sediment grabs, confirmed that the sediments of this pit comprise unconsolidated sludge material with possible traces of authigenic material (such as Mn oxyhydroxides and organic carbon). A peeper or dialysis array sampler was also deployed in January 02 to assess the dissolved phase chemistry of the sediment-water interface. The presence of an extended nepheloid layer and soft surface sediments also prevented definition of the sediment-water interface for the peeper samples. The peeper data are considered to represent general sediment porewater chemistry and are used as being indicative of near surface sediment porewaters.

The freeze core (~2 m in length) contained two regions of “laminated” or striped sediments, each of around 10-20 cm in thickness, and each consisting of dark brown material. The bulk of the core was uniform orange/light brown, of similar colour and consistency above and below the laminated zones (Figures 3.1.18 and 3.1.19). The angle of the laminated sections through the horizontal width of the core was approximately 45 degrees to horizontal. This is unlikely to be real and is attributed to the corer penetrating the sediments obliquely. These laminated regions contained elevated Mn relative to Fe though other metals were largely consistent with Fe down core (Figure 3.1.19).

**ARD treatment Sludge Characterization and Properties.**

The solid phase of the treatment sludge is primarily the result of oxidation of ferrous iron in the acid mine drainage waters upon raising the pH through addition of CaO.H₂O (lime) in the aerated solution. Gypsum (CaSO₄.2H₂O) also precipitates in the limed solution, and is a major constituent in the sludge.

Although the freeze core taken in the Main Zone pit cannot be referenced to the absolute depth from the sediment water interface, the data it provides are still useful as a general
indication of the in-situ sediment characteristics. Distinct laminations suggest that the core captured a sequence of sediments deposited during a change in the depositional phase, either over the winter when discharge ceased or during a period or periods during which discharge was episodic.

Given the high sludge discharge rate, sediment traps were not deployed deeper than 50 m in the water column (where they would be rapidly filled with settling sludge). Thus, only results from traps shallower than 50 m are presented here. The ratio of metals in the sludge and those in the sediment traps were similar for all metals except Mn, Mo and Ba. These three elements occurred in considerably higher concentrations in the traps, relative to the composition of the bulk sludge retrieved by the freeze corer. In contrast, Fe, Co, Ni, Cu, Zn, As and U contents in the trap samples were similar to those in the bulk sludge. These observations suggest collectively that there is an additional solid-phase source in the surface waters for Mn, Mo, Sb and Ba.

The flux rates of selected metals over time are displayed in Figure 3.1.17 as average fluxes per m² of surface area. While the total flux for most metals increased with depth, the flux per m of water column did not. The general pattern of sediment deposition between the three sediment trap depths (10, 20 and 50 m) was a similar flux per m at 10 m and 50 m though a reduced flux at 20 m. As noted above this was not the case for Mn, Mo, Sb and Ba where the surface (10 m trap) flux was considerably higher per m of water column (80, 204, 89 and 168 % greater than at 50 m respectively). The total flux for Fe was remarkably similar at 10 m and 50 m depth as a function of water column depth, within 1 % averaged over the two-year study.

All metals displayed a lower rate of deposition per m of water column at 20 m depth than at 10 m. This implies that a surface supply may be present for all metals, and that deeper in the water column, sludge becomes a proportionately more important source. The average Mn flux per m of water column was remarkably consistent at both 20 m and 50 m depth at 7.63 and 7.64 mg/m²/day/m_depth respectively over the study period. This rate would equate to the removal of 2800 ppb of Mn from the water column per year. If the particulate Mn supplied through sludge is subtracted from this figure (using Fe as a proxy for sludge) then the authigenic Mn precipitation rate is calculated to be on the order of 2500 ppb per year. This is equivalent to the entire pool of dissolved Mn found in the water column at its peak in Oct 02. By March 03, the dissolved Mn concentration was below detection limit in the upper water column, implying near-quantitative precipitation (or adsorption onto particle surfaces).

A considerable total carbon content was measured in the MZP sediment traps but because particulate organic carbon was not specifically measured, the total C cannot be differentiated
from detrital organic particles. However, the general pattern of carbon deposition relative to Fe was one of increased C in the top 10 m of the water column and the carbon flux, relative to Fe, in summer phytoplankton growth periods. This would suggest that a significant portion of the carbon in the 10 m sediment traps may be attributable to organic carbon. Organic carbon comprised approximately half of the total carbon in the freeze cored sediments, implying that a significant fraction of the particulate organic carbon flux reaches the lake floor and is buried in the sediments.
Figure 3.1.17: Main Zone pit lake particulate metal flux to the sediments at 10 m, 20 m and 50 m depth – Aug 01 to June 03.
Figure 3.1.18: A close up of the Main Zone Pit sediment freeze core, March 02, showing lamination.

Figure 3.1.19: Mn and Zn ratios to Fe (by weight) in the MZP Freeze Core – March 2002. Note: photograph of Freeze Core aligned to sample depths. Photograph contrast enhanced to display lamination.
3.2 Waterline Pit Lake Biogeochemistry

A two-year study of the geochemical and physical behavior of the Waterline Pit Lake (WPL) was undertaken between June 2001 and June 2003. This section presents the results of this study with an emphasis on the aquatic geochemistry of the pit lake. The physical behavior of the pit lake was the focus of another thesis (Leung, 2003) and the physical data from that work are used here (predominantly) to support the geochemical results.

The WLP is a meromictic, circum neutral (pH 7.5), brackish lake with a high aspect ratio (surface area / depth). The lake is ~43 m deep, although only a small fraction of the surface area (2.6 ha) reaches this depth (see Figure 2.3 in the Site Description). Initially the Waterline pit lake was not considered a high priority within the overall Equity Pit Lake Project. The Main Zone pit lake and the Main Zone limnocorral experiments were to comprise the bulk of the sampling and analytical effort. On the first sampling date (June, 01) only a surface sample was taken of the WPL as opposed to a full vertical profile of the Main Zone pit lake (21 depths). The CTD cast taken on the initial sampling session indicated an interesting physical structure to the Waterline Pit (Figure 2.5.8). On the second sampling session (Aug 17, 01) a more extensive investigation of the Waterline pit was undertaken with samples for dissolved and total metals taken every 5 m from the surface to the lake bottom (~35 m). Dissolved oxygen measurements obtained during the third sampling session (Oct 3, 01) indicated an anoxic hypolimnion below 10 m. The strong chemocline, anoxic monimolimnion and high metal concentrations within the WLP proved to be an interesting study point and the project was expanded to include a further limnocorral experiment in the Waterline pit lake coupled with a more comprehensive study of its geochemistry and physical characteristics. Twelve chemical sampling sessions were conducted, one every two months (on average), over the period of two years.

Between July 27, and July 28, 02 an accidental discharge of ARD treatment sludge entered the Waterline Pit Lake. The sludge came from an open channel carrying waste from an ARD lime treatment plant to the Main Zone Pit, where it is normally discharged. This channel broke its banks and the resulting spillage ran into the shallow southern end of the WLP at the surface. The ARD treatment sludge is oxic, dense and contains a large percentage of metal oxyhydroxide solids and gypsum. The path and impact of the sludge discharge into the WLP was monitored via weekly CTD casts and a chemistry profile on Aug 7, 02 (one week after the spill). As the WLP is meromictic, changes in the chemistry of its hypolimnion are typically small over
intra-annual time periods. This spill represented an unusual input to the hypolimnion of the pit lake and the geochemical results of this event are also discussed in this section.

The Waterline Limnocorral experiment aided in the understanding of the geochemistry of the WLP under normal, non-experimental, conditions as well as the likely response of the pit lake to a change in the nutrient and redox regime. The design and results of the Waterline limnocorral experiments are given in section 3.3.

The physical behavior of the WLP is outlined in section 2.5.2. A raw description of the spatial and temporal changes in parameter concentrations is given in this Results section. All interpretation and analysis of the results is presented in the discussion section 4.2. Values prefixed with a (±) symbol indicate 1 standard deviation unless otherwise stated. The concentration profiles are discussed in relation to the various density stratifications (layers) within the pit lake. It is useful to refer to Section 2.5.1.1 and Figure 2.5.1 prior to reading this section. As a reference, a small figure depicting the profile of the total metal concentration with depth is inserted within the written section for each metal. These figures are not formally numbered as a complete set of dissolved and total metal concentrations for each metal and each sampling date can be found in Figures 3.2.2 through 3.2.10. These are the figures formally referred to in the text.

3.2.1 Waterline Pit Lake – Major element chemistry.

The waters of the WLP are dominated by sulphate (6.6-16 mM) as the major anion and calcium (4.7-10 mM) as the major cation. The mean WLP sulphate concentration is approximately 24 to 57 % that of seawater though the ionic strength, at ~0.03, is only 5 % that of seawater due to much lower Na and Cl concentrations. Mg (1-2.3 mM) and Na (0.4-2.1 mM) are also present in elevated dissolved (<0.45 μm) concentrations when compared to average lake waters (Health Canada, 1987; Peacey et al., 2002; Stumm and Morgan, 1996; Zhang et al., 1999), although are comparable to other mine pit lakes (Ramstedt et al., 2003) and lakes in more rapidly eroding catchments (Burgis and Moris, 1987). Charge balance calculations, assuming oxidation states given from speciation calculations, indicate that the major ions for the WLP are represented by those elements analyzed. In these calculations alkalinity was assumed to represent carbonate alkalinity. Over 80 % of the total sulphate charge can be accounted for by Ca²⁺, Mg²⁺ and Na⁺ representing the counter cations. The metal pool accounts for ~4 % of the total sulphate charge in
the hypolimnion. These calculations are indicative only as far as the unknown carbonate and the hydroxide anion concentrations (pH gives only the proton activity), as well as the speciation of the major cations, allow. The concentrations of Mg, Na, K and SO$_4$ increased with depth, closely following the slope of conductivity. Ca deviated slightly at depth (35 m) from the correlation with conductivity (Figure 4.2.1.), decreasing in concentration relative to the other major elements (e.g. Na, Mg, SO$_4$). The profile for silicate was marked by a maximum in the epilimnion of 160 µM and a near uniform concentration in the hypolimnion of between 30 and 50 µM.

3.2.2 Waterline Pit Lake – Redox chemistry and nutrients.

The redox state of the water column can greatly influence the speciation, transport and aqueous/solid phase distribution of many metals and metalloids. For this reason the redox chemistry of the WLP was followed via several key parameters such as dissolved oxygen, nitrate, nitrite, dissolved/particulate Fe and ammonium. Figure 3.2.1 shows the depth profile data for dissolved oxygen (saturation %), phosphate, nitrate, nitrite and ammonium. Dissolved oxygen (D.O.) was only saturated within the epilimnion, rapidly dropping to below detection limit (0.02 ml/L) through the chemocline/pycnocline at between 4 and 11 m, depending on the season. The calculated pe at equilibrium with the atmosphere and at the pH of the WLP epilimnion (7.54) was 13.6 to 15.0 within the range of temperatures encountered, manually calculated using equations 3.2.1 and 3.2.2.

\[
\frac{1}{2} O_2(g) + 2H^+ + 2e = H_2O(l), \quad \log K = 41.55, \quad -\Delta G^\circ = 237 \text{ kJ mol}^{-1} \quad (3.2.1)
\]

\[
p_e = \frac{1}{2} \log K + \frac{1}{2} \log(p_{O_2}^{1/2}(H^+)^2) \quad (3.2.2)
\]

The saturation of D.O. in the WLP was strongly controlled by the position of the first chemocline (as measured by the conductivity profile). The epilimnion was close to saturation with respect to D.O. for the entire year with the highest saturation values, around 100 %, during the summer and fall periods. Winter D.O. saturation was typically between 80 % and 90 %. Due to higher saturation capacity, the colder waters actually contained more dissolved oxygen than the warmer summer waters. The D.O. concentration at 2 m depth (middle of the epilimnion) varied by around 20 % over the two years of this study, ranging from 9.15 mg/L to 11.02 mg/L.
Unfortunately D.O. was not sampled below ~10 m as it was assumed that surface infusion of atmospheric D.O. was the only source of dissolved oxygen to the deeper waters and, once depleted below the chemocline, it would not re-appear at depth. Further analysis of CTD data and metal profiles suggest that intrusion of possibly oxic water may occur from time to time at depth in the WLP, as discussed below. Any oxygen intrusion in to the hypolimnion of the WLP would be unlikely to persist due to rapid reaction with the large pool of dissolved Fe (presumably Fe$^{2+}$) and the formation of Fe-oxyhydroxide solids.

Nitrate averaged 4.7 mg/L (s.d. ±0.6) in the epilimnion and was rapidly depleted over the chemocline to below detection limit within the hypolimnion. No seasonal trends in nitrate concentrations were observed. Nitrate was only detected in the hypolimnion once, on the 25 Jan 02 although at low concentrations (0.15 to 0.3 μmol). Nitrate is an important nutrient in oxic systems and electron donor and nutrient in anoxic systems. The concentration of nitrite (the reduction product of nitrate) varied much more than that of nitrate though the data collected are not sufficient to suggest a seasonal trend. Unlike nitrate, nitrite was occasionally detected at low levels (<0.2 μM) within the hypolimnion though again no seasonal or spatial trends in concentration could be observed.

 ammonium is present in elevated concentrations throughout the hypolimnion of the WLP with a general increase in concentrations with depth from 35 μM in Layer 2 (below the chemocline) to 100 μM at 35 m depth. The largest change in NH$_4^+$ over the study period occurred below 20 m between Aug 17, 01 and Oct 3, 01 where concentrations decreased by 47 % at 35 m. By Jan 21, 02 ammonium concentrations had increased again (99 % at 25 m through to 135 % at 35 m). For the duration of the study period ammonium concentrations remained relatively stable in the hypolimnion. Despite unfavorable thermodynamic conditions NH$_4^+$ was always present in the epilimnion at concentrations ranging from 10 to 20 μM.

The photosynthetic biological activity of the WLP was very low though not absent. A small peak in fluorescence was present in the late summer/fall for both the 2001 and 2002 seasons. Chlorophyll was only measured on two dates (June 21, 02 and June 13, 03), neither of which displayed a fluorescence peak, though a small amount of chlorophyll was detected (0.02 μg/l). The low level of algal activity in the lake is somewhat perplexing in that dissolved phosphate concentrations in the WLP are an order of magnitude higher than those in the Main Zone Pit lake where significant algal blooms occur during the summer. Between Oct 01 and Jun 02 P concentrations in Layer 2 decreased in a near linear fashion from 0.1 μM to below detection limit at < 0.01 μM. By Aug 7, 02, P concentrations in this layer had again risen and remained at
an average of 0.2 μM until March 03. The deep hypolimnion below Layer 2 exhibited relatively stable dissolved P concentrations between Aug 01 and Jan 02. By March 21, 02 a small increase (−0.04 μM) in dissolved P occurred in Layers 4 to 6 (20 m to 35 m). The Aug 7, 02 profile, taken a week after the accidental sludge discharge into the WLP, displayed a marked increase in dissolved P between 20 m and 30 m with a peak at 25 m of 1.7 μM, the highest value recorded in the pit lake. Between late summer (Aug 27, 02) and winter (Jan 21, 03) P concentrations in the hypolimnion below 20 m gradually declined to below detection limit, increasing again to −0.2 μM by March 03.

The source of P to the WLP is not known though the major tributary (Berzelius Creek overflow) and the perennial seeps all recorded lower dissolved P concentrations than those found in the epilimnion of the pit lake. An interesting point is that the melt water/slush above the ice (beneath the snow) in March 03 contained 6.3 μM of dissolved P, well over an order of magnitude greater than that found in the pit lake.

3.2.3 Waterline Pit Lake – Metals (Biogeochemistry and Distribution).

The biogeochemistry of the Waterline pit (WLP) is dominated by the density structure of the water column and the presence of a strong chemocline between 5 and 10 m from the surface. The chemocline is shallowest in the early summer (~5 m) and deepest in the late fall (~10 m). This chemocline presents a physical barrier to water column mixing and reduces the transport of atmospheric oxygen into the hypolimnion. Biological and chemical oxygen demand below the chemocline is higher than oxygen supply, generating anoxic conditions and lowering the system pe. The following geochemical results are given in relation to the vastly different metal behavior between the oxic epilimnion and the anoxic hypolimnion.

The determination of small changes in metal concentrations over time are complicated by errors introduced by sampling and analysis methods such as contamination, instrument drift, matrix effects, incomplete digestions and post sampling changes in sample chemistry (e.g. precipitation and adsorption to sample vessels). Considerable effort is taken to minimize the effects of these errors though it is evident from quality control analysis (duplicates, repeats etc.) that some degree of error does occur. This error is quantified in Appendix A: Methods. Between-analysis variance was ascertained using standard reference materials for each ICP-MS run as well as repeat matrix matched reference samples. Temporal changes in metal concentrations at a
given depth must be qualified against possible variance due to analytical error. Quality control analysis indicates that a >10% change in concentrations is likely to be real and significant. All samples for a single date and single depth profile were analyzed in the same ICP-MS run. These data are shown in Figures 3.2.4 to 3.2.10.

Layer 3 is a small intrusive stratum (from 17 m to 20 m) and as such the regular sampling depth of 20 m represented a zone of mixing between Layer 3 and Layer 4 (Figure 2.5.8, page 40). The discussion of spatial changes in metal concentrations between Layers 2, 3 and 4 refer to a single profile taken on June 13, 03 when Layer 3 was more thoroughly sampled.

**Manganese.** The concentration profiles for total and dissolved Mn, for each sampling date, are presented in Figure 3.2.2 (page 93). Mn was found entirely in the dissolved (<0.45 μm) fraction throughout the water column of the WLP. Particulate Mn was not detectable within the analytical variance. “Mn” in this discussion refers to dissolved Mn unless otherwise specified.

Epilimnetic Mn concentrations were typically slightly less than half those of the hypolimnion, increasing over the summer/fall period during the deepening of the chemocline. The highest epilimnetic Mn concentrations (1.8 to 2.1 ppm) were found during the late fall/winter with the lowest concentrations (1.2 to 1.4 ppm) being present in the early summer. In the early summer, the cline in Mn concentrations between Layer 1 (epilimnion) and Layer 2 (hypolimnion) was approximately 1 m higher in the water column than Fe, returning towards the Fe chemocline during the fall epilimnion deepening. The concentrations of Mn in layer 2 were relatively stable (between 3 to 4.1 ppm) throughout the study period with no indication of a temporal trend. As with other metals, Mn was seen to increase in concentration at the base of Layer 2 between 10 and 17 m on August 7, 02 (a week after the accidental sludge discharge to the WLP) by 900 ppb or 26%. This peak in dissolved Mn declined to concentrations typical of the bulk of layer 2 over the course of the summer. As the Mn peak at 15 m decreased, the Mn concentration at 20 m increased (Aug 7, to Oct 9, 02), possibly due to downward migration of Mn.

As with most other metals, the concentration of Mn decreased from Layer 2 to Layer 3 (to 2.5 ppm; June 13, 03). The reduction in Mn concentrations in this layer, relative to Layer 2 was of the same degree (42%) as that for Zn, Co, and Ni though slightly greater than that for Fe (35%)
and less than that of As (50%). Below Layer 3, Mn concentrations increased to levels similar to Layer 2 (3.8 ppm) and were relatively uniform with depth. No seasonal or temporal trend in Mn concentrations could be seen for Layers 4 to 6 (20 m to 35 m).

The flux of Mn to the sediments (as recorded by sediment traps deployed from July 24, 02 to June 13, 03,) was, relative to the total pool of Mn in the water column, considerably lower than other metals analyzed. Over the fall/winter of 02/03 sediment traps were left deployed at 3 m and 30 m depth for 304 days. It can be assumed that the sediments retained in the traps over such an extended deployment represent solids that are at least pseudo-stable under the conditions at the deployment depth. The Mn flux recorded at 30 m over this time period would require 223 years to remove the total pool of Mn from the WLP. This is in contrast to 60 years for Ni, 13 years for Zn, 1.3 years for Sb and only 21 days for Cu. It is clear from both the ratio of Fe:Mn and the total flux rate of Mn to the sediments recorded during the accidental sludge discharge to the WLP (July 28, 02) that the sludge contained a significantly higher fraction of Mn than the natural precipitates. The Mn flux recorded between July 24 and Aug 1, 02 would require only 1.4 years to remove all Mn from the WLP.

Iron. The concentration profiles for total and dissolved Fe, for each sampling date, are presented in Figure 4.2.3 (page 94). Fe is a major element in the WLP and is found in the highest concentration of all the metals analyzed. In the anoxic hypolimnion Fe is the fourth most significant cation (by total charge) after Ca, Mg and Na. Epilimnetic Fe concentrations are relatively low with dissolved Fe typically being close to the analytical detection limit (~1 ppb). The highest epilimnetic Fe_diss concentrations (~10 to 60 ppb) occur during the fall deepening of the chemocline (Oct, 01 and Oct, 02) as Fe_diss is mixed up from the hypolimnion. Together with dissolved Fe, particulate Fe is highest in the epilimnion in the late fall with concentrations reaching ~1.6 ppm. Both particulate and dissolved Fe are at their lowest concentrations in the epilimnion during the winter and early summer, periods of chemocline stability or shallowing. The dissolved Fe concentration increases rapidly across the chemocline to reach ~13 to 25 ppm at 10 m depth. The profile of Fe concentration through the hypolimnion below 10 m is positively and linearly correlated with conductivity apart from in Layer 3 (17 to 20 m) where concentrations decrease by approximately 35 % (June 13, 03) over that expected
from conductivity values. The removal or dilution mechanism operating for Fe in Layer 3 also operates for several other metals (Mn, Co, Ni, Zn, As, Cd) to varying degrees.

Total and dissolved Fe concentrations in Layer 2 decreased by 3600 ppb between March and June 02, increasing again over the summer and fall. Over the course of the two year study the \( \text{Fe}_{\text{diss}} \) concentrations in Layer 2 generally trended upward, starting at \(~13\, \text{ppm}\) in August 01 and reaching \(~20\, \text{ppm}\) in June 03. The major change in hypolimnetic Fe concentrations over the two years of study appeared between 10 m to 17 m depth (Layer 2), below the oxic/sub-oxic chemocline and above a secondary pycnocline at 17 m. \( \text{Fe}_{\text{tot}} \) increased by 9.7 ppm or 56\% at 15 m depth on Aug 7, 02. It appears as though an input of Fe was associated with an accidental discharge of ARD treatment sludge into the Waterline Pit Lake on the July 28, 02. A profile of dissolved and particulate metal concentrations taken on the August 7, 02 shows a peak in (predominantly dissolved) Fe at 15 m that was not present in the earlier (June 21, 02) profile (Figures 3.2.3, 3.2.11). Due to the high \( \text{pH} \) and \( \text{pH} \) of the lime treatment process, the dissolved metal concentration of the sludge is comparatively very low (e.g. \( \text{Fe}_{\text{dissolved}} = <20\, \text{ppb}, \text{Fe}_{\text{total}} = 600\, \text{ppm} \)) with Fe being converted to Fe-oxyhydroxides and possibly Fe-sulphate solids (e.g. jarosite, melanterite). A profile of optical backscatterance taken a few days after the sludge discharge (August 1, 02) indicates that particulate material either entered or formed in the WLP water column, peaking at depths of 11 m and 16.5 m. Over the 10 months after the sludge discharge Fe concentrations decreased at 15 m though remained slightly above pre-august 02 levels.

Below Layer 3 there was no apparent seasonal or temporal trend in Fe concentrations. Layer 4 (25 m) Fe concentrations were relatively stable throughout the study period varying between 30 and 35 ppm. Fe concentrations in Layer 5 varied between 32 and 40 ppm, peaking in January 03. Again no seasonal trend was evident in Layer 5. A large increase in \( \text{Fe}_{\text{diss}} \) (from 39 to 52 ppm) was seen at 35 m between Oct 1, 01 and Jan 25, 02. By March 21, 02 (the next sampling date), the excess dissolved Fe appears to have been converted to particulate form (Figure 3.2.3). This represented the largest pool of particulate Fe detected below the chemocline over the study period.

Sediment traps were deployed in the WLP during the summer/fall of 2002 and over the winter of 2002/2003. The flux of Fe particulates from the epilimnion to 3 m averaged 14 (±3) mg/m\(^2\)/day over the summer of 2002. The integrated average from Aug 16, 02 to June 16, 03 (304 days) Fe flux at 3 m was 133 mg/m\(^2\)/day, an order of magnitude higher than that recorded during the summer. This is probably due to the inclusion of the October chemocline deepening
where particulate Fe is formed as high Fe hypolimnetic waters are eroded into the epilimnion. The adsorption of Fe-oxyhydroxides to the side of the sediment traps may also preferentially accumulate Fe in traps left for long periods in oxic water. The Fe flux recorded in sediment traps deployed at 30 m depth appear to record the deposition of sludge on July 28, 02 with flux rates declining by an order of magnitude over the three weeks after the spill. At the highest recorded flux rate (11800 mg/m$^2$/day), during the week of July 28, 02, the entire pool of Fe in the WLP would precipitate out within 53 days. This rate slowed to 880 mg/m$^2$/day (713 days) over the next two weeks. At the flux rate recorded over the late fall/winter (380 mg/m$^2$/day; traps deployment = 304 days) it would take 4.5 years to remove all Fe from the WLP.

**Cobalt.** The concentration profiles for total and dissolved Co, for each sampling date, are presented in Figure 3.2.4. Co concentrations followed a similar profile with depth to Mn and Ni, displaying the lowest concentrations in the epilimnion and having a relatively uniform distribution with depth apart from a decrease in Layer 3. Co was found entirely in the dissolved fraction (< 0.45 μm) throughout the water column and for the duration of the study, Co in the following discussion should be taken as dissolved unless specified.

Co concentrations in the epilimnion were at their lowest during the early summer (12 ppb), increasing over the summer and fall to a maximum of 18 ppb. Concentrations increased rapidly across the chemocline into Layer 2 reaching 40 ppb at 10 m. As with a host of other metals, Co was introduced into the base of Layer 2 between June 21, and Aug 7, 02. A peak in Co had formed by Aug 7, 02 and had mixed throughout Layer 2 by the end of the fall (Oct 9, 02). The conservative nature of Co within Layer 2, in the absence of inputs, is highlighted by the fact that almost a year later (June 13, 03) the total pool of Co in Layer 2 remained very similar.

The decrease in Co in Layer 3 (17 m to 20 m) to 26 ppb was of the same order (40%) as that for Mn, Ni and Zn. Co increased again into Layer 4 to concentrations similar to that of Layer 2 (35 to 40 ppb) and decreased with depth towards 28 ppb over Layers 5 and 6 (25 m to 40 m). The ratio of Co to Ni remained constant over the hypolimnion from 10 m to 40 m ([Co] = 0.825[Ni] - 9.321;
R² = 0.94). The ratio of Co to Fe in sediment traps deployed for 304 days at 30 m depth (15223:1 ±516) was an order of magnitude greater than that in the water column directly above the sediments (1553:1 ±98) suggesting that Co was not readily scavenged or retained on Fe solids under the conditions at 30 m depth. Only the removal rate of Mn was slower than Co, relative to the total pool of Co in the water column. The flux rate recorded for the 304 days between Aug 16, 02 and June 13, 03 would require 113 days to remove all Co from the water column. Co displayed the largest relative slow-down (of all metals measured) of sedimentation rates between the period of sludge deposition (July 28, 02) and traps deployed over the late fall/winter. The flux rate during the period of sludge deposition was 645 times greater than that over the following 10 months. Ni, Cu and U recorded similar slowing of sedimentation rates over this period of 538, 519 and 499 times respectively.

**Nickel.** The concentration profiles for total and dissolved Ni, for each sampling date, are presented in Figure 3.2.5. Within analytical detection limits, Ni was found entirely in the dissolved (< 0.45 μm) fraction throughout the water column of the WLP. Unless otherwise stated, “Ni” refers to dissolved Ni in this discussion. In conjunction with Mn, Co, and Zn, concentrations of Ni were at their lowest in the epilimnion of the WLP. Unlike Co, concentrations of Ni decreased in the epilimnion between Jun 21, 02 and Aug 7, 02 from 37 ppb to 30 ppb, increasing again over the course of the summer/fall to 38 ppb. The concentration profile in the top 10 m of the water column closely followed that of the chemocline though no rigorous correlation could be drawn with conductivity. Over the two-year period of study, Ni concentrations at 10 m, the top of Layer 2, trended upwards from 48 ppb in August 01 to 63 ppb in June 03. This trend largely reflects a 16 ppb increase in concentrations over the summer/fall of 2002 and a general increase in Ni throughout the water column from 10 m to 25 m between March 21, and June 21, 02.

As with Co, Mn, Zn, As and Fe, Ni decreased in concentration in Layer 3 by 40% (in comparison to the base of Layer 2), increasing again into Layer 4. Ni concentrations in Layer 4 (20.5 m to 28 m) closely matched those of Layer 2 between Oct 01 and June 02. The input of Ni into the base of Layer 2 between June 21 and Aug 7, 02 appears to have been mixed over the
entire depth of the layer by Oct 9, 02. Layer 2 remained 10% (6 ppb) higher in Ni than Layer 4 for the duration of the study to June 13, 03.

Layer 4 saw an increase in Ni between March 21, and June 21, 02 from 56 ppb to 62 ppb. For the next eight months Ni decreased steadily in this layer by 0.05 ppb/day (+0.01), returning to pre-June 02 concentrations for the six months from Jan 03 to June 03. The flux of Ni from this layer is hard to quantify from a single point though a flux of 0.05 ppb/day over a 2 m to 5 m depth would be sufficient to account for the Ni flux recorded in the sediment traps between Aug 8, 02 and June 13, 03. Ni in Layer 5 (28 m to 30.5 m) was relatively constant, varying within a 9 ppb range from 46 to 55 ppb. Ni in Layer 6 (30.5 m to bottom) also varied within a 9 ppb range over the two years of study, mostly reflecting a rise of 5 ppb between Jan and March 02. Concentrations from March 02 to June 03 remained relatively constant at 44.2 ppb (+1.5).

The time required to remove all Ni from the water column at the sedimentation rate recorded between Aug 16, 02 and June 13, 03 is 59 years, the third slowest after Mn and Co. For perspective, the Ni flux to sediment traps at 30 m depth recorded during the period of accidental sludge discharge to the WLP (July 28, 02) would only require 41 days to remove all Ni from the water column. The ratio of Fe:Ni was more than an order of magnitude greater in the sludge impacted sediments than those recorded in traps left over the fall/winter of 2002/2003 (304 days deployment).

Copper. The analysis for Cu was plagued with contamination problems and unexplained variance. Those data that did appear rigorous indicated that Cu is found in concentrations between 1 to 10 ppb in the surface waters and becomes rapidly depleted to near or below detection limit in the hypolimnion. Unlike many other metals mentioned here, a significant particulate fraction of Cu was found in surface waters. The major tributary to the WLP, the Berzelius Creek overflow, contains higher dissolved Cu (4.7 ppb average) than the surface waters of the WLP (1.2 ppb average) and may be a significant source for the peak in Cu found in the WLP epilimnion. All other metals concentrations in the Berzelius Creek overflow, apart from barium, are well below those concentrations found in the WLP.

Although copper was largely absent from the hypolimnion (< 0.1 ppb D.L), there was a significant flux of Cu to the sediments. The Cu flux recorded at 30 m depth over the 304 days from Aug 16, 02 to June 13, 03 would require only 21 days to remove the total detectable Cu pool present in the water column on June 13, 03. 93 days would be required to remove the larger Cu pool present on Aug 27, 02 at this same flux rate (0.7 mg/m²/day). The period of sludge
discharge to the WLP (July 28, 02) saw more than an order of magnitude increase in the Cu flux to the sediments as well as in the ratio of Fe:Cu in the sediments. Although the water column data are somewhat erratic for Cu, the Aug 27, 02 Cu profile indicates that some Cu may have been released during settling of the sludge through the water column.

**Zinc.** The concentration profiles for total and dissolved Zn, for each sampling date, are presented in Figure 3.2.6. Zn is a major trace element in the WLP and is at elevated concentrations throughout the water column. The general depth profile of Zn concentrations closely follows that of Co, Ni and, for the top 20 m of the water column, Mn. Unlike most metals studies here, dissolved Zn concentrations decreased in the epilimnion over the course of the summer during the chemocline deepening. Zn was found to be predominantly in the dissolved (< 0.45 µm) fraction throughout the water column for the duration of the study. A particulate fraction of Zn did form in the epilimnion during the late summer/fall possibly in response to the chemocline deepening or adsorption to algae. A peak in fluorescence was observed at the same depths as the particulate Zn in the epilimnion. Epilimnetic Zn concentrations typically ranged from 400 to 500 ppb though peaked at 860 ppb on June 21, 02.

Prior to June 21, 02 the increase in Zn concentrations across the chemocline into Layer 2 was of a much lower magnitude (~20 %, 100 ppb) than that post June 02 (~40 %, 250 ppb). An input of Zn into Layer 2 between March and June 02 elevated the Zn concentrations from 490 to 660 ppb. Zn peaked in Layer 2 at 770 ppb in Aug 02 and remained elevated at 706 (±30) ppb for the duration of the study to June 13, 03.

In both the 01 and 02 seasons, Zn concentrations decreased at the base of Layer 3 (20 m) between October and March. As with Layers 1 and 2, Zn increased sharply between March and June 02 from 400 to 560 ppb at 20 m. Unlike Layer 2 there was no general increase in Zn concentrations in Layer 3 over the course of the study. The decrease in Zn concentrations from Layer 2 to Layer 3 (46 %, 350 ppb, June 13, 03) was similar to that for Mn (42 %), Co (42 %) and Ni (40 %) though less than that for As (50 %) and greater than that for Fe (26 %).

Zn concentrations peaked in Layer 4 at 25 m depth, ranging from 660 ppb to 830 ppb throughout the study. The temporal trend in this layer was marked by sharp increases in Zn
concentrations in Oct, 01, Aug 7, 02 (80 ppb) and June 13, 03 (170 ppb). Between these dates Zn
trended downwards towards a low of 705 ppb and 660 ppb respectively. Zn concentrations in
Layer 5 (30 m) were at their highest in Oct 01 (800 ppb), decreasing at a relatively constant rate
of 1.32 ppb/day (±0.3) over the next 260 days to June 21, 02 (490 ppb). Layer 5 Zn
concentrations increased again over the summer and fall of 2002, peaking in Oct 02 at 605 ppb.
As with Layer 5, Zn concentrations in Layer 6 also peaked in Oct 01 (535 ppb), decreasing at a
constant rate over the 260 days to June 21, 02 (340 ppb) at 0.74 ppb/day (±0.05). A small jump
in Zn was seen between June 21 and Aug 7, 02 to 410 ppb, in conjunction with a small increase
in conductivity. Zn concentrations in Layer 6 remained relatively constant between Aug 7, 02
and June 13, 03.

The flux of Zn to the sediments was highest over the period of sludge discharge to the
WLP (650 mg/m²/day), decreasing two orders of magnitude in the following two weeks (8.2
mg/m²/day). The ratio of Fe to Zn also increased over the same period from 18:1 to 105:1,
indicating that the sludge reaching the sediments was richer in Zn relative to Fe than the natural
sediment flux. The final ratio of Fe:Zn in the sediment traps deployed over the fall/winter of
02/03 (90:1) was similar to that in the water column in the vicinity of the 30 m sediment trap
(62:1 at 30 m, 97:1 at 35 m). The flux rate of 8.2 mg/m²/day would require 13 years to remove
the total pool of Zn from the water column, on the same order as that for Mo (19 years) and U
(25 years). Zn and Mn had similar changes in the recorded flux to the sediments between the
period of sludge deposition (July 28, 02) and the following 10 months (Aug 16, 02 to June 13,
03; 304 days). Over this period the recorded Zn flux at 30 m depth slowed by 150 times while
Mn sedimentation slowed 158 times. This change in flux rates between these dates was lower
than that for Co, Ni, and U though greater than that for Fe, As, Mo, Cd, and Sb (32 ±8.6 times).

**Arsenic.** The concentration profiles for total and dissolved
As, for each sampling date, are presented in Figure 3.2.7. The profile of As through the water column of the WLP
closely followed that of Fe with near quantitative removal
from the oxic epilimnion and a maximum close to the lake
sediments. The increase in As concentration across the
chemocline was of a similar slope to that of Fe although at a
slightly lower point in the water column (0.5 to 1 m).
Dissolved As was only detectable in the epilimnion during ice-over and once on Aug 27, 02 (mid summer) albeit at low levels (0.2 to 1.9 ppb). The presence of particulate As in the epilimnion occurred during the fall chemocline deepening, in conjunction with particulate Fe. A maximum concentration particulate As at 2 m of 39 ppb was reached in Oct 01.

Concentrations in Layer 2 varied markedly over the course of the two-year study from 400 ppb to 1700 ppb, reflecting periodic inputs, changes in the chemocline depth and subsequent oxygenation. The major change in As concentrations in Layer 2 was in response to an intrusion at 15 m depth between June 21 and Aug 7, 02. This intrusion is possibly attributable to an accidental discharge of ARD treatment sludge into the WLP on July 28, 02 though there is some evidence in the optical backscatter profiles that an intrusion may have been present prior to this event. Together with Mn, Ni, Co, Zn and Fe, As concentrations are lower in Layer 3 than in Layers 2 and 4. The reduction in As concentrations (50%, 350 ppb) from Layer 2 to Layer 3 is greater than for the other metals listed and continues into Layer 4. The rate of increase in As concentrations with depth between Layer 3 and Layer 4 is also somewhat suppressed in comparison to the these metals. Whereas Co, Ni, and Zn concentrations decrease below 25 m, those for As increase steadily from Layer 3 through to the bottom of the pit lake to reach a maximum concentration of ~2000 ppb. The ratio of Fe to As also steadily increases between Layer 3 and the bottom of Layer 6. The final ratio of As to Fe at the bottom of the pit lake (26:1) matches that in Layer 2 (24:1).

Sediment traps deployed at 30 m depth for 7 or 8 days and 304 days had remarkably similar ratios of As to Fe (17:1 (+0.7, n = 4) and 16:1 (+0.2, n=2) respectively). The in-situ or “normal” flux of As to the sediments cannot be predicted from sediment trap data as the input of ARD treatment sludge to the WLP on July 28, 02 appears to have dramatically increased the sediment load during the period of trap deployment. Those traps deployed two weeks after the sludge deposition (Aug 16, 02 to June 13, 03) indicate that the removal rate of As from the water column is quite large in comparison to the total pool of As present. At 24 mg/m²/day, 2 years would be required to remove all As from the water column (at June 13, 03 concentrations), a greater relative sedimentation rate than all metals measured apart from Sb (1.4 years) and Cu (0.6 years). The relative change in As flux from the period of sludge deposition to that recorded over the fall/winter is lower (20 x decrease) than that for all other elements measured indicating that the contained relatively less As than the natural sediments. This is confirmed by analysis of pure sludge in which only low concentrations of As, relative to Fe, were found.
**Molybdenum.** The general shape of the Mo concentration profile closely follows that of conductivity and hence sulphate throughout the water column of the WLP. The temporal correlation of Mo to conductivity was not rigorous as Mo was considerably more variable than conductivity. Mo was found to be entirely within the dissolved (< 0.45 \( \mu \text{m} \)) fraction in the WLP. "Mo" in this discussion refers to dissolved Mo unless otherwise specified. While the ICP-MS response to Mo in standard reference materials (TM-25.2) was within specified 95 % confidence limits, the response to the pit lake matrix was less stable. The analytical variance for Mo was considerably higher than that for other metals and it appears as though much of the temporal variation in Mo concentrations between June 02 and June 02 can be attributed to analytical error.

Epilimnetic Mo concentrations ranged from 1.2 to 3 ppb, being lowest in the early summer and increasing with the depth of the chemocline as Layer 2 waters were mixed up. Mo concentrations are uniform in Layer 2 and increase in a near linear fashion through Layers 3 to 6. The profile of Mo with depth remained remarkably consistent for the first 6 months of the study from Aug 17, 01 to March 21, 02. A 2 ppb increase in Mo was seen at 15 m, 30 m and 35 m between March 21, and June 21, 02. Between June 21, and Aug 7, 02 a further increase in Mo was recorded in the upper portion (5 m to 11 m depth) of Layer 2 of 1.5 ppb. There was no plume of Mo at 15 m depth between June 21 and Aug 7, 02 suggesting that the intrusive waters were either low in Mo or Mo was mixed throughout Layer 2.

Unlike the majority of the metals discussed here (Mn, Fe, Co, Ni, Zn and As) Mo concentrations do not decrease in Layer 3. No temporal change was found for the shape of the Mo concentration profile below 20 m over the course of the study.

The flux of Mo to the sediments, as recorded in sediments traps deployed at 30 m depth for 304 days between Aug 16, 02 and June 13, 03 was relatively small in comparison to the total pool of Mo in the water column. At a flux rate of 0.02 mg/m\(^2\)/day, 19 years would be required to remove all Mo from the water column. This rate is comparable to that for U (25 years) and Zn (13 years) though much slower than other metals such as Cu, As, Fe and Cd, Sb and Ba.
Cadmium. The concentration profiles for total and dissolved Cd, for each sampling date, are presented in Figure 3.2.8. For the duration of the study the highest Cd concentrations in the WLP were found at the chemocline between the oxic epilimnion and the sub-oxic hypolimnion. The majority of this Cd peak was always in the dissolved fraction (>90 %) with the particulate fraction varying from 0 to 10% over the year. This peak ranged in concentration from 3.5 to 9 ppb with the highest values in late winter/early summer. The only particulate fraction detectable in the true epilimnion (0 m to 5 m) were present in the late summer/fall, a period of chemocline deepening and the formation of particulate Fe in the epilimnion. For the initial 6 months of the study Cd_{tot} was found to be elevated in the epilimnion (2 to 6 ppb) and depleted throughout the hypolimnion (< 1 ppb).

The concentration of both dissolved and particulate Cd increased markedly at between March 21, and June 21, 02 in the epilimnion, at 15 m and from 25 m to 35 m. By June 21, 02 the “March 21, 02” peak in Cd was maintained at 8 m depth despite the chemocline rising to 4.5 m depth, where a second Cd peak had formed. This would indicate that the increase in conductivity from 4.5 m to 8 m depth between these dates occurred without significant mixing of waters at or below 8 m depth. There did appear to be a source of Cd to the epilimnion of the WLP between Oct 3, 01 and Jan 25, 02 as the increase in Cd_{diss} concentrations above the chemocline cannot be accounted for by scavenging from the low Cd waters in the hypolimnion despite a 1 m deepening of the chemocline between these dates.

Percentagewise, Cd concentrations in the WLP hypolimnion varied more than any other metal studied here. The lowest total pool of Cd in the hypolimnion was recorded between Aug 17, 01 (the first depth profile sampled) and March 21, 02. Over this period Cd_{diss} concentrations gradually increased from < 0.05 ppb to 0.6 ppb with the largest increase in Layer 4 (20 m and 25 m). As with epilimnion, the largest recorded increase in Cd_{diss} in the hypolimnion occurred between March 21, and June 21, 02 at 15 m where concentrations rose by 1200 % (3.7 ppb). During the same period both Cd_{diss} and Cd_{particulate} concentrations increased from 25 m to 35 m depth though by only 270 % (0.8 ppb). Cd was distinguished from most other metals studied here by the presence of a significant particulate fraction in the hypolimnion throughout the study period. Prior to March 02 particulate Cd typically accounted for between 70 and 100 % of total
Cd below Layer 2 (17 m to 40 m). Over the summer/fall of 2002, Cd\textsubscript{diss} became the dominant fraction with an influx of predominantly dissolved Cd starting at 20 m depth in March 02 and spreading to the entire water column below 20 m by Aug 29, 02. From March 02 through to June 03, Layer 3 (as represented by samples taken at 17 m and 20 m) consistently contained predominantly dissolved Cd (60 to 100%). This is notable as between Aug 28, 02 and January 23, 03 particulate Cd had once again become the dominant fraction below 25 m and continued to be until the last survey in June 03.

The overall pattern of Cd distribution in the WLP hypolimnion was of low concentrations of largely particulate Cd prior to March 02 with a large increase in dissolved Cd between March and June 02. Over the year from June 02 to June 03, Cd was both removed from the hypolimnion and “formed” a dominant particulate fraction. The total pool of Cd in the water column on June 13, 2003 was of similar magnitude to that present in Jan 25, 2002.

The flux of Cd to the sediments relative to the total pool of Cd in the water column (as recorded by sediment traps deployed at 30 m over the period Aug 16, 02 to June 13, 03) was greater than that for the majority of metals measured and of a similar order to that for As and Sb. At a flux rate of 0.07 mg/m\textsuperscript{2}/day, 2.3 years would be required to remove all Cd from the water column of the WLP. The Cd flux recorded at 3 m was of the same order as that recorded at 30 m depth indicating that the majority of the Cd flux to the sediments is sourced from the top 3 m of the water column. The ratio of Fe:Cd in the sediments is an order of magnitude lower than that in the water column at 30 m depth (where the sediment traps was deployed) which would suggest that Cd is largely retained in the sediments under the conditions present in the WLP hypolimnion.

**Antimony.** The concentration profile for Sb was marked by a maximum of predominantly (> 85 %) dissolved Sb in the epilimnion of between 1.7 to 4.3 ppb. Across the chemocline Sc concentrations declined rapidly with oxygen to reach a near uniform concentration (0.2 to 0.8 ppb) with depth between the bottom of the chemocline and 30 m depth. There was no decrease in Sb concentrations in Layer 3 as recorded for most other metals. A slight increase in dissolved Sb between 30 m and 35 m was observed in all
surveys between Oct 3, 01 and Aug 7, 02 as well as in June 13, 03. As with Cd though to a lesser
degree, a particulate Sb fraction was present throughout the hypolimnion for many surveys. The
particulate Sb fraction typically averaged between 20 % and 30 % of the dissolved
concentrations.

On Jan 25, 02 a large peak in dissolved Sb (3.3. ppb) was recorded at 35 m. It is not
known if this data point is real though it appears in both the dissolved and total samples and is at
a depth where more moderate increases in dissolved Sb were observed on other dates. A small
increase in both dissolved and particulate Sb formed at the base of Layer 2 (15 – 17 m) between
June 21, 02 and Aug 7, 02, the period of the accidental sludge discharge to the WLP. By Aug 28,
02 this Sb peak had disappeared from Layer 2 without an increase in the Sb concentrations
within Layer 3 (at 20 m) as occurred with other metals (Mn, Ni, Cd) though with an increase in
particulate Sb at 25 m (Layer 4). The particulate Sb present on Aug 28, 02 between 25 m and 35
m was gone by Oct 9, 02 though the dissolved Sb concentrations remained stable. If it assumed
that this particulate Sb precipitated to the sediments a total flux of 2.06 mg/m2, only 11 % to 15
% of that actually recorded in the sediment traps at 30 m over the period Aug 16, 02 to June 13,
03 (304 days). It is obvious that additional Sb precipitation occurred between Oct 02 and June 03
despite water column concentrations remaining stable.

The Fe to Sb ratio in sediment traps deployed at 3 m depth was an order of magnitude
higher than those deployed at 30 m depth despite much higher concentrations of Sb in the waters
above 3 m depth. This would suggest that Sb is preferentially removed to a solid phase in the
hypolimnion of the WLP. The flux of Sb to the sediments relative to total pool of Sb in the water
column is second only to Cu. At a recorded flux rate of 0.05 mg/m²/day (Aug 16, 02 to June 13,
03, 304 days), only 1.4 years would be required to completely remove the Sb pool from the
water column of the WLP.

**Barium.** The profile of Ba was largely uniform throughout the WLP, ranging from 10 to 16 ppb
over the two-year study period. The analytical variance for Ba tended to be slightly higher than
that for other metals and, within that context, the detection of a particulate fraction was
hampered. Even without considering analytical variance, Ba was always predominantly
dissolved (> 90%). A small particulate fraction detected from 20 m to 35 m depth on June 21, 02
appears to be real. Conductivity and sulphate increased at these depths on this sampling date, the
particulate Ba may be due to the formation of Barite. Barite is calculated to be above saturation
(s.i.= 0.3) in the WLP (PHREEQC, wateq4f database). No seasonal or temporal trends in Ba
concentrations were observed. No increase in Ba concentrations was noted in response to the accidental sludge discharge into the WLP on July 28, 02 despite elevated Ba present in the sediment traps deployed over the same period. No decrease in Ba concentrations was recorded in Layer 3, unlike most other metals analyzed (Mn, Fe, Co, Ni, Zn, As, Cd).

The major tributary to the WLP, the Berzelius Creek overflow, contains slightly higher dissolved Ba (18 ppb average) than the epilimnion of the WLP (12.8 ppb average) and may be responsible for a small peak in Ba in the surface waters on June 21, 02, a period of relatively high flow from this source.

The flux of Ba to the sediments as recorded from Aug 16, 02 to June 13, 03 (304 days) was the same in the 3 m sediment trap and the 30 m sediment trap (0.11 mg/m$^2$/day) suggesting that the Ba flux is sourced from above 3 m. The flux of Ba over this same period would remove the total WLP Ba pool in 9.1 years.

**Uranium.** Within detection limits, U was found entirely in the dissolved ($< 0.45 \mu m$) fraction at all depths and dates in the WLP. “U” refers to dissolved U in this discussion unless otherwise stated. The overall shape of the U depth profile closely followed that of conductivity below the chemocline. U concentrations between the surface and 15 m (Layers 1 and 2) ranged from 0.6 to 0.8 ppb for the duration of the study period. From 17 m to 35 m (Layers 3 to 6), concentrations increase with conductivity, ranging from 1.8 to 2.3 ppb. There was no decrease in U concentrations in Layer 3 as recorded for most other metals. Like Ba, U displayed very little variation in concentration across the chemocline between the oxic epilimnion and the sub-oxic hypolimnion. U correlated with conductivity across the chemocline on only two sampling dates (Aug 7, and Aug 28, 02) when a slight increase in U concentrations (0.1 ppb) was recorded at the base of the chemocline. This $U_{\text{diss}}$ increase at the top of Layer 2 was possibly in response to the sludge
discharge into the WLP on July 28, 02. There were no distinct temporal or seasonal trends in U concentrations over the period of study.

The ratio of Fe to U in sediment traps deployed at 3 m depth (oxic) was very similar to that found in the water column in the hypolimnion ((2.0833 ±5200, n = 6) and (2.0036 ±2183, n = 48) respectively). The Fe:U ratio in sediment traps deployed at 30 m depth (anoxic) was 2 to 5 times higher than that in the water column suggesting greater retention of U in the sediments under oxic conditions. At the flux rate recorded in sediment traps deployed at 30 m between Aug 16, 02 and June 13, 03, it would take 25 years to remove all U from the WLP water column. This is of a similar order to Mo (19 years), which displays a similar concentration profile with depth. The flux recorded over the same time period at 3 m depth (0.0012 mg/m²/day) was one third of that at 30 m (0.0034 mg/m²/day).
Figure 3.2.1: Waterline pit lake profiles for phosphate, nitrate, nitrite, ammonium and dissolved oxygen – June 2001 to June 2003.
Figure 3.2.2: Waterline pit lake dissolved and total manganese profiles – Aug 01 to June 03.
Figure 3.2.3: Waterline pit lake dissolved and total iron profiles – Aug 01 to June 03.
Figure 3.2.4: Waterline pit lake dissolved and total cobalt profiles – Aug 01 to June 03.
Figure 3.2.5: Waterline pit lake dissolved and total nickel profiles - Aug 01 to June 03.
Figure 3.2.6: Waterline pit lake dissolved and total zinc profiles – Aug 01 to June 03.
Figure 3.2.7: Waterline pit lake dissolved and total arsenic profiles – Aug 01 to June 03.
Figure 3.2.8: Waterline pit lake dissolved and total cadmium profiles – Aug 01 to June 03.
Figure 3.2.9: Waterline Fe at 15 m depth, 25th Jan, 02 to 11th March, 03; Comparison between samples analysed (ICP-MS) on the same day and on different days (over 12 months).

Figure 3.2.10: Correlation of Sulphate and Conductivity and Iron and Conductivity in the Waterline Pit Lake at 20 m (Jan 02 to Oct 02).
Figure 3.2.11: Waterline pit lake dissolved metal profiles prior to and after the accidental sludge discharge on July 28, 2002.
3.3 Waterline Pit Lake Limnocorral Experiments

Objective. The Waterline Pit contains several metals (Fe, Cd, As, Zn) at concentrations above environmental and drinking water standards, as set by the National Recommended Water Quality Criteria of the USEPA (USEPA, 2002). The geochemical controls on the distribution, speciation and concentration of these metals are various suggesting that in-situ remediation will require a combination of chemical manipulations. The current status of the Waterline Pit hypolimnion is sub-oxic/anoxic but not significantly sulphidic (within detection limits).

Adsorption to iron oxyhydroxides and subsequent precipitation controls the concentrations of some metals within the epilimnion (Fe, As, Co, Ni) though not all (Zn, Cd, Sb). Given this geochemical setting, the objective of the Waterline Limnocorral study was two-fold: 1. To assess the capacity of algal growth in the epilimnion to reduce metal inventories though uptake, adsorption, pH adjustment and precipitation and; 2. To increase the reducing conditions in the hypolimnion to sulphidic levels to initiate the production of metal sulphide phases and promote their removal to the sediments through subsequent precipitation. The experimental approach used to address these objectives will be discussed in this chapter.

Experimental Design. The location of the limnocorral experiments is given in Figure 2.2 (Section 2.0) and the design plan in Figure 3.3.8 (this section). Eight cylindrical limnocorrals, each 2m in diameter, were installed in the Waterline Pit, of a similar design to those installed in the Main Zone Pit. The corrals were constructed of translucent, low metal polyethylene sheeting and a PVC frame and ribs made of flexible poly-pipe maintained the cylindrical form of each. High-density foam provided floatation (Figure 3.3.8). Four limnocorrals were located on a raft in the shallow (~10m) southern section of the Waterline Pit. Each of these was connected to the sediments through a weighted sleeve at its base in order to ascertain the sediment interaction with the overlying water column.

Four additional limnocorrals (~12m long) were place in the deeper (~40m) northern section of the pit. These were open to the water column at the base and were used to assess water column chemistry only. Each set of four limnocorrals contained a control (to which no additions were made), a “high nutrient” limnocorral, a “medium nutrient” limnocorral and a “high nutrient and ethanol” addition limnocorral (see Table 3.3.1). The timetable of nutrient and ethanol additions can be found in Figure 3.3.1. A single ethanol addition (~ 2.5 mmol L⁻¹, if mixed over
1m depth) was introduced at a depth of 8m in limnocorals WLL-12 and WLL-16 only. The ethanol was bubbled prior to introduction with nitrogen gas to remove dissolved oxygen and diluted approximately 9:1, using water taken from 8m depth in each respective corral.

Samples for metals and nutrients were taken from discrete depths using Tygon tubing and a peristaltic pump. Sampling was undertaken weekly during the summer and multi-weekly into the fall and winter (see Figure 3.3.1). An inline filter system with a 0.45μm cellulose acetate filter was incorporated for all “dissolved” metal and nutrient samples. Typically five depths were sampled per limnocorral per date. Profiles of conductivity, temperature, fluorescence, transmissivity and optical backscatter were collected from each corral on each sampling date using a Seabird SBE 19 CTD. Additional samples were taken on occasion for chlorophyll (GFF filter), size fractionated metals (polycarbonate filters) dissolved oxygen, dissolved organic carbon (DOC, particulate organic carbon (POC) and sulphides (Zn acetate preserved).

Twin sediment traps of 47 mm internal diameter were deployed at 8m depth and retrieved at the end of the experiment. These traps were not retrieved more frequently so as to not introduce oxygen below the chemocline during the experiment.

<table>
<thead>
<tr>
<th>Limnocorral Code</th>
<th>Additions</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>WLL-9</td>
<td>High Nutrients (~2.3 μmol l⁻¹ wk⁻¹)</td>
<td>Attached to sediments</td>
</tr>
<tr>
<td>WLL-10</td>
<td>Medium Nutrients (~0.23 μmol l⁻¹ wk⁻¹)</td>
<td>Attached to sediments</td>
</tr>
<tr>
<td>WLL-11</td>
<td>Control (no additions)</td>
<td>Attached to sediments</td>
</tr>
<tr>
<td>WLL-12</td>
<td>High Nutrients and Ethanol (2.5mmol L⁻¹)</td>
<td>Attached to sediments</td>
</tr>
<tr>
<td>WLL-13</td>
<td>High Nutrients (~2.3 μmol l⁻¹ wk⁻¹)</td>
<td>Open to water column</td>
</tr>
<tr>
<td>WLL-14</td>
<td>Medium Nutrients (~0.23 μmol l⁻¹ wk⁻¹)</td>
<td>Open to water column</td>
</tr>
<tr>
<td>WLL-15</td>
<td>Control (no additions)</td>
<td>Open to water column</td>
</tr>
<tr>
<td>WLL-16</td>
<td>High Nutrients and Ethanol (2.5mmol L⁻¹)</td>
<td>Open to water column</td>
</tr>
</tbody>
</table>

Table 3.3.1: Waterline Pit limnocorral experimental design with nutrient and ethanol addition schedule.
Figure 3.3.1: Timeline of nutrient additions. WLL-10 and WLL-12 are used as examples of medium and high nutrient addition corrals respectively.

3.3.1 Biological Response

As discussed in section 3.2.1, the Waterline Pit does not naturally maintain a significant algal biomass. This had been attributed to the low nutrient status of the waters and, before the limnocorral study, possibly heavy metal toxicity. The low nutrient status is relative however; the Main Zone Pit does have a lower dissolved phosphate concentration than the Waterline but has a significant algal bloom during the summer.

Despite elevated metal concentrations in the epilimnetic waters of the Waterline Pit, the addition of relatively low amounts of nutrients produced large algal blooms. Those corrals with high nutrient additions also developed large phototrophic bacterial blooms beneath the chemocline in anoxic waters (see Figure 3.3.2, page 108). These anoxic blooms appeared (Limn 16) within two weeks of the first nutrient additions, a week behind the epilimnetic blooms. The fluorescence values and chlorophyll concentrations of the anoxic blooms were comparable and often exceeded their oxic counterparts. The anoxic bloom in WLL-9 did not appear until the late summer, some time between the end of August and mid September. The Waterline Pit Limnocorrsals developed a much larger chlorophyll concentration (slightly less than one order of
magnitude) than their counterparts in the Main Zone Pit. This is counter-intuitive as the Main Zone pit already supported a summer algal bloom prior to nutrient additions where as the Waterline Pit did not.

Large epilimnetic blooms were maintained throughout the summer, from a week after first nutrient addition (July 13, 2002) until at least mid October. Only WLL-12 and WLL-16, both high nutrient and ethanol addition corrals, suffered a decrease in fluorescence in mid summer. The bloom in WLL-12 steadily decreased from the first week of August through to the end of August, growing again into September and October. At the end of August the bloom in Limnocorral 12 was almost absent in the surface waters though was maintained in the hypolimnion. In WLL-16 the bloom in the epilimnion decreased in size between Aug 1, and Aug 7, 2002. This was prior to the ethanol addition, which therefore could not have influenced this decline. The WLL-16 bloom had fully recovered by the next week. On Aug 7, the WLL-16 anoxic bloom was considerably larger than the oxic bloom.

Microscopic investigation indicated that the majority (~75%) of the algae present in at least one limnocorral were blue greens of the genus *Synechococcus*. The bulk of the remaining ~25% consisted of flagellates from the genus *Chrysochromulina* and assorted micro-flagellates (see Table 3.3.2, page 109). Diatoms were not identified in algal samples. Dinoflagellates were a minor component only (Stockner, 2002).

**Carbon and Nitrogen.** Measurements of the particulate carbon (POC) and dissolved organic carbon (DOC) concentrations in the limnocorral were few but the results are consistent. Surface water POC concentrations in high nutrient limnocorral were on the order of 2 to 3 mg L$^{-1}$ during the height of the algal blooms. DOC was on the order of 1 to 1.5 mg L$^{-1}$ in controls and 3 to 10 mg L$^{-1}$ in the high nutrient corrals. DOC profile data are restricted to one control (WLL-15) and one high nutrient / ethanol limnocorral (WLL-16) and one date (Aug 29, 2002) during the growth period. These data indicated that the DOC values were uniform through oxic to anoxic waters in the control though elevated DOC occurred at the redox-cline in WLL-16. The carbon contents measured in the sediment traps for the Waterline experiment are not reliable as a source of carbon flux data due to the extended intervals between trap retrievals and the possibility of in-situ bacterial decomposition. Traps were not retrieved with greater frequency in an attempt to maintain anoxic conditions and collect metal sulphides. The traps were located at ~8m depth in the anoxic zone and thus collected authigenic solid phases both from the anoxic zone and those exported from the overlying epilimnion.
There was ample evidence of the removal of carbon from traps during deployment. Two traps were retrieved in late summer from the ethanol-addition corrals. These both showed greatly elevated integrated carbon flux concentrations in comparison to traps that were left for longer (collected in mid winter). Sulphide generation (detected by odour not analysis) in traps where no water column sulphides were detected indicates that the traps provided a substrate for sulphate reducing bacteria and that carbon oxidation was occurring. Despite the inferred loss of carbon compounds through decomposition, the carbon contents measured on the trap samples do reflect at least semi-quantitatively the respective strength of the overlying summer blooms. The data indicate that measurable export did occur (Figure 3.3.3).

The carbon to nitrogen ratio found in sediment traps closely matched the Redfield Ratio of 6.6 for most samples from the high nutrient corrals. One medium nutrient corral (WLL-10) and one control differed in that the average ratio of C:N was almost double the Redfield value at 12.1. The flux of nitrogen to the sediments cannot be estimated due to possible loss of soluble N species such as NH₄⁺ through bacterial uptake and N₂ through denitrification during mineralization of organic matter.

The sediments of WLL-16 contained 5 times more carbon than WLL-12 (both ethanol addition limnocorral). The sediments of WLL-16 also had a distinct green colour upon drying, possibly indicating the presence of chlorophyll-containing algae or phototrophic bacteria, or reduced iron compounds in the mineral fraction (e.g. Lyle et al., 1983). An unknown source of additional sediment mass appeared to exist in WLL-16 when compared to the other high nutrient / ethanol limnocorral, WLL-12. Three times more mass was collected in the sediment traps in WLL-16 in comparison to WLL-12 though only twice as much Fe. Although WLL-16 also contained more Carbon than WLL-12, this could account for less than 25% of the difference in sediment mass between the two limnocorals.

**Sulphides.** One measure of the activity of sulphate reducing bacteria is the concentration of dissolved sulphide and "dissolvable sulphide". The former consists of sulphide that will pass through a 0.45μm filter and react with Zn acetate to form a stable ZnS solid phase. Dissolvable sulphides are defined here as the unfiltered total sulphides (including any metal sulphide species) that would dissolve under the acidic conditions of the spectrophotometric sulphide analytical procedure. This measurement was imprecise in that the fraction of metal sulphides that would dissolve under these conditions was unknown. Instead, the parameter is used as an indication of the presence or absence of solid phase sulphides in the water column.
Dissolved sulphides were only detected in the ethanol addition corrals (WLL-12 and WLL-16). No dissolved sulphide was detected for the first 42 days after the addition of ethanol. Significant concentrations of dissolved sulphides appeared in the hypolimnion of WLL-12 some time between Aug 28, and the Sept 17, 2002. The highest [HS⁻] (≈54 μmol) detected in September 2002 was near the chemocline at 6 m, 2 m above the ethanol injection point. The concentration was five times less in the true hypolimnion (≈11 μmol). Dissolved sulphides were also present in WLL-16 at this time but at values near the detection limit (<1μmol). Sulphide concentrations in WLL-12 increased throughout the experiment with the highest concentrations (2380 μmol) being found in March 03, the last month in which sulphide samples taken. Sulphides were still detected in WLL-12 in June 03 by smell and black precipitates were evident, presumably FeS or other metal sulphides. WLL-16 was not sampled in June 03, though as of March 03 sulphides were present in more modest concentrations (25 to 35 μmol) in that corral than in WLL-12 where all sulphide profiles indicated a water column maximum as opposed to a sediment source. Concentrations were always less at 9 m than 8 m depth.

Sulphate-reducing bacteria (SRB) were detected in the Waterline pit limnocorrals, using a sulphate growth medium (S. Baldwin, written communication). Samples were taken for SRB detection on Aug 19, 2002 and these indicated that the two ethanol-addition limnocorrals and the high nutrient limnocorral WLL-13 contained the highest concentrations of SRB activity. Samples from all limnocorrals showed a reduced sulphate concentration in the growth medium after two months, possibly indicating some SRB activity in all limnocorrals (S. Baldwin, 2003, written communication).
Figure 3.3.2: Fluorescence (as calculated chlorophyll) from three limnocorals, 25 days after first fertilization (Aug 6, 2002).

Note the development of a bloom beneath the chemocline in WLL-12 (right). This fluorescence profile was taken one day prior to the only ethanol addition into WLL-12.

Figure 3.3.3: Carbon flux in Waterline Pit Limnocorals (deployed from July 17, 2002 to March 14-18, 2003.

The data show replicate traps for each limnocoral. The flux numbers are shown as an indication of the pattern of carbon deposition only as carbon values are likely to be impacted by significant in-situ mineralization and loss. Limnocorals 12 and 16 show similar patterns (elevated carbon) though are not shown as the traps for these corrals had different deployment times.
<table>
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<tr>
<th>Class/Species</th>
<th>No. Cells/mL</th>
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<td>Small microflagellates</td>
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</tr>
<tr>
<td><strong>Group total</strong></td>
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<td>Dinophyceae (dinoflagellates)</td>
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<tr>
<td>Peridinium sp1</td>
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</tr>
<tr>
<td><strong>Group total</strong></td>
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<tr>
<td>Chlorophyceae (coccoid greens, desmids, etc.)</td>
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<td></td>
</tr>
<tr>
<td>Ankistrodesmus sp.</td>
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</tr>
<tr>
<td><strong>Group total</strong></td>
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<td>0.026</td>
</tr>
<tr>
<td>Cyanophyceae (blue-greens)</td>
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<tr>
<td>Synechococcus sp. (&lt;2 um)</td>
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</tr>
<tr>
<td>Oscillatoria sp2</td>
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<tr>
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</tr>
<tr>
<td><strong>GRAND TOTAL</strong></td>
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</tr>
</tbody>
</table>

Table 3.3.2: Algal genus composition of a high nutrient limnocorral (WLL-12), Aug-12, 2002 (Stockner, 2002).
3.3.2 Physical Response

Limnocorals introduce several artifacts that must be taken into account when interpreting the results of experiments and extrapolating these to whole lake responses. The presence of the limnocorals, for example, is expected to reduce the mixing in the epilimnion in comparison to the open pit lake through sheltering from wind (reduced fetch) and some degree of internal wave deflection / energy adsorption from the corral wall. The Waterline pit is predominately salinity stratified with only the top 8m being subject to thermal stratification.

Comparison with CTD collected beside the corrals from the open water column indicates that the mixing within the corrals was reduced in comparison to that immediately outside the walls. The likely impact of such reduced mixing on the chemistry of the limnocorals is that the mixing of hypolimnetic waters with oxygenated waters in the mixolimnion would be more limited. This would have the effect of reducing Fe-oxyhydroxide formation and subsequent metal sequestration and consequent export from the mixolimnion. The available data support this hypothesis (Figure 3.3.4, page 112).

As shown in Figure 3.3.4, the starting conditions (A) on July 13, 2002 were similar in all limnocorals and the Waterline Pit. By Sept 17, 2002 (B), the chemocline was significantly deeper and sharper in the open pit (in comparison to the limnocorals) and the transmissivity was much reduced in the surface waters of the lake in comparison to the control limnocoral (WLL-11). The reduced transmissivity in the lake is attributed to Fe-oxyhydroxides that formed when the chemocline deepened.

Temperature. The temperature within the limnocorals closely matched that of the Waterline Pit throughout the experiment. The surface waters started at ~12°C in mid July, decreased slightly to ~10°C in early August and increased again to ~12°C in late August. By Sept 17, the water temperatures at the surface had decreased significantly to ~8°C and by Oct 11, were at close to maximum thermal density at just over 4°C. During the winter (January-March), temperatures near the surface graded from 4°C at depth (1m in January, 2m in March) to near 0°C at the surface. Temperatures below the thermocline / halocline were relatively constant throughout the summer at ~5°C. In mid winter this temperature dropped to 4°C.
**Conductivity.** The conductivity profiles match the sulphate concentrations closely. Sulphate is the dominant anion and is expected to control both the conductivity and density stratification within the pit and limnocorral waters. Throughout the experiment the epilimnetic conductivity did not change significantly. It can be expected that the lack of external water input (other than minimal precipitation) to the limnocorals would result in a conservative mixing profile with the total salt load for the corrals remaining constant. This did not appear to be the case when the deepening of the chemocline occurred in the limnocorals in the fall. It can be seen in Figure 3.3.6 that a somewhat conservative mixing occurred in WLL-12 between Aug 28, 2002 and Sept 17, 2002 with the epilimnetic conductivity increasing as a response to mixing with deeper waters. Conductivity was not conservative during the deepening and broadening of the chemocline between Sept 17, and Oct 10, 2002. Deep (but < 6m) waters within WLL-12 became less saline without a consequent increase in mixolimnion conductivity. Why this is the case is not clear.

In addition to conductivity, the Total Dissolved Sulphur content of the waters was measured. The ICPMS method used for the determination of total dissolved sulfur would likely include both sulphate and dissolved sulphides. Due to the sulphate dependence of conductivity in the Waterline Pit waters, the dissolved Sulphur parameter could be used to support conductivity measurements. In relation to the apparent non-conservative conductivity profile during the fall chemocline deepening in the corrals, the Total Dissolved Sulphur concentrations at 8 and 9 m in WLL-12 for the October 10th sampling date suggest that the chemocline may have deepened to below 6 m. The Sulphur data suggest that the CTD cast on Oct 10, 02 may have been too shallow to reach true hypolimnetic conductivity values (chemical sampling extended deeper into the water column than the CTD profile). Sulphate can be lost through the formation and precipitation of sulphide minerals. The total removal of metals in WLL-12 by this date was on the order of 10 μmol, much too low to account for the non-conservative sulphate profiles (assuming removal in mono or bi metal sulphide / sulphate complexes).
Figure 3.3.4: Conductivity, temperature, fluorescence and transmissivity profiles of the southern raft limnocorals (WLL-9 to WLL-12) and the Waterline Pit.; A. July 13, 2002 (start of nutrient additions) B. Sept 17, 2002 (after 67 days).

Figure 3.3.5: Depth of chemocline as estimated by conductivity and temperature profiles for each limnocorral. "Top" refers to the upper chemocline limit, "Bottom" refers to the lower limit.
**Figure 3.3.6:** WLL-12 conductivity profiles (binned at 0.1m intervals) for 28 August 02, 17 September 02 and 10 October 02.

**Figure 3.3.7:** XRD output for WLL-14 (medium nutrient) sediment trap material, March 03. The diffraction pattern for goethite is shown.
Figure 3.3.8: (A) Cross section of Limnocorrall design. Sediment traps deployed at 8.2 m depth. (B) Plan view of the Waterline Limnocorrall deployment.
3.3.3 Chemical Response (Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Cd and Sb).

The following results for selected metals and metalloids in the Waterline limnocorral are given in mass order from Mn through to Sb. These parameters are presented in the same order in graphical form in Appendix B (Figures B.1 to B.48). Throughout this section (and the thesis), “dissolved” indicates that fraction of an element or compound that passes a filter with 0.45 μm nominal pore size. The term “dissolved” is thus operationally defined and has little true chemical meaning. In a study of an oxic ARD impacted river system, a significant colloidal fraction was identified that passed through a 0.45 μm filter and even a smaller fraction that passed through a 0.1 μm filter though not a 0.001 μm ultra filtration apparatus [Kimball, 1995 #314]. Several 0.1 μm filtered samples were taken in the WLP and limnocoral waters which showed little difference in metal concentrations when compared to the < 0.45 μm fraction. These data are discussed below where relevant.

The overall aim of the limnocoral experiment was to explore the potential for the removal of hypolimnetic metals from the water column through the induction of sulphide generation. The basic energy source for the reduction of sulphate to form sulphides and subsequent sulphide minerals is reduced carbon in the form of autochthonous organic carbon fluxes from the epilimnion, plus ethanol added directly to the hypolimnion. Two basic redox regimes were in effect in the limnocorals, an oxic epilimnion and an anoxic hypolimnion. In interpreting the chemical response to the experimental manipulations, an emphasis has been placed on understanding the oxic and anoxic processes as well as those of the chemocline where they meet.

The limnocorals were installed in the second week of July, 2002 and the first samples were taken on July 13, primarily for measurements of dissolved metal (0.45 μm filtered) and nutrient concentrations. Only surface samples were taken for Total Metals (unfiltered). Nutrient additions were made after sampling (within one day) and sampling was carried out weekly throughout the summer (until August 28, 02). Two fall (Sept 17, 2002 and Oct 10, 2002) and two winter (Jan 24, 2003 and Mar 13, 2003) sampling sessions were also conducted.

Manganese. As would be expected, on the July 13, 2002 all the limnocorals started with similar Mn profiles, representative of the Waterline Pit itself. Surface concentrations in the epilimnion (top ~4m) were on the order of 2000 ppb. These increased over the chemocline to
~3500 ppb in the hypolimnion. No significant differences could be seen laterally between the northern (no sediments) and southern limnocorrals (attached to the sediments). Mn was found almost entirely within the dissolved fraction for all samples at all dates (within the uncertainty of analysis). Even by day 47 (Aug 28, 02) the only significant change to the Mn concentration profile in any limnocorral was a slight reduction (from ~3000 to ~2500 ppb) at 6 m depth in the no-sediment limnocorrals (WLL-13 to 16). This reduction reflected a deepening of the redox cline in these limnocorrals with water of lower Mn content mixing down as well as possible MnO\textsubscript{x} precipitation.

Despite a reduction of Mn concentrations in the newly oxygenated upper hypolimnion upon the deepening of the chemocline, there was no subsequent increase in Mn in the epilimnion. By winter, day 196 following the first additions to the limnocorrals, Mn concentrations in the epilimnion showed a reduction in all nutrient addition corrals but not in the controls. This decline continued into March (day 241). The average March 03 epilimnion concentrations (1 m and 3 m samples) of Mn in the nutrient addition corrals was 544 ppb (±940 ppb, 95\% c.i., n = 12) while control concentrations were 2328 ppb (± 330 ppb, 95\% c.i., n = 4).

During the progressive deepening of the chemocline in September, Mn was found to be elevated at 6 m (near the chemocline) but iron was not. However, by October Fe and Mn profiles at 6 m both displayed oxic / epilimnion concentrations lower than those in the hypolimnion. Even into January and March 03, in the control, only the 9 m deep sample represented hypolimnetic waters. Epilimnetic Mn concentrations increased in the controls during the winter deepening of the chemocline due to mixing up of higher Mn concentrations at depth.

In March 03, additional samples were taken in the heart of the chemocline at 7 m depth in the WLL-13 (High Nutrient), WLL-15 (Control) and WLL-16 (High Nutrients and Ethanol) corrals. These showed a peak in Mn, in excess of 5000 ppb, for both nutrient addition corrals but no such peak in the control. Mn was almost entirely within the dissolved fraction in the peaks at 7 m depth. In several cases the Mn chemocline (defined by the gradient from low epilimnetic to increasing hypolimnetic concentrations) appeared to be higher in the water column than that of Fe (e.g. Figure B.45, 6m).

Mn can be expected to have been remobilized through Mn-oxide reduction in the sediment traps of the Waterline limnocorrals due to their long deployment time. Indeed the lowest Mn settling fluxes appeared in the traps that were suspended in the corrals that received carbon supplements as ethanol. The low rates of particulate Mn capture in these traps are
consistent with the higher settling fluxes of organic carbon in the ethanol-bearing corrals and the related stronger reducing conditions in the water column. The greatest retention of Mn in the sediment traps occurred in the high nutrient and medium nutrient limnocorrals despite the detectable odour of H$_2$S in the traps during retrieval. WLL-9 provides a notable exception to this pattern. The low Mn flux in this corral was similar to that in the controls and the ethanol addition corrals, but the reason for this anomaly is unclear.

**Iron.** The profiles of dissolved and particulate Fe in the limnocorrals indicate that the distribution of the element was controlled primarily by the redox state of the water column. Dissolved Fe in the oxic epilimnion was typically below detection limit (~10 ppb) throughout the experiment. Relatively minor dissolved Fe was detected in some limnocorrals in the epilimnion on some dates (max. 66 ppb). These levels compare to hypolimnetic Fe concentrations of ~15000 ppb. In contrast to the dissolved fraction, a significant pool of particulate Fe was present in the epilimnion for the duration of the experiment.

Limnocorrals not attached to the sediments in the deeper northern section of the pit lake consistently contained more than double (See Figure 4.3.1) the particulate Fe content of the southern (attached to the sediments) limnocorrals for the bulk of the summer and fall, even as particulate Fe steadily declined in the northern limnocorrals during the summer. The southern limnocorrals were more variable though a decreasing trend in Total Fe from late fall into winter was can be seen in the data. After initial sampling, the [Fe]$_{tot}$ in the epilimnion of the Waterline pit outside the limnocorrals was considerably higher than that of the limnocorrals during the summer / fall. During the two winter sampling sessions the pit and limnocoral Fe concentrations were of the same order. The winter [Fe]$_{tot}$ in the controls was higher than that of the nutrient addition corrals.

The hypolimnetic Fediss (8 m and 9 m) was two orders of magnitude greater than that of the epilimnion on most sampling dates. From the third week of the experiment (August 6, 02), southern hypolimnion Fe$_{disc}$ concentrations were slightly less than those of the northern limnocorrals. This also appeared to be the case in the lake outside the corrals. For the duration of the summer both the 8 m and 9 m samples should have been well within a uniform sub-stratum of the hypolimnion and not subject to errors (in comparing depths) associated with sampling a cline in concentration. By August 28, 02 a difference in the deepening of the chemocline between the northern and southern limnocorrals was apparent in the 6 m Fe$_{disc}$ concentrations. The 6 m depth in the southern limnocorrals displayed Fe$_{disc}$ concentrations intermediate between epilimnetic and hypolimnetic values indicating that this depth was within the chemocline. The
same depth in the northern limnocorral contained Fe concentrations characteristic of the epilimnion indicating a deeper chemocline. A significant particulate Fe fraction was present at 6 m in the northern limnocorral on this date, also an indication of the oxidation of dissolved Fe from the hypolimnion during chemocline deepening.

There was little change in the Fe concentration profile between the end of August and September 17, 02. By October 10, 02 there was a significant reduction in Fe in the hypolimnion of all limnocorral (~1/3 to ½). Indicating a deepening redoxcline. Only the southern limnocorral were sampled in January 03. By this date dissolved Fe was all but absent in WLL-9 down to 9m (~0.5m above the sediments). The sediment control (WLL-11) had about one-half of its original Fe_{diss} concentration at 9 m. Both WLL-10 and WLL-12 displayed elevated Fe_{diss} at 9m (~20000 ppb) though only WLL-12 showed any significant dissolved Fe at 8 m (884ppb). By March 03 the redoxcline was above 8 m for all but WLL-9 and WLL-11, indicating a slightly shallower redoxcline in all limnocorral. At this time, the redoxcline depth in the northern limnocorral was comparable to or shallower than the southern limnocorral in all instances, marking a reversal from the summer / fall pattern. The hypolimnetic Fe concentrations were higher in March 03 than for the start of the experiment in July 02 for all but WLL-9.

The sediment traps showed various degrees of conservation of Fe in comparison to water column losses. The particulate fraction collected in the traps ranged from 10% to 97% of the original water column inventory; none exceeded the losses from the water column. Traps in the northern limnocorral control and nutrient addition limnocorral (ethanol free) displayed the highest proportionate capture of Fe_{part} (~70 to 97%). XRD analysis of sediment trap material identified a large component of amorphous material (high background scatter) and possibly some goethite (FeOOH)(Figure 3.3.7) in the control and medium nutrient limnocorral.

**Cobalt.** Throughout the experiment the epilimnnetic Co in the controls was found almost entirely in the dissolved fraction and at concentrations close to half that of the hypolimnion. Typical control concentrations were ~15 to 17ppb in the epilimnion and ~30 to 39ppb in the hypolimnion. Neither hypolimnnetic nor epilimnnetic Co concentrations displayed any significant change in the controls corrals, other than that associated with the deepening of the chemocline over the fall which reduced hypolimnnetic Co by ~10ppb. The pattern of Co loss from the epilimnion of the nutrient addition limnocorral was similar to that seen for Mn.

There did not appear to be any relation between the rate of Co removal from the epilimnion and the amount of nutrients added. In fact the greatest removal of epilimnnetic Co (to <1 ppb) appeared in a medium-nutrient limnocorral (WLL-10, Figure B.13). The least Co
removal for a nutrient addition limnocorral was in WLL-12, possibly due to the greater reducing conditions and rapid Mn oxide reduction at the chemocline.

Around 25% of Co was in the solid phase at 6 m in WLL-9 on October 10, 02, during the deepening of the chemocline and the generation of particulate Fe. The same proportion of particulate Mn was also found solely at this depth in this limnocorral. Some degree of partitioning of Co to the solid phase was apparent in all but the control limnocorals by March 03. Co delivery to the hypolimnion is suggested by the occurrence of congruent peaks of Mn and Co in the redoxcline of WLL 9, WLL-10, WLL-13 and WLL-14 in March 03. Further, the increase in hypolimnetic Co in March 03 accounted for more than 2/3 of that removed from the epilimnion. Such inferences of export or removal can only be estimated due to the coarse nature of the sampling frequency, both spatially and temporally.

The most significant removal of Co in the hypolimnion of the limnocorals was found where ethanol was added (WLL-12). By winter 03 the dissolved Co concentrations in WLL-12 had fallen to 0.34 ppb in the hypolimnion at 8 m. This value represented some 8% of the total Co (4.3 ppb). Between January 24th and March 18th 03, the depth of this dissolved Co minimum has risen to 6 m (Figures B.26 and B.27) while total Co concentrations rose to 15.8 ppb at 8 m and 34 ppb at 9 m depth. In the other limnocorral that received ethanol (WLL-16), the Co concentration decreased in the hypolimnion between September 17, 02 and October 11, 02. Sulphides were detected at moderate levels (< 3 μmol) at the same depths as the inferred Co removal. By March 03 the Co_diss concentrations at 8 m and 9 m in WLL-16 increased again, possibly due to the upward mixing of Waterline pit water from underneath the limnocorral. Sulphides were detected at 6 m in March 03 though not at 8 and 9 m, where they were previously present.

Nickel. The control limnocorral and Waterline lake profiles of Ni and Co match closely and suggest similar geochemical influences on both elements in this setting. Ni in the epilimnion of the limnocorals was found entirely within the dissolved (<45μm) fraction for the most part with < 10% particulate Ni being observed during the height of the algal blooms. A slight removal of epilimnetic Ni from the nutrient addition limnocorals was observed over winter, as for Co although to a lesser degree. Initial concentrations for Ni were ~40 ppb in the epilimnion and ~60 ppb in the hypolimnion. The concentration difference appeared to be redox controlled. Deepening of the chemocline led to removal of Ni from the newly oxygenated hypolimnetic waters without distinctly increasing epilimnetic Ni through mixing up. Although the total volume of the epilimnion increased over the length of the experiment, by March 03 the control
limnocorals still displayed ~40 ppb epilimnetic Ni and somewhat higher (65 – 70 ppb) hypolimnetic dissolved Ni contents.

Other than that associated with the deepening chemocline, Ni was not removed from the hypolimnion of the controls or ethanol-free limnocorals during the experiment. Where ethanol was added, there was a significant increase in solid phase Ni content and subsequent removal of the metal from the hypolimnion. Particulate Ni first appeared in the hypolimnion of both WLL-12 and WLL-16 between the September 17, and the October 11, 02 (between day 67 and day 91 of the experiment). On October 11, a significant percentage of the particulate Ni (~65%) was in the colloidal fraction (0.1 to 0.45 μm)(Figure 3.3.9). This stands in contrast to particulate Cd being observed in the August 28, 02 (day 47) samples and particulate Zn in the September 17, 02 (day 67) samples. By March 18, 03 (day 249) in WLL-12, dissolved and total Ni at 8 m (the depth of the ethanol addition) had fallen to <1 ppb, and 3.9 ppb respectively.

The flux of Ni to the sediments (as represented by the sediment trap results) was greatest in the limnocorals to which ethanol had been added (~120-220 μg/m²/day for the length of the experiment). The flux was higher for the fall / winter period (17th September, 02 to 18th March 03) than the previous summer trap deployment (17th July 02 to 17th September, 02). The Ni flux was similar in both the control and ethanol-free corrals: 22 to 50 μg/m²/day.

Copper. The Cu data obtained during the project are not considered reliable due to problems of intermittent contamination of the ICPMS. Consequently only a very brief summary is presented here. Total Cu in the Waterline pit lake is typically below detection limit in the hypolimnion (< 1 ppb) and on the order of 2 ppb in the epilimnion. Where reliable Cu data exist, the particulate fraction generally comprises > 50% of the total inventory.

Zinc. Zinc concentrations present one of the water quality concerns in both the Waterline and Main Zone pit lakes. Typical epilimnetic concentrations in the Waterline pit lake are on the order of 400 to 600 ppb. Slightly higher values, up to 700 to 900 ppb, occur in the hypolimnion just below the chemocline. The Zn concentration in the limnocorals at the beginning of the experiment (~700 ppb) distributed uniformly across both the epilimnion and the hypolimnion (e.g. Figure B.1). Little change occurred in the control limnocorals from the starting date of July 13, 2002 through to September 17, 2002. By October 11, the chemocline had deepened considerably and this apparently drove a reduction in the Zn concentration to ~550 ppb over the length of the water column in the control corrals.
Over the duration of the experiment Zn in the control limnocorral remained almost entirely within the dissolved (<0.45 μm) fraction. A slight increase in the proportion of particulate Zn was observed in the controls during the summer though this was gone by fall (September 17, 02). The nutrient-addition limnocorral all showed considerable partitioning of Zn to the solid phase (> 0.45 μm) within the first three weeks of the experiment. This could not be rigorously correlated with the fluorescence signal from the same depths, although in general the proportion of solid phase Zn was higher in the high nutrient corral than in their medium-nutrient counterparts. The degree of carbon export recorded by the sediment traps and implied by POC analyses support the inference that higher particulate zinc was associated with the 50 to 300 % increase in biomass (see the biological response section above) seen in the high-nutrient relative to the medium-nutrient corral.

During the course of the summer Zn was removed from the epilimnion of the corral to which nutrients were added. Within three weeks from the start of nutrient additions, up to a third of the dissolved Zn had been removed from the epilimnion. The removal was initially rapid and continued to the end of August, 2002. Little additional removal occurred between August 28, 2002 and the end of the experiment in March 03 (day 47 through to day 249). By the winter, the particulate fraction of Zn had disappeared from the nutrient addition limnocorral though the total Zn concentrations remained the same, suggesting that the particulate Zn had returned to the dissolved fraction (<0.45 μm) in January and March 03.

There was evidence of Zn transport from the epilimnion to the chemocline in WLL-9 between August 28, and September 17, 2002. On both dates WLL-9 displayed a peak in (primarily dissolved) Zn at 6m. In the same corral between January 24 and March 18, 2003, the dissolved Zn fraction at 9 m depth declined by 40 % at the same time as the particulate fraction increased by 20 %. Unlike WLL-9, Zn removal was not seen in WLL-13, the other high nutrient, no-ethanol corral that was not attached to the sediments. Similarly, no evidence of Zn removal was observed in WLL-10 at 8 m, although no 9 m sample was taken from this corral due to concerns about contamination induced by contact of the sampling equipment with the corral wall.

Zn removal from the hypolimnion of the ethanol-addition limnocorral occurred much earlier and to a much greater degree than that of WLL-9. Dissolved sulphide was first detected in WLL-12 and WLL-16 on September 17, 2002 (day 67). By this date 90% of Zn had been removed from the dissolved phase in the hypolimnion of both these limnocorral. Most of the Zn inventory was still present in the water column however, albeit in solid form. Total Zn
concentrations fell by less than 20% relative to late August (day 47) levels. Over the next two months the particulate Zn fraction slowly settled from suspension at a rate of 1 to 1.7% per day (calculated from the removal rate between day 67 to day 91). By January 24, 2003, dissolved Zn was below detection limit in the hypolimnion of WLL-12 and total Zn had been lowered to ~45 ppb. The Zn flux to the sediment traps was a factor of two or three greater in the ethanol amended corrals than compared to their ethanol-free counterparts. For the nutrient-addition limnocorrals, the pattern of Zn flux roughly followed that of the removal from the epilimnetic waters with the settling flux highest in the high-nutrient corrals and lowest in the controls.

**Arsenic.** The distribution of As in the Waterline limnocorrals closely followed that of Fe and was strongly dependant on the position of the chemocline. At the start of the experiment dissolved As was at 1 to 2 ppb in the epilimnion and graded to ~400 ppb in the hypolimnion. These concentrations dropped to below detection limit (0.5 ppb) in the epilimnion by day 25 (August 6, 2002) and increased again to between 2 and 10 ppb for the remainder of the experiment (to day 249). Within the hypolimnion of all limnocorrals As was found almost exclusively found in dissolved form.

During periods of chemocline deepening a small fraction of particulate As was observed, typically near the chemocline. This coincided with the removal of As from the newly oxidized portion of the hypolimnion as the chemocline deepened. By late fall (day 91) dissolved As had been removed to ~2 ppb (from 215 ppb on day 67) in the hypolimnion of WLL-11 (control). This coincided with a significant removal of Fe (from 12.5 to 5.2 ppm). Arsenic was similarly removed in WLL-9 though latter in the season, between day 91 and day 196. In all other limnocorrals dissolved As was maintained at above 150 ppb in the hypolimnion (9 m sample) and tended to increase in concentration over the length of the experiment in those corrals that were open to the water column at the bottom (WLL-13 to WLL-16). There was marked increase in As at 8 m in WLL-16 between October 02 and March 03 from 314 to 838 ppb. This increase could not be explained by As precipitation from the epilimnion where As concentrations were below 10 ppb between those dates, and must reflect incursion of As-laden water from below.

The Fe:As weight ratio (85) was highest in the sediment trap sample from the ethanol amended corral (WLL-12) and substantially lower in the high and medium-nutrient corrals (36 and 34 respectively in WLL-9 and WLL-10) as well as in the control (32 in WLL-11). The Fe:As ratio was lower across the board in the deep, open-bottom corrals (average = 21, stdev. = 4).

**Molybdenum.** As with the majority of metals in the Waterline pit lake, at the start of the experiment Mo was found predominantly in the dissolved (< 0.45 μm) form in both the
epilimnion and the hypolimnion of the limnocorrals. Epilimnetic concentrations were typically half that of the hypolimnion at ~1.6 ppb. Hypolimnetic Mo ranged from ~2.8 ppb just below the chemocline to ~3.2 ppb at 9m. The Mo distribution and concentrations in the control remained reasonably constant throughout summer. During the deepening of the chemocline in the late fall values in the hypolimnion fell and were similar to those in the overlying epilimnion, epilimnion values did not change over this period implying that the decrease with depth was not due to mixing of the two strata. For most cases the removal of Mo from the limnocorrals had a pattern similar to that of Mn.

A marked removal of dissolved Mo and increase in the particulate fraction occurred in the hypolimnion of WLL-12 between day 91 and day 196 (Figures B.25, B.26 and B27), along with the detection of significant quantities of dissolved sulphide. A significant particulate and colloidal Mo fraction was observed in WLL-12 at 9 m depth in a series of size-fractionated samples taken on October 11, 2002. Similar behaviour was seen only with Ni and Sb (Figure 3.3.9). Some fractionation of Mo was observed in WLL-16 at 7 m on March 18, 2003 (Figure B.45) in the presence of dissolved sulphide concentrations of ~35 μmol. Metals expected to form sulphide minerals under these conditions (Cd, Zn, Co, Ni) were also fractionated into the particulate phase at that time.

The presence of significant algal biomass (as recorded by POC and fluorescence measurements) in the nutrient amended limnocorrals did not cause a change in the fractionation of Mo nor removal of Mo from the epilimnion (e.g. Figure B.3).

Cadmium. Although samples for total Cd analyses were not taken at the beginning of the experiment, measurements made in the open Waterline pit indicate that Cd must have been present predominantly in dissolved form in all limnocorrals on July 13, 2002. Particulate Cd concentrations in the open pit lake remained low (typically < 10 % of the total Cd, on a few occasions rising to near 20 %) throughout the sampling campaign. Although Cd is a relatively scarce constituent in the lake – total concentrations did not exceed 9 ppb during the course of the experiment.

The stimulation of algal blooms in the nutrient amended limnocorrals promoted partitioning of Cd to the solid phase. The fractionation was surprisingly constant at 40-45 % through the summer in WLL-9, despite changing total Cd concentrations. This same degree of fractionation (45%) was observed in WLL-10 on Aug 28, 2002 during the height of the algal bloom. Peak fractionation was recorded on Sept 17, 2002 in WLL-12 (50%) and WLL-16 (56%). Both dissolved and particulate Cd was removed from the epilimnion of the nutrient addition
limnocorral throughout the summer and was at its lowest concentration at the end of the experiment in March 2003. Less removal was observed from the epilimnion of the control corral. The calculated fluxes for the two control limnocorals were quite different from each other with WLL-11 recording a ~40% greater Cd removal from the epilimnion than that of WLL-15. The calculated total fluxes of Cd from the epilimnion in the high nutrient limnocorals WLL-9 and WLL-12 were remarkably similar (within 5%) over the course of the experiment.

Cd was partitioned to the solid phase in the hypolimnion of both ethanol-amended corral (WLL-12 and WLL-16) during the mid to late summer. In both cases the particulate fraction of Cd was detected before sulphides were detected. Cd occurred at the chemocline predominantly in the dissolved phase (Figures B.23, B.42 and B.4) while the particulate proportion ranged between 40 to 90 % above and below this horizon. Throughout the late fall and winter the particulate fraction was removed from the epilimnion and hypolimnion of the corral. Total dissolved Cd removal reached 89 % in WLL-12, 74 % in WLL-9, 38 % in WLL-11 and 21% in WLL-15. No significant particulate Cd (>5%) was found in the hypolimnion of the control limnocorals throughout the experiment.

By Day 249 (March 18, 2003) dissolved Cd concentrations were below detection limit (~0.05 ppb) at 9 m depth in WLL-9. This coincided with the detection of “dissolvable sulphides” though no dissolved free sulphide. No “dissolvable sulphides” were detected in the controls or medium nutrient limnocorals.

Antimony. As with the Waterline pit, Sb concentrations were elevated in the epilimnion of all limnocorals at the start of the experiment (~5 ppb) and declined across the chemocline to lower values of ~ 0.5 ppb in the hypolimnion. Throughout the water column, the element occurred almost entirely in the dissolved (<0.45 μm) fraction and, in the control corral, it appeared to be conservative throughout the summer and fall.

Sb did not fractionate to the particulate phase in the presence of algal blooms in the nutrient addition limnocorals, nor was any significant export of Sb observed from the epilimnia during the summer. In the late fall (between Sept 17, and Oct 11, 2002) concentrations in most nutrient amended limnocorals fell 10 to 60% as a result of chemocline deepening and mixing with hypolimnion waters of lower antimony content.

The partitioning of Sb to the particulate phase and subsequent removal from the water column occurred in both the ethanol and nutrient amended limnocorals (WLL-12, WLL-16, WLL-9). Particulate Sb was first evident at 8 m depth in WLL-12 within three weeks of ethanol addition. By day 67 (September 17, 2002), all hypolimnetic Sb was in the particulate phase in
both ethanol addition limnocorals and particulate Sb had started to form in the hypolimnion of WLL-9 (high nutrient addition). The detection of particulate Sb in WLL-9 coincided with that of particulate Cd in the hypolimnion. On the 11\textsuperscript{th} October, 02 a size fractionated metals sample was taken at 8m in WLL-12 (ethanol addition) and WLL-11 (control) (Figure 3.3.9). This sampling detected a significant (~20\%) “colloidal” fraction of Sb in WLL-12, along with colloidal Ni and Mo phases. This size fraction (0.1 \mu m < x > 0.45 \mu m) was absent in the control. By day 249 (March 18, 2003) Sb contents were below the analytical detection limit (~0.05 ppb) in the hypolimnion of WLL-12.
Figure 3.3.9: WLL-11 and WLL-12 size fractionated metals at 9 m depth (% passing indicated filter size), Oct 11, 2002. Total (unfiltered) metals set as 100 % (indicated as >20 µm).
4 Discussion

4.1 Main Zone Pit Lake Biogeochemistry

4.1.1 Main Zone pit lake biology

Under standard lake classifications systems (such as the Trophic State Index) the level of phytoplankton “biomass” in the Main Zone pit lake, as measured by chlorophyll concentrations, would rate as mesotrophic (2 to 8 μg/L chlorophyll) (Nelson Institute., 2004). This is somewhat surprising given the elevated dissolved concentrations of some elements such as Zn and Mn and the low phosphate concentrations. Under the same Trophic State Index the phosphate concentrations would rate the Main Zone pit as oligotrophic.

The issue of elevated dissolved metal concentrations, particularly Zn, was investigated with regard to the inhibition of algal growth. While the size of the summer algal blooms did increase with decreasing Zn concentrations, low water temperatures appear a better candidate for bloom inhibition in the spring / early summer. Algae, particularly blue-greens, are not growth inhibited by metal concentrations on the order of those found in the MZP (Kalin et al., 2001; Shehata et al., 1999; Simmons et al., 2004). It is more likely that the removal of phosphate through adsorption to Fe-oxyhydroxides in sludge and neutralized ARD inputs to the MZP inhibit algal growth to a greater degree than the dissolved metal content (Gunnars et al., 2002; Ler and Stanforth, 2003; Simmons et al., 2004). Figure 3.1.2 (section 3.1.1) shows a significant decrease in dissolved phosphate concentrations in the vicinity of the algal bloom on Aug 14, 2002 suggesting near quantitative uptake of this nutrient during growth periods.

Although not presented as part of this thesis, a limnocorral study of algal removal of metals from the surface waters of the MZP was conducted as part of the wider pit lake study. This limnocorral experiment essentially induced an increase in algal biomass in the surface waters of the MZP through nutrient additions. The marked increase in phytoplankton biomass with the addition of moderate concentrations of nutrients (~ 1 μmol L\(^{-1}\) wk\(^{-1}\)), despite the presence of elevated dissolved Zn concentrations, suggests that Zn was not inhibiting under these conditions (Figure 4.1.1). While these limnocorral experiments appear to prove the efficacy of using algal biomass to adsorb / uptake metals from the water column, the diagenetic effects of increasing the organic carbon loading to the sediments through such a strategy need to be addressed. This is further discussed in the conclusions section of this thesis (section 5.0).
Figure 4.1.1: Zn, Cu, Cd and Fluorescence in the Main Zone pit lake limnocrails for control (left graphs), medium nutrient additions (centre graphs) and high nutrient additions (right graphs) on Aug 14 –15, 2002 (51-52 days from the start of weekly nutrient additions).
Limnocorral design was similar to those described in section 3.2.2 for the Waterline limnocorral experiments.

4.1.2 Geochemical and physical aspects of the deposition of ARD treatment sludge into the Main Zone pit lake.

The MZP is the final repository of an average of 130,000 m$^3$ yr$^{-1}$ of ARD treatment sludge containing between 5 and 8% solids. This equates to approximately 1.3% of the volume of the MZP on an annual basis. The typical solid phases comprising the bulk of the ARD neutralization sludge are gypsum and metal-oxyhydroxides. This section discusses the current impacts of sludge deposition on the MZP geochemistry, while the following section (4.1.3) discusses the management implications of a future change in the mixing regime and the $\rho_e$/pH conditions of the pit lake. It is important to emphasise that the MZP does not represent a typical mine pit lake in that sludge deposition and artificial maintenance of the water balance impact the physical and geochemical characteristics of the pit lake. The unique nature of the MZP however allows assessment of the use of mine pit lakes as metal-oxyhydroxide waste repositories.

During active sludge deposition into the MZP a density current is supported by the high solids content of the sludge and drives mixing within the pit lake. This mixing typically creates a uniform water column with regards to conductivity (dissolved ion content) and temperature below the epilimnion (2 to 10 m depth). Small variations with depth are apparent in the dissolved metal concentrations during sludge deposition indicating that the mixing is not always complete with regards to trace elements. Consideration of the dissolved and particulate metal profiles as well as the CTD measurements for conductivity, temperature and transmissivity indicate that the degree of mixing is greatest in the water column below 50 to 80 m during sludge deposition. Current measurements support this conclusion. This sludge driven mixing inhibits the formation of thermal or halocline stratification and increases the supply of dissolved oxygen to the deep water column (Figure 4.1.9). Although sludge deposition can be observed as a distinctive plume of particulate metals in the water column below 50 to 80 m depth, the actual % volume of sludge in the water column is generally very small. Figure 3.1.8 shows that on August 26, 2002, during active sludge deposition, that the water column at 80 m depth contained only 1 part in 4000 sludge despite the strong transmissivity and particulate metal signal at this depth. The total pool of sludge in the 10 m layer from 75 m to 85 m on this date would equate to less than one hour of sludge input during pumping (assuming a pumping rate of 50 L/s).
A change in the sludge composition in July 12, 2002 to one of slightly higher solids content appears to have reduced the amount of mixing induced by the sludge deposition. This sludge was generated from the treatment of a lower acidity influent stream (diversion pond re-treatment) combined with re-circulated sludge as a nucleation agent. The re-circulation of sludge into the lime-ARD reaction chamber is the basis for the “high-density sludge” process (Vachon et al., 1987). This post July 12, 2002 sludge appears to settle faster and inject fewer particulates into the upper water column than the previous sludge composition. Although more neutral in language, a consultant study of the relative physical behaviour of the “old” and “new” sludge types during deposition found that the “new” sludge type did not disperse through the water column to a greater degree than the “old” sludge type (Lorax Environmental Services., 2002). While the “new” sludge type was only discharged to the MZP in the latter half of the 2002 ice-free season, this information is relevant to the future deposition of sludge into the MZP as PDC-Equity (the mine operators) are currently upgrading the ARD treatment plant to a permanent high density sludge (HDS) system.

The moderate alkalinity of the MZP (30 to 40 mg/L CaCO₃ equiv.) is supported by excess lime and carbonate in the sludge (Norecol Environmental Consultants Ltd., 1991) as well as carbonate alkalinity in the natural groundwaters (Morin, 1990; PDC - Equity Division, 2003). Some small degree of buffering may also be present in the form of major ion exchange with protons at the sludge surface (Uhlmann et al., 2004). It is likely that the total concentration of dissolved metals in the pit lake is reduced with sludge deposition through increasing the pH of influent ARD drainages (run-off from pit walls, seeps etc.) and the subsequent formation of metal oxyhydroxides and scavenging oxy-anions (e.g. As and Sb).

It was apparent from the dissolved and particulate metal concentration profiles in the MZP that, for most metals, sludge deposition did not directly effect the dissolved metal concentrations. Whilst the whole-water-column concentrations of dissolved Ni, Cu, Zn and Cd did increase significantly during the early summer, shortly after the start of the seasonal sludge deposition, this also coincided with the freshet and a peak of dissolved metals at the surface of the lake (Figures 3.1.12-15). Consideration of the timing and location of the changes in dissolved concentrations of these metals supports the suggestion that ARD from both the pit walls and seeps into the pit lake is the likely source. The dissolved concentrations of these metals actually decreased over the summer of 2002 despite continued sludge deposition to the pit, indicating that some removal through adsorption to the sludge solid phases may have occurred. Direct evidence of sludge supply/removal of dissolved metals was mixed as dissolved concentrations within the
sludge plume were observed to both increase and decrease slightly over that in the general water column above the plume on different dates.

Significant dissolved Mn does exist in the sludge (1.4 ppm), treatment plant effluent waters (avg. = 25 ppm) (PDC - Equity Division, 2003), and the ephemeral acidic seeps into the MZP (~45 ppm). The continued increase in dissolved Mn concentrations over the sludge deposition period indicates that the sludge is likely to be the major source for this metal. The Waterline pit lake over flow also contains significant dissolved Mn (~1.5 ppm) and may be responsible for up to 3.5 % (at an outflow into the MZP of 20 L/s) of the total MZP Mn pool during the summer/ fall period. The Waterline overflow is also likely to be a significant source for Zn, Sb and Ba in the epilimnion of the MZP. Particulate Mn, Sb and Ba also appear to have a surface source in the sediment trap record (higher fluxes recorded in the top 10 m than in the top 50 m of the MZP water-column).

While sediment pore-waters (from peeper / dialysis samplers deployed in March 2002) displayed elevated dissolved Mn, mass balance considerations rule out re-suspension of sediments upon sludge discharge as a source. Although use of the peeper data is restricted as the vertical location of the samples within the sediment profile could not be ascertained, the concentration profile over the length of the array (32 cm) was reasonably uniform. The pore-water concentrations of most metals suggested that the sediments are likely to be, at most, a mild source for dissolved As, Cu and Mo and a sink for other metals (Ni, Zn, Cd, Ba and U). Ficks' first law of diffusion was used to estimate the maximum efflux / influx of these metals if a 1 cm gradient between pore water and the open water column concentrations existed (Li and Gregory, 1974). With no correction for tortuosity or formation factor in the sediments or counter ion diffusion, the sediments were calculated to contribute less than 1 ppb of As and Cu to the water column per year (averaged over whole lake sediment area and water column volume). These are maximum values given possible pore water concentrations and do not reflect likely real effluxes.

It is evident from changes in the water column particulate and dissolved Mn concentrations as well as freeze-core and sediment trap samples that significant precipitation of Mn solids occurs, probably on an annual basis. There are several mechanisms that may be invoked to explain the near quantitative loss of dissolved Mn from the water column over the winter period. Under the MZP geochemical conditions it is likely that Mn can form solids as inclusions in the structure of authigenic calcite (Neumann et al., 2002) or through the formation of Mn-oxyhydroxides (Haack and Warren, 2003; Kay, 2001). Although Mn is predicted to be in the form of Mn-oxyhydroxides under the oxygenated conditions of the MZP the formation of
this phase is extremely slow kinetically without a catalyst such as bacterial oxidation or heterogeneous catalysis by solid surfaces (even auto-catalysis) (Davidson, 1992; Scott et al., 2002; Stumm and Morgan, 1996). The reduction of Mn(IV) to the soluble Mn(II) species by Fe(II) (Postma and Appelo, 2000; Villinski et al., 2003) in the MZP may also hinder the formation of Mn-oxyhydroxides during sludge deposition. The Fe-oxyhydroxides present in the sludge may have reductive capacity through the inclusion of mixed Fe(II) – Fe(III) species in the amorphous solids. The reduction of metals at the surface of Fe-oxyhydroxides is well documented (Belzile et al., 2001; de Vitre et al., 1991) and is a possible mechanism for the maintenance of dissolved Mn in the MZP during sludge deposition periods.

Dissolved Fe was only detected in the epilimnion during ice-over and once in the deep water column. Between January and March 2002 dissolved Fe was detected between 30 m and 80 m depth. Sludge disposal into the MZP had also resumed between these dates. It appears as though both dissolved Fe and Mn were added to the MZP with or slightly before the early spring sludge disposal of 2002. Despite a surface peak in particulate Fe present throughout the summer and fall in the MZP, dissolved Fe was not detected suggesting that photo-reduction (Kieber et al., 2003; Rose and Waite, 2003) does not play a significant role in the MZP or that reduced Fe is rapidly re-oxidized (Davidson, 1992) or adsorbed to existing Fe-oxyhydroxides (Jeon et al., 2003).

The pH of the waters would be an indication of ARD seeps if a large enough volume of ARD entered the pit waters. The alkalinity of the MZP waters is on the order of 30 to 40 mg/L (CaCO₃ equivalent). While the acidity of the ARD seeps into the MZP was not measured, ARD on the Equity mine site typically has an acidity of 10 to 15 g/L. This would equate to between 250 to 500 L of pit water being required to neutralize one litre of ARD water. Those few acidic seeps that were observed in the MZP after rainfall typically had very low flow rates on the order of 1 L/sec. The top 1 m of the water column in the MZP could therefore neutralize up to five ARD seeps running at 1 L/sec for one day before depletion of their alkalinity. Given this crude accounting, it is not surprising that no significant drop in pH was seen in the surface waters of the MZP over the study period, at least on the four dates on which data were collected.

Particulate Fe was elevated in the epilimnion, over mid water column concentrations, for most sampling dates (Figure 3.1.11). It is difficult to assign the source of the surface particulate Fe peak to sludge deposition or ARD seeps into the surface of the pit lake as both are likely to have similar source compositions and similar metal ratios. The particulate Fe pool in the top 6 m of the water column June 20, 02 could have been supplied by seeps sampled two days prior, after
a rainfall event. Only two acidic seeps could be found after this rainfall event with an average individual flow estimated to be around 0.5 L/sec. At 1 L/sec the strongest (highest Fe concentrations) of these seeps could supply the whole June 19, 2002 Fe pool in the surface waters with about five days of flow. It is conceivable that the total Fe surface peak (together with several other metals present in elevated concentrations) could have been supplied by moderate flows of ARD seeps and run-off from mine walls after the June 17 / 18 2002 rainfall event. If the Fe surface Fe peak in June 02 was supplied by ARD seeps, the associated volume of ARD would have come close to exhausting the alkalinity of the surface waters. Unfortunately surface water alkalinity was not measured on this date.

Barium appears to be controlled by the elevated sulphate concentrations within the MZP through the formation of Barite (BaSO₄). Barium has been shown to have an adsorptive affinity with hydrous ferric oxides at circum neutral pH (Mishra and Tiwary, 1999) and would be expected to behave similarly with the ARD treatment sludge. Only one concentration profile taken during sludge deposition showed any partitioning of Ba to the solid phase (March 03) and Ba concentrations remained remarkably stable (temporally) within the pit. The lack of significant Ba concentrations in the sludge can be attributed to the low solubility of barite even at low pH (<1.0). Barite can be expected to precipitate within the active ARD generation zone and not to be transported significantly in the aqueous phase to the treatment plant (Figure 4.1.2).

In summary, the deposition of sludge to the Main Zone pit lake decreases stratification and increases the delivery of dissolved oxygen (primarily through mixing) and alkalinity to the deep water column. Only limited D.O. is entrained in the sludge itself, most probably due to the low volume of sludge relative to the MZP volume. Both of these processes (mixing and excess alkalinity) aid in the stability of the sludge in the sediments. The circum neutral pH, elevated pe and high concentrations of particulate matter in the water column also aid in the mitigation of untreated ARD waters entering the pit on a seasonal basis. On a regulatory note, the sediments of the Mainzone Pit Lake exceed the B.C. Contaminated Sites Regulation (B.C. Reg. 375/96, Schedule 4) for Co and Ni but are within standards for Ba, Sb and Mo. No “generic” regulations are available for As, Cu or Zn, which also occur in elevated concentrations in the sludge. Given the current water column conditions, the bottom of the Main Zone pit appears to be the most desirable location for this material.

4.1.3 Main Zone pit lake redox and pH conditions - implications for management.
The deposition of sludge into the MZP has the potential to both remove and release dissolved metals into the water column depending on the pH, pe and ionic competition for adsorption to surface sites on the solid phase (Cummings et al., 2000; Norecol Environmental Consultants Ltd., 1991; Tessier et al., 1996). The sludge itself offers some alkalinity (5 mg/L CaCO$_3$ equiv.) (Norecol Environmental Consultants Ltd., 1991) and buffering capacity to the MZP waters and sediments (Uhlmann et al., 2004). The pH range of the MZP (pH 7 to 8.5) encompasses the point of zero charge on the surface of many Fe-oxyhydroxide solids (Langmuir, 1997; Stumm and Morgan, 1996) and is also within the range of the adsorption edge for the major ions found in the MPZ (Ca$^{2+}$ and SO$_4^{2-}$) onto this solid phase (Stumm, 1992). The implications of changes in the pH / pe regime of the MZP to the stability of the sediments (sludge) and the water quality of the pit lake are discussed below.

The future pH / pe conditions within the MZP are likely to change upon the cessation of sludge disposal into the lake. As outlined in sections 2.5.1 and 4.1.2 (above), sludge deposition both increases the alkalinity of the pit lake and increases the delivery of dissolved oxygen to the bottom waters. The delivery of acidity into the MZP is evident from seeps sampled in early summer and is likely to continue for the foreseeable future (ARD generation has been known to proceed for centuries after mining) (Pereira et al., 1995). An acid base accounting model using empirically measured and estimated ARD inputs to the MZP and alkalinity inputs from pit wall and groundwater sources predicted a net neutralizing capacity of the pit waters over time (Morin, 1990). Although the sludge itself contains significant alkalinity (Norecol Environmental Consultants Ltd., 1991), the long term stability of these sediments depends on maintenance of alkalinity from other sources. A net consumption of the buffering capacity in the sludge over time would, depending on the relative decrease in ARD inputs over time, lead to the eventual release of metals through the lowering of the MZP pH and metal desorption / hydroxide dissolution. The maintenance of groundwater flow through the pit lake therefore would appear to be critical to ensure perpetual stability of these sediments.

Although low pH conditions appear unlikely to develop in the MZP, reducing conditions are also of management concern. The mesotrophic algal productivity together with freeze core (sediment) organic carbon concentrations suggest that delivery of reduced compounds to the sediments could, in the absence of active water column mixing, promote anoxia. Considerable reductions in dissolved oxygen saturation (30 to 35 %) are already observed in the MZP despite artificially maintained mixing. In the absence of oxygen, organic carbon export to the sediments from phytoplankton production in the epilimnion would provide a reductant and energy source...
for Fe and Mn oxyhydroxide reducing bacteria. Given the nature of the MZP sediments—being largely Fe / Mn oxyhydroxides with other metals either adsorbed to these phases or also present as oxyhydroxides—this is likely to be detrimental to the pit lake water quality (as seen in the Waterline pit lake).

The total particulate organic carbon (POC) present in the water column on Aug 26, 2002 (during the summer algal bloom) would equate to 10 mg C/m$^2$ if transported in its entirety to the sediments. The maximum value of organic carbon found in the “varved” section of the freeze core was 6.8 mg/g or, at the estimated density of the sediments (0.09 g/cm$^3$), roughly equivalent to the August 26, 2002 POC pool distributed over 2 cm depth. This carbon pool, if entirely labile, would be sufficient to liberate the bulk of the Mn-solid phase in the sediments (over the same 2 cm depth) through Mn reduction.

Another potential removal mechanism for oxygen in the MZP is the oxidation of Mn to form MnO$_x$ solids. The observed removal of Mn in the upper water column between January and March 2003 would have consumed approximately 10 % of the water column D.O. inventory (assuming MnO$_2$ formation). Thus, under stratification and associated oxygen supply limitation, continued Mn-oxyhydroxide formation could be a significant factor in D.O. depletion in the hypolimnion.

4.1.4 Main Zone limnocorral experiments - implications for management.

Although the results of nutrient addition experiments to limnocorals deployed in the MZP over the summer/fall of 2002 are not presented as part of this thesis, the strategy of these manipulations will be briefly reviewed here. Two nutrient (N and P) addition regimes (medium and high additions) were tested for the induction of algal growth and subsequent sequestration of metals by the algal biomass. An excerpt of data from these limnocorals 50 days after first nutrient additions is given in Figure 4.1.1 above. This shows that effective removal of Zn, Cu and Cd was promoted by nutrient additions. Thus, this metal removal strategy may be effective in improving the water quality of the epilimnion of the MZP (and other pit lakes) although it has potentially deleterious ramifications in the MZP given the possible diagenetic impact that the transport of reduced organic carbon to the sediments could have on those deposits.

Under the well oxygenated conditions currently observed in the MZP, however, the bulk of organic carbon exported from the epilimnion would be expected to be mineralized with
oxygen as the terminal electron acceptor. But as discussed in section 4.1.3 above, under conditions of restricted oxygen renewal (stratification) additional carbon export to the hypolimnion would increase the biological oxygen demand, thus increasing the likelihood of deep water anoxia. As the surface peak in metal concentrations (Mn, Fe, Cu, Zn) in the MZP appear to be sourced largely from the Waterline pit outflow, ARD seeps and pit wall run-off, nutrient amendment of the surface waters would be a temporary and seasonal management strategy only. The current management regime of pumping all MZP discharge waters from 20 m depth coupled with the maintenance of the water level below the decant elevation currently negates the need for amendment of these surface waters. At present, nutrient additions offer no advantage over the current management scheme. Should such amendments be considered in the future, careful assessments must be made to avoid increasing hypolimnetic oxygen demand and anoxia at the lake floor as this could yield unwelcome geochemical consequences.
4.2 Waterline Pit Lake Biogeochemistry

The vast majority of all metals in the WLP were found in the “dissolved” fraction (< 0.45 μm). In this discussion element concentrations refer to “dissolved” metals, unless otherwise specified.

4.2.1 Waterline Pit Lake - Major element geochemistry.

As is typical with mine waters originating from sulphide ore bodies, sulphate is the dominant anion of the WLP and is probably derived from sulphide mineral (e.g. pyrite and pyrrhotite) oxidation. A second source of SO$_4^{2-}$ to mine waters is the saturation and subsequent dissolution of sulphate minerals, found in evaporites and oxidized ore bodies, though this is unlikely at the Equity site. For the most part, the WLP walls are non-sulphide bearing and appear to be un-oxidized. The western wall of the pit contains significant oxidized material near the pit rim and is a mottled yellow colour, evidence of sulphide mineral oxidation. Another source of sulphate to the hypolimnion of the WLP is the old underground workings. These are hydraulically connected to the WLP through two adits at ~15 to 20 m and 33 to 36 m below the lake surface. The “roof” of these underground workings collapsed several years after mine closure, exposing the voids to the surface. Unconsolidated waste rock was used to backfill the holes, increasing the hydraulic conductivity of the cover and introducing oxidized sulphide material. As will be discussed later in this section, there is evidence for drainage from these adits entering the WLP at depth.

For the sake of perspective, the total pool of sulphate present in the WLP could be supplied by the complete oxidation of between 40 to 50 m$^3$ of pure pyrite mineral. The non-conservative nature of Fe is illustrated by the fact that only around 3 m$^3$ of pure pyrite would be required to supply the WLP Fe pool. Obviously the oxidation of sulphide minerals requires contact with atmospheric or dissolved oxygen or oxidized solutes such as Fe(III). The total rate of sulphide oxidation depends on the surface area of the exposed sulphide mineral, in turn depending on the geology of the host rock and the sulphide crystal dissemination (Hutchinson and Ellison, 1992; Morin, 1990). The total sulphate pool of the WLP represents only 1.3 % of the amount of sulphate in the ARD collected from the Equity Mine site in 2002 (PDC - Equity Division, 2003). If sulphate is considered to be conservative in the WLP, ignoring the fraction exported each year through the outflow, and the rate of ARD generation in 2002 is assumed, then
only ~0.2 % of the total Equity waste rock would be required to supply the WLP sulphate since filling started in 1993. This would equate to approximately 50,000 m$^3$ of waste rock material eroding (oxidizing) at a rate of 0.01% per year. Although these figures are estimates based on further estimates, such “back of the envelope” calculations are useful to ascertain order of magnitude relationships and to identify the likely source of contaminants. It should be emphasized that the amount of sulphate exported from the WLP each year is equal to approximately 1/5 of the total sulphate pool in the WLP. As the deeper layers of the pit lake appear to be relatively stable with respect to conductivity and geochemistry, it can be assumed that the loss of sulphate from the WL outflow is balanced by inputs through sulphide oxidation within the pit catchment.

The exothermic nature of the sulphide oxidation reaction (FeS$_2$ + 3.5 O$_2$ + H$_2$O = Fe$^{2+}$ + 2H$^+$ + 2SO$_4^{2-}$; FeS$_2$ $\Delta$H$^\circ$ = -178.2; H$_2$O $\Delta$H$^\circ$ = -285.8; SO$_4^{2-}$ $\Delta$H$^\circ$ = -909.2; Fe$^{2+}$ $\Delta$H$^\circ$ = -89.1) as well as the salts released are likely to inhibit the formation of ice or freezing conditions in the immediate zone of ARD generation. The major impact of surface freezing during the winter months is the restriction of atmospheric oxygen and groundwater transport to the zone of active sulphide oxidation. The general cooling of the ground will also have the effect of favoring the products in exothermic sulphide oxidation (Atkins, 1990).

The volume of the visible layer of oxidized sulphide material on the west wall of the WLP appears to be on the same order as the waste rock required as a source of sulphate calculated as above (see section 2.5.1.9). The underground workings, connected by two adits to the WLP hypolimnion, could be a further source of sulphate and other products of sulphide oxidation. Calculations using the average (three stations) sulphate generation rate from the Main Zone Pit walls (Morin, 1990) of 11 mg/m$^2$/day indicate that direct ARD generation from the WLP walls are likely to have only a very minor impact on the sulphate loading to the WLP. These calculations suggest that <1 % of the sulphate pool of the WLP can be attributed to direct oxidation and flushing of the WLP walls (rock face).

Unlike the Main Zone pit lake, the SO$_4^{2-}$ and Ca$^{2+}$ concentrations in the WLP do not appear to be controlled by the solubility of gypsum (epilimnion S.I. = -0.69, hypolimnion S.I. = -0.21). Titration using the PHREEQC speciation software indicates that concentrations of both calcium and sulphate are required to be 40 % greater before gypsum precipitates. This control is not pH, alkalinity or temperature sensitive within the normal parameters of these pit waters. Although carbonate was not specifically measured, the alkalinity of the WLP waters was quite high (1.5 to 3.6 meq/L), and increased with depth. At the WLP pH of around 7.5, speciation
calculations suggest that the alkalinity is predominantly bicarbonate supported. If bicarbonate is assumed to be the major alkalinity source, calcite is over saturated (S.I. = 0.46 to 0.48) for the WLP waters. Another source of alkalinity is NH$_3$ though at pH 7.5, ammonia is predicted to be converted mostly to NH$_4^+$. This reaction may be partly responsible for maintaining the circum neutral pH of the pit waters though the alkalinity potential of NH$_3$ is consumed in raising the pH, thus the product species (NH$_4^+$) does not add to the standing alkalinity of the pit waters. The biologically mediated mineralization of organic matter (OM) is likely to produce both NH$_3$ and bicarbonate through the reaction (4.2.1). The products of (4.2.1) are ammonia and carbon dioxide though these are subject to further protonation / oxidation to become ammonium and carbonate / bicarbonate.

\[
\begin{align*}
\text{Organic Matter} & : 424\text{FeOOH} + (\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 848\text{H}^+ \\
& \rightarrow 424\text{Fe}^{2+} + 106\text{CO}_2 + 16\text{NH}_3 + \text{H}_3\text{PO}_4 + 742\text{H}_2\text{O}
\end{align*}
\]  

(Libes, 1992)

In the WLP oxygen and nitrate are rapidly depleted below the epilimnion, allowing for the reduction of other oxidants such as Fe-oxyhydroxides by OM. Fe-oxyhydroxides are a common electron acceptor in anoxic sediments (Cummings et al., 2000; Davidson, 1992; Roden and Wetzel, 2003) and are likely to be particularly important in the WLP where they form a major fraction of the sediments. After reaction (Eq. 4.2.1), the further hydration of CO$_2$ to form bicarbonate yields a proton while the oxidation of ammonia to ammonium consumes a proton. Under oxic conditions and given the carbon to nitrogen ratio in organic matter, 6.6 times more protons would be produced than consumed during mineralization, assuming total conversion to bicarbonate and ammonium (respectively). Given the consumption of 8 moles of protons per mole of CO$_2$ produced during Fe-oxyhydroxide reduction by organic matter (Eq. 4.2.1), a net consumption of 1.4 moles of protons is expected, thus increasing the pH of the system.

The circum neutral pH of the WLP was at first somewhat perplexing given the obvious evidence of ARD on the pit walls and the lack of significant neutralizing capacity in the local geology (Equity Silver Mines Ltd, 1991). It is possible that the pH of the WLP is maintained by anoxic OM mineralization reactions such as Fe-oxyhydroxide and sulphate reduction. Alkalinity may also be produced through the reaction of water and dissolved carbonic acid with aluminosilicates in the pit walls and in contact with groundwater (Stumm, 1992). Several of the major rock forming minerals of the Goosley geological sequence, in which the Equity mine site sits, are aluminosilicate minerals known to generate bicarbonate alkalinity upon weathering. One
of these rock types, andesite, is composed primarily of plagioclase and biotite type minerals. The weathering reactions and the generation of bicarbonate alkalinity are represented in equations 4.2.2 (general aluminosilicates) (Das and Kaur, 2001) and 4.2.3 (biotite) (Stumm and Morgan, 1996).

\[
\text{Na, K, Mg, Ca (silicate)} + H_2CO_3 \rightarrow H_4SiO_4 + HCO_3^- + Na + K, Mg, Ca - \text{solid - products (general silicate mineral weathering by carbonic acids). (4.2.2)}
\]

\[
KMg_3AlSi_3O_{10}(OH)(s) + 7H_2CO_3 + \frac{1}{2}H_2O \Rightarrow K^+ + 3Mg^{2+} + 7HCO_3^- + 2H_4SiO_4 + \frac{1}{2}Al_2Si_2O_5(OH)_4(s) \quad (4.2.3)
\]

The introduction of net acid neutralizing rock containing these minerals was responsible for an increase in the pH of the ground waters of the backfilled Southern Tail pit on the same property (Morin, 1990) and may be responsible for the generally high alkalinity of the natural groundwater on the site (PDC - Equity Division, 2003)(Mike Aziz, pers. comm. March 04).

For Na and Mg, the rate of input through weathering of local rocks such as aluminosilicates (e.g. biotite for Na) and dolomite (for Mg) and discharge (e.g. through the outflow to the Main Zone pit) are likely to be the controlling factors. Both Na and Mg are generally conservative (Libes, 1992) and no solid phase precipitates were calculated to be close to saturation for either of these elements. The concentration of these elements will increase in the pit waters until a balance is achieved between inputs and outputs. Na and Mg are likely to have only a minor role in the geochemistry of the WLP, mainly impacting the saturation of state of minerals such as calcite and gypsum through competitive equilibrium with major anions such as carbonate and sulphate. The ARD waters collected at the Equity site do contain considerable Mg and Ca though low Na (PDC - Equity Division, 2003). This may indicate that the ARD waters are dissolving the products of previous carbonic acid weathering of the natural geological units such as calcite and dolomite or mixed Ca-Mg carbonate minerals. Na does not produce a relatively insoluble solid phase with carbonate.

Major elements were only measured on one date for the WLP and so it is unknown if these conservative elements are at a steady state or are accumulating in the hypolimnion. Although natural lakes tend to have a wide range of solute concentrations depending on the nature of their catchment and inputs from pollution, a survey of Australian lakes has found that Na tends to be the dominant cation and bicarbonate and Cl, followed by sulphate, tend to be the
dominant anions (Hart and McKelvie, 1986). A review of other lake chemistry literature suggests that the WLP has highly elevated calcium and sulphate contents (by one to three orders of magnitude) compared to most natural lakes but is within normal ranges for K and Mg (Berner and Berner, 1987; Burgis and Moris, 1987).

Ca, Mg, Na and $\text{SO}_4$ increase with depth in a near linear fashion throughout the hypolimnion, with similar slopes, despite the presence of several density stratifications (Figure 4.2.1). The strong correlation of sulphate with conductivity, as well as these other elements (Ca, Mg and Na), would suggest that the concentration of these other elements also follows the conductivity profile. Unfortunately only three analyses exist for the major elements in the WLP on the same date (Oct 3, 01) and so extrapolation of the data is risky. Nevertheless, if it is assumed that the input ratios among these four elements are constant, then Na and possibly Mg were in slight excess at 30 m on that date (Oct 3, 01). This may be evidence of sulphate removal at depth through either sulphate mineral precipitation (e.g. Jarosite) or sulphate reduction and sulphide mineral precipitation. Sulphate, being the major anion, is also predominantly responsible for the density stratification and stability of the WLP. Even under conditions of sulphate reduction at depth a decrease in sulphate would not be seen in the profile, as the removal of sulphate (sulphide mineral precipitation) would cause the WLP water to become buoyant with respect to that overlying it and cause convective mixing to occur. In waters where the density structure is dominated by sulphate this mechanism would obscure the sulphate removal signal.

The maximum of silicate in the epilimnion of the WLP suggests that a removal mechanism for silicate is present in the hypolimnion. The major freshwater tributary to the epilimnion is extremely low in dissolved silicate (<0.3 $\mu$Mol) and perennial seeps along the east wall of the pit lake contained 63 $\mu$Mol dissolved silicate, a third of the concentration found in the epilimnion. The weathering of silicate minerals is enhanced under acidic conditions and the silicate in the WLP epilimnion may be supplied by a relatively small volume of ARD waters present as surface run-off during periods of precipitation. Equilibrium speciation calculations indicate that none of the major inorganic aqueous species of Si are redox sensitive and as such no change in valence state and possible physical / adsorptive properties were predicted across the chemocline. The only Si mineral phase at or above saturation was $\text{ZnSiO}_3$, though this was also not redox sensitive within the range of $\text{pE}$ possible in the WLP (15 to --6).
4.2.2 Accidental sludge discharge – 28 July 02.

On or about the 28th of July 2002, an open channel carrying ARD treatment sludge to the Main Zone pit broke its banks and discharged sludge into the Waterline Pit lake. This discharge was running for between 1 to 2 days and entered the pit at the surface of the southern end. Unlike the Main Zone pit lake, sludge is not normally discharged into the Waterline pit. The chemistry sampling and CTD profiles taken before and after the accidental sludge discharge were collected at the northern end of the pit lake, some 400 m from the sludge entry point. A comparison between the dissolved metal and CTD profiles on June 21, 02 (pre-spill) and Aug 7, 02 (post-spill) is given in Figure 3.2.11, and the bulk composition of the ARD sludge is given in section 4.1.1.

It is apparent from the chemistry and CTD sampling that the sludge discharge impacted both the epilimnion and upper hypolimnion of the WLP through the addition of turbidity, heat and various metals. The sludge is primarily composed of metal oxyhydroxide and sulphate mineral phases and is expected to be warm and oxic in comparison to the WLP hypolimnetic waters. An attempt was made to correlate the measured metal concentrations and ratios to Fe in the sludge to those found in the sediment traps and water column (plume at 14 to 17 m) on Aug 7, 02, one week after the sludge deposition. These calculations did not provide any rigorous correlation between the two although the order of magnitude of metal ratios to Fe were similar in the sludge and sediment trap samples for many metals (Co, Cu, Zn, Sb).

There is some ambiguity about the impacts of the sludge discharge in the WLP as the depth of the apparent “plume” of metals (12 to 16 m) is also just above Layer 3 where intrusions of “groundwater” are also seen. There is some evidence in the Optical Backscatter (OBS) profiles taken the week before the sludge discharge that an intrusion may have already been present at the same depth. Careful consideration of the CTD profiles and the chemistry data of the period between March 25, 02 and Aug 7, 02 indicates that the “plume” of metals present at 15 m depth on Aug 7, 02 was probably caused by the input of sludge whereas the general increase in Cd and Zn concentrations in the same layer (Layer 2) were most likely caused by an intrusion of ARD impacted waters and an increased pe during the early summer.

4.2.3 Redox calculations.
It is obvious from the lack of detectable NO$_3$ within 1 m below the chemocline that the pe drops to below +7.15, the pe$_w$ of natural, neutral waters in equilibrium with atmospheric carbon dioxide and the NO$_3$ / NO$_2$ redox couple (Figure 4.2.6) (Stumm and Morgan, 1996). The NO$_3^-$ /NH$_4^+$ redox couple was used to calculate the pe at 35 m on Jan 21, 02, the only date on which nitrate was detected in the hypolimnion (PHREEQC). The pe at equilibrium for 0.02 mg/l nitrate and 1.9 mg/l ammonium is 6.04. This is well above the precipitation point for the majority of the iron oxide solids and the jarosite suite of minerals (Figure 4.2.5). The pe returned by the nitrite / ammonium redox couple at the peak values of nitrite found in the WLP at 35 m (5 ppb, June 21, 02) is 5.85. Nitrate would have been well below detection limit (picomolar) at this depth. Only slightly lower pe values (5.7 to 5.8) are returned by the range of nitrite values found in the hypolimnion during the period of study (for those above the detection limit of 0.005 µmol).

These predictions follow the general pe values that are returned for a simplified N-O-S-H system as represented in Figure 4.2.6 (Hydra / Medusa software, (Puigdomenech, 2003)). There is some doubt about the nitrate and nitrite values as indicators of redox conditions, however, as nitrite was detected in the limnocorral experiments in the presence of free dissolved sulphides where the pe would be much lower than the stability field for nitrite.

The large concentration of dissolved Fe in the hypolimnion of the WLP suggests that the pe at depth, particularly at the sediment-water interface is at or below that of Fe-oxyhydroxide reduction (pe$_w$ = +2)(Stumm and Morgan, 1996). Calculations using PHREEQC indicate that at 35 m depth (June 13, 03) dissolved Fe would become prominent in the water column below a pe of 4, above which Fe-oxyhydroxides and jarosite dominate. The generation and transport of dissolved Fe in ARD is usually as Fe(III) in the highly oxidizing, low pH environment of sulphide oxidation. The circum neutral pH of the WLP would support the presence of the reduced Fe(II) dissolved species; Fe(III) would precipitate out as an oxide in this environment. The most likely source of Fe(II) under neutral pH conditions is through reduction of Fe(III) to Fe(II) by bacterial Fe-oxyhydroxide reduction (Cummings et al., 2000).

Sediment trap data, XRD analysis and visual inspection of the WLP sediments show that a considerable pool of Fe-oxyhydroxides precipitates to the sediments and is stable on at least a multi-month basis. The calculated Fe flux to sediment traps at 30 m depth was considerably lower for traps left for 10 months as opposed to traps left for two weeks in mid-august 2002. As for manganese, the lower Fe flux rate could be attributed to loss of Fe-oxyhydroxides from the longer-term sediment traps through reductive dissolution. However, if the Fe flux is assumed to cease during the winter months, then the flux rates obtained in traps left for 8 days and those left
for 304 days were remarkably similar (within 20%). This suggests that precipitated Fe-oxyhydroxides may in fact be largely stable on an annual basis.

The next major oxidant (electron acceptor) after Fe-oxyhydroxides in the WLP is almost certainly sulphate, although arsenate could also play a role. The product of sulphate reduction, hydrogen sulphide, was not detected in the water column of the WLP, but it is possible that the rate of sulphate reduction is slow enough that all hydrogen sulphide produced is consumed in the formation of highly insoluble metal sulphides (e.g. CdS and ZnS) before free sulphide can be detected. Bacterial reduction of arsenate coupled to the oxidation of organic matter has been shown to be important in a hypersaline lake with high sulphate and arsenic contents (Oremland et al., 2000). Arsenate reduction occurs before the reduction of sulphate and may be an important oxidant in the WLP. The As(V) / As(III) redox couple would control a $p_e$ range around 0 to -1 as calculated for 35 m waters (June 03). This redox range is slightly below that of FeOOH reduction (~+1) (Stumm and Morgan, 1996). More As(V) might be present in the hypolimnion than suggested by thermodynamic calculations due to the oxidation of As(III) on the surface of Fe-oxyhydroxide solids (Belzile et al., 2001).

The evidence for the possible $p_e$ of the WLP hypolimnion is mixed. It is obvious that the $p_e$ is above that required for the reduction of U(VI) to U(IV), upon which the solid uraninite is precipitated. PHREEQC calculations indicate that a $p_e$ of close to -1 is required for U reduction and uraninite saturation (35 m, June 03). The Waterline limnocorral experiments did show that U was not immediately reduced (removed) even where $H_2S$ was detected ($p_e < 3$). This may reflect inadequacies in the thermodynamic constants available for U geochemistry. Indeed, many U-sulphate and U-sulphide mineral and aqueous species are known to exist (Wanner and Forest, 1992) but are not present in the commonly available speciation databases (phreeqc, wateq4f, minteq). Furthermore, kinetic considerations are also not included in the thermodynamic modeling.

The relative solubilities of the transition metal sulphide minerals provide a further tool for the determination of the redox conditions in reducing waters. The removal of metals in the hypolimnion of the WLP below 25 m does not follow that of the sulphide mineral solubility sequence ($CuS < CdS < ZnS < FeS_2 < As_2S_3 < CoS < NiS$) (Huerta-Diaz et al., 1997; Sillen and Maretll, 1964) past that of Cd, further suggesting that significant sulphate reduction may not be occurring in the deep hypolimnion of the WLP. Cu and Cd are effectively removed to the sediments in the WLP possibly indicating that trace levels of sulphate reduction may be occurring. Cu and Cd are also known to be adsorbed to Fe-oxyhydroxides and their removal
from the water column could be explained by this mechanism (Buerge-Weirich et al., 2002; Tessier et al., 1996). The presence of Fe-oxyhydroxides in the WLP sediments would be thermodynamically unfavorable under sulphide generation – the pe of free Fe formation (dissolved Fe) is calculated to be close to 4 (Figure 4.2.5) while free sulphide (H$_2$S) is calculated to appear in the water column at a pe of -4.5. Despite this, dissolved sulphide and Fe-oxyhydroxides do coexist under some natural circumstances (Motelica-Heino et al., 2003).

Various manipulations of the pe and S(VI)/S(-II) redox couple were tested in PHREEQC in order to reproduce the degrees of metal removal at 35 m in the WLP and obtain an equilibrium H$_2$S concentration. These calculations indicate that, despite the large Fe concentrations, that CdS and ZnS could be precipitated with up to 100 µMol of dissolved S(-II) in the water column, before FeS$_2$ would be precipitated. While dissolved Cd concentrations reached a minimum of 0.02 ppb in the deep hypolimnion, we do not see removal of dissolved Zn below 329 ppb from the water column in the WLP, indicating that the rate of sulphide production could be below that of complete Zn removal (balanced against Zn inputs). The much greater concentrations of dissolved Zn than dissolved Cd in the WLP hypolimnion decreases the saturation point of ZnS relative to CdS over that of their equimolar K$_{sp}$ values. While CdS will still precipitate before ZnS, the pe “window” between the two species is very small (~0.1 pe unit).

The removal of Sb from the water column below the chemocline may also be an indication of the redox conditions of the water column. The mineral SbO$_3$(s) is predicted to precipitate at a pe from 1 to -0.5 in the WLP (35 m depth, June 13, 02). Below a pe of -0.5 SbO$_3$(s) again becomes under-saturated due to the formation of the soluble Sb complexes Sb(OH)$_3$ and HSbO$_2$. To further complicate identification of controls on Sb concentrations below the chemocline, antimony is known to readily adsorb to Fe-oxyhydroxides (Belzile et al., 2001; Filella et al., 2002; Thanabalasingam and Pickering, 1990). This adsorption affinity would be lessened at the neutral pH of the WLP however due to the anionic speciation of Sb in oxic waters.

The profile of dissolved Mo largely follows that of conductivity through the WLP water column with little indication of scavenging in the epilimnion or at the chemocline. Mo is known to be subject to a geochemical “switch-point” where, at a pe of close to -2, the typical aqueous speciation changes from a largely conservative oxy-anion to a thiomolybdate anion that is preferentially scavenged (Erickson and Helz, 2000). As Mo does not appear to follow a scavenged profile in the WLP is can be assumed that the pe is above -2 or kinetic / competition factors are involved.
In summary, the evidence allows two possible $p_e$ regimes to be derived for the WLP hypolimnion. If the removal of Cu, Cd, and Sb from the water column is controlled by adsorption to Fe-oxyhydroxides then a sensible $p_e$ range would be between 6 and 2. If these metal distributions are instead controlled by the precipitation of sulphide minerals then the $p_e$ is likely to be close to −2, where CdS can precipitate without complete ZnS precipitation. The most probable $p_e$ regime in the deep hypolimnion of the WLP is of low rates of sulphate reduction with consequent CdS precipitation in the water column ($p_e \sim -2$) with a higher sediment $p_e$ maintained by Fe-oxyhydroxide reduction ($p_e \sim 4$). The presence of Fe-oxyhydroxides in the sediments would impact the $p_e$ of the sediments through the oxidation of more reduced species at the surface of this phase (Belzile et al., 2001; de Vitre et al., 1991; Fredrickson et al., 2000; Yashida et al., 2002). A small increase in the dissolved Sb concentrations near the sediments supports the oxidation of Sb sulphate precipitates at the surface of Fe-oxyhydroxides. Sb was first precipitated in the limnocorral experiments after Cd though at the same time as Zn (Figures B.23 and B.24), further supporting the control of this element by sulphide precipitation.

The apparent conundrum of both sulphate reduction and the presence of Fe-oxyhydroxides in the WLP can be explained by the kinetic and spatial separation of the two $p_e$ regimes. Fe-oxyhydroxides are supplied from oxidation of Fe(II) at the epilimnion / hypolimnion boundary and delivered to the sediments, passing through the lower $p_e$ of the deep water column. The residence time of the Fe-oxyhydroxides in the deep water column, as they settle towards the sediments, may not be long enough for their reduction and a subsequent raising of the water column $p_e$. The loss of surface adsorbed species from the Fe-oxyhydroxides as they pass into greater reducing conditions is well documented and may explain the increasing concentrations of many metals in the deep water column including Mn, As, Co and Ni. Both Fe-oxyhydroxide reduction and sulphate reduction can occur in the same location due to the difficulty in accessing the surface of the mildly hydrophobic Fe-oxyhydroxide surfaces in electron transfer (Burgos et al., 2003; Motelica-Heino et al., 2003).

4.2.4 Controls and processes in the epilimnion.

The major physical influences on the biogeochemistry of the WLP epilimnion are density differences between lake waters and inflow waters, wind stress at the surface, solar heating, the influx of atmospheric oxygen and the outflow of water from the southern end of the pit into the Main Zone pit lake. Although the equation of state for the WLP waters was not completed in
time for inclusion in this thesis, a rough estimate of the density of the water can be calculated from the conductivity and the temperature of the water. From these calculations the estimated difference in density between the hypolimnion (Layer 2) and the epilimnion (March 03) was 50 mg/l with the density of the epilimnion waters at 1000.465 g/l. This density difference was sufficient to maintain a distinct pycnocline between the epilimnion and Layer 2 over the entire two-year study period.

Despite a tripling of the depth of the epilimnion over an annual cycle, the changes in the conductivity of this layer were very consistent between years. The conductivity in June for all three years varied by less than 4% (1018 μS/cm, s.d. 20, n = 3), this is remarkable as the inter-annual variation was as much as 18%. The consistency of conductivity values in the epilimnion over a seasonal basis is perplexing if the major influence on mixing between the epilimnion and Layer 2 is considered to be wind driven mixing. Winds are typically variable in intensity and duration between seasons and years and would be expected to increase the inter-annual variability in mixing in the epilimnion. It is difficult to match the deepening of the chemocline with the influx of intrusive waters from deeper in the water column (Adit 1) to the epilimnion as the increase in conductivity in the epilimnion over the summer period could also be a function of the mixing up of Layer 2 waters and the input of fresh waters from the Berzhelius Creek overflow. The next two sections (4.2.5 and 4.2.6) discuss the likely presence of an influx of water to Layers 2 and 3 from a submerged adit (Adit 1) connected to old underground mine workings. This intrusion of waters from below the epilimnion is crucial in understanding the volume and chemistry of the epilimnion on a seasonal basis.

The behavior of metals in the epilimnion, relative to that in the hypolimnion, was largely determined by the oxic/anoxic status of the water column and the concentration of major anions. The most notable change between the two limnia occurred for dissolved Fe and As. Both of these metals were absent or of very low concentration in the epilimnion for the entire period of the study. As the pycnocline is eroded in the late summer / fall high concentrations of dissolved Fe and As are mixed up from the epilimnion and are quickly partitioned to the solid phase through the oxidation of Fe and the adsorption of As to the Fe-oxyhydroxides (Davidson, 1985; Dixit and Hering, 2003; Le Guern et al., 2003; Stumm and Morgan, 1996). If the profile of conductivity changes over the pycnocline was taken as “conservative” mixing between the epilimnion and Layer 2 then Figure 4.2.3 displays the relative loss of oxygen and Fe from the water column over and above that expected from mixing. For these calculations Fe was sourced solely from the hypolimnion at the first depth of complete oxygen depletion and oxygen from 0 m depth, hence
values at 0 m and 10 m are conservative by definition. Fig. 4.2.3 shows that the depth of greatest loss of both dissolved oxygen and dissolved Fe relative to conductivity is at the pycnocline. It is probable that this is the zone of most active dissolved Fe oxidation and Fe-oxyhydroxide formation. Fe-oxyhydroxides are strong adsorbants for many metals including As, Cd, Cu and, to a lesser extent, Zn, Ni, Sb, Co, U and Mn (Belzile et al., 2001; Blake et al., 1998; Buerge-Weirich et al., 2002; Carlson et al., 2002; Dong et al., 2000; Ferris et al., 1998; Swelund and Webster, 2000; Thanabalasingam and Pickering, 1990). The partitioning of some metals to a small particulate fraction during the late fall occurs at the same time as increased particulate Fe in the epilimnion. This effect was most notable for As, Cd, Zn, Sb and to some extent Ni. This time period also coincided with a small algal bloom in the epilimnion and partitioning of metals to organic matter cannot be ruled out, particularly for Zn and Cd, which also show a strong affinity for adsorption to this phase (Reynolds and Hamilton-Taylor, 1992; Yee et al., 2004).

As with Fe, a comparison between the change in conductivity over the pycnocline and the relative change in dissolved metal concentration was conducted for the other metals measured. There was no rigorous relationship between the two but rather several metals followed the general trend of conductivity changes in the epilimnion. Mn, Co and Ni follow a similar response to conductivity changes in the epilimnion though are less conservative. The change in metal concentration across the pycnocline for Mn, Co and Ni is approximately double that of conductivity with Co showing the greatest changes of the three. The Waterline Pit lake limnocorral experiments appeared to show Mn-oxyhydroxides as an important phase in controlling the distribution of several metals including Co, Mo, Ba and U (Section 4.3, page 171). This may also be the case in the pit lake itself. Rhodochrosite is calculated to be slightly under-saturated in the epilimnion though over-saturated in the rest of the water column. The Mn oxyhydroxides birnessite and manganite are both calculated to be over-saturated in the epilimnion. The slow kinetics of Mn oxidation appear to limit the precipitation of these solid phases in the WLP (Chapnick et al., 1982; Stumm and Morgan, 1996). The flux of Mn to sediment traps at 3 m depth over the fall/winter of 2002-03 accounted for 104% of the Mn in the water column above 3 m. The fact that dissolved Mn concentrations declined by only 25% over this time period can be explained by dissolved Mn being mixed up into the epilimnion from the hypolimnion during the chemocline deepening of the late fall, coupled with slow oxidation of Mn-oxides in the near surface waters.

The change in dissolved Co and Ni concentrations across the chemocline (Figure 4.2.10) was typically of the same order as that for Mn with Ni being slightly more conservative than Co.
relative to conductivity. The limnocorral experiments as well as the literature indicate that Co has a greater affinity for Mn-oxyhydroxides than Ni (Haack and Warren, 2003; Kay, 2001; Tonkin et al., 2004). Ni and Co both have a sparingly soluble oxide form when oxidized from the (II) to (III) redox state (Stone and Morgan, 1987). The reduced concentrations of Ni and Co, relative to conductivity, in the epilimnion thus may be due to the precipitation of their oxide forms.

While dissolved Mo and dissolved Zn typically "decreased" in concentration across the chemocline to a greater degree than conductivity (by around 25%), this relationship also varied considerably over the two-year study (Figure 4.2.11). For the winter of 2002 Zn was conservative with conductivity across the chemocline while in June, 02 both Mo and Zn were in excess in the epilimnion relative to conductivity changes. While scavenging of Mo from the water column by Fe-oxyhydroxides has been postulated as an important control on Mo cycling in other lakes (Achterberg et al., 1997), this does not appear to be the case for the WLP. The ratio of Fe:Mo in the sediment traps was considerably greater than that in the water column indicating that little Mo is cycled with Fe to the sediments.

The most conservative element relative to conductivity was U suggesting that there is a control on U concentrations that is independent of small changes in the major ion content or redox state of the water column. This is unlikely to be adsorption to Fe and Mn-oxyhydroxides, because although known for U, the U concentration across the chemocline in Oct 02 changed little, despite there being the highest concentration of particulate Fe in the epilimnion. Thus, the ultimate control on the U distribution in the pit is unknown.

The profiles of Cu, Cd and Sb differ markedly to those of other metals in that they indicate significant depletion from the water column below the chemocline. These elements also displayed a detectable particulate fraction in both the epilimnion and hypolimnion at different times. There are two possibilities for the former: (1) the elements are supplied at the surface through run-off from the pit walls, seeps or Berzhelius Creek; and/or (2) they are predominantly supplied by the influx of groundwater from Adit 1 and enter the epilimnion as the influx waters become progressively less dense over the summer. The metal concentrations of Berzhelius Creek are considerably lower than those in the epilimnion of the WLP for most metals and are not likely to be a source of Cd. Sb and Cu were detected at elevated concentrations in Berzhelius Creek, which may have been a prominent source of these elements to the WLP epilimnion. In contrast, the influx of Cd to the top of Layer 2 in June 02 suggests that option (2) above may operate for this metal. The Cd concentration peaks at the chemocline, which can be attributed to
adsorption onto oxyhydroxides in the epilimnion, desorption at the chemocline as the pH decreases into Layer 2, and precipitation at depth, possibly as CdS. The peak at 8 m depth persisted from January through June, 2002, although on June 21, 02 a second peak in dissolved Cd appeared at 4 m coincident with a general increase in Cd content throughout the epilimnion and Layer 2. It is speculated that these changes could have been brought about by the spreading of Cd-rich waters from Adit 1.

The barium distribution across the chemocline changes least of all the elements considered. The water column of the WLP is supersaturated throughout with respect to barite (BaSO₄) and this rapidly forming phase probably controls the concentration of Ba in the epilimnion.

4.2.5 Controls and processes in Layer 2, the upper hypolimnion.

The pycnocline (top of Layer 2) rose at a rate of 0.01 m per day between January and March, 2002, reaching its shallowest level in early summer. The rate of rise was remarkably similar in both winter sampling sessions indicating that a reasonably constant influx of water occurs in Layer 2 over the winter-spring period. The total influx of water into Layer 2 is estimated to have been 300 m³/day and 360 m³/day for winter 02 and 03 respectively. This equates to an inflow rate of 3.5 to 4.2 L/sec., of the same order as the lowest flow rates recorded from the WLP overflow (5 L/sec.) and around 20 % of the outflow recorded during the summer of 2002 (~20 L/sec). The groundwater flow rate is likely to be at its lowest in winter due to the frozen ground surface, snow / ice cover, increased pore vacuum in the soils and the lack of significant recharge. The thermocline in most natural lakes deepens right up to the point of freeze-over in late fall (Roger Pieters, pers. com., March 15, 04), and this is also true of WLP. The thermocline on Jan 21, 02 was deeper than in the previous October. Despite these variations, the rate of subsurface inflow may well be constant throughout most of the year, with the deepening of the epilimnion over the late summer/early fall masking the inflow signature.

The rate of pycnocline deepening over the summer and fall of 2002 was remarkably constant at 0.066 m/day ($r^2 = 0.998$, $n = 4$) between Aug 7 and Oct 9, 02, and can be attributed to wind-generated mixing. Alternatively, if the hydraulic head above the adits in the WLP (Figures 4.2.8 and 4.2.9) is greater than the density difference between the Layer 2 waters and the intruding waters then the less dense intrusive waters may enter the pit at the mouth of the adits and “float” up the pit wall to reach neutral buoyancy. If the neutral buoyancy point is in the...
epilimnion then the top of Layer 2 may become eroded into the epilimnion as a function of the
flow rate of the intrusion. The broadening of the pycnocline observed in June 21, 02 may be a
function of this process.

Close inspection of the conductivity profiles indicates that the evolution of Layer 2 is
closely aligned to the intrusions in Layer 3. As is discussed in the next section (4.2.6), it appears
likely that ARD impacted groundwaters enter the WLP at depth from two adits connected to old
underground workings. As the freshet progresses the density of the inflow waters decreases,
most probably as the ARD impacted waters in the old mine workings are mixed with
progressively more “natural” groundwater. This may induce the flow of lighter intrusive waters
over the top of denser ARD waters into the pit at the bottom of Layer 2. The bottom of Layer 2
matches the top of adit 1 (15 m) well (Figure 4.2.9) and the conductivity profiles show that
conductivity in this layer increases from 15 m upwards over the early summer period (Figure
4.2.11). The volume of Layer 2 increased by almost a third between March 21, 02 and June 21,
02 without a significant change in conductivity. This would suggest that a large volume of water
entered this layer that was of similar dissolved ion content (probably primarily sulphate). If,
during the winter period, the waters at the top of Adit 1 (bottom of Layer 2) were at the same
density as those in the pit lake at this depth (as would be expected) then these waters may have
been flushed from the adit by increased hydraulic head above them during the spring freshet.
This would have increased the volume of Layer 2 with water of the same basic density / salt
content.

It appears that as the summer progressed that the influx waters became increasingly
“saline” or conductive and gradually increased the conductivity of the whole of Layer 2 over the
summer/fall of 2002 (Figure 4.2.11). This would be consistent with a reduction in the percentage
of “natural” groundwater in the influx as the groundwater head reduced over the summer. A
complication in this hypothesis is that the rate of influx of this secondary “higher conductivity”
plume between June 21, and July 23, 02 was of a very similar rate to that of the influx of waters
over the previous freshet period (March 21, to June 21, 02) of 6.3 and 5.8 cm/day respectively
(cm rise in the chemocline). This secondary plume may in fact be representative of flushing of
sulphate weathering products from the vadose zone above the underground workings.
Unfortunately there was no chemical sampling conducted between June 21, 02 and the accidental
sludge discharge to the WLP on July 28, 02 so the plume of increased metal concentrations
present on the Aug 1, 02 sampling date cannot be conclusively attributed to either this change in
influx waters or the sludge discharge.
Coincident with these hydrographic variations, the concentrations of most metals within Layer 2 changed between March and June 2002. Fe, As and to a smaller extent Mn all decreased in concentration while Cd and Zn increased markedly. The response of these metals to the intrusion of waters to Layer 2 over this time period is discussed below.

Iron - The 17 % (3600 ppb) decrease in Fe in Layer 2 between March and June 02, could be in response to an oxygenation event (possibly during the freshet or ice-breakup) or dilution, or both. Given the 32 % increase in the volume of Layer 2 over this time period, attributing the decline in Fe content to dilution would require that inflow waters contained 53 % less Fe than that in Layer 2 in March 02.

The presence of low but detectable levels of dissolved oxygen between the chemocline and 10 m depth on June 21, 02 indicates that the intrusive waters were either oxic or mixed with oxic epilimnion waters. Figure 4.2.3 shows the calculation of oxygen and Fe deficits in the top 10 m of the water column assuming conservative mixing (and using conductivity as the conservative parameter) between an anoxic hypolimnion and Fe-free epilimnion. The profile for 21 June 02 shows that the calculated deficit of Fe in the water column approximates the dissolved oxygen excess. What this figure demonstrates is that as the chemocline progressively shallows during the spring, there is a source of oxygen and a removal and/or dilution mechanism for Fe between 4 m to 10 m depth. An increase in turbidity from the chemocline to 15 m depth over the same time period may be attributed to the precipitation of Fe-oxyhydroxides, which complicates determination of the effect of the accidental sludge discharge to the WLP on July 28, 2002. The increase in metals at 14 m to 17 m (August 7, 2002) may reflect settling of Fe-oxyhydroxide particulates formed during the spring chemocline shallowing or the accidental sludge discharge event.

Arsenic and to some extent Mn also decreased in conjunction with Fe at this time in the 4 to 10 m depth interval. Arsenic may have adsorbed to Fe-oxyhydroxides but Mn is less likely to have been removed through this mechanism. Without knowing the concentrations in the intrusive waters to Layer 2, it is difficult to separate dilution from precipitation effects on the concentration of metals during the spring 2002 period.

Cadmium - Like Zn, Cd concentrations increased over the whole of Layer 2 over the freshet period of 2002, most prominently in the upper half. Cd occurred almost entirely in the dissolved fraction at this time and is likely to have been sourced from the intrusive waters from Adit 1. The increase in Cd concentrations from bottom to top in Layer 2 on June 21, 02 occurred despite the near uniform conductivity profile (Figure 4.2.11). This distribution points to a
removal mechanism for Cd operating in the hypolimnion of the WLP despite the apparent desorption of Cd at the chemocline, described above. The distribution of Cd and the pattern of particulate fractionation between March and June 2002 suggests that Cd “rich” waters from Adit 1 intruded primarily into the upper half of Layer 2 and were subject to a decreased pe and possible removal via CdS precipitation once in situ. The concentration of dissolved Cd in Layer 2 gradually decreased over the summer of 2002, implying ongoing net removal.

**Barium** - As noted earlier, calculations performed using PHREEQC show that Ba concentrations are near saturation with respect to barite throughout the water column, and are supersaturated below the chemocline at 15 m depth. The computed saturation indices should be treated with some caution though as they represent thermodynamic equilibrium amongst all competing species, including jarosite and gypsum. Barite precipitation kinetics in natural waters are fast, suggesting that the calculated saturation indices may in fact underestimate the extent of control of this phase on the dissolved barium distribution.

**Zinc** - Like Cd, dissolved Zn concentrations increased by 35 to 120 % throughout Layer 2 between March 21, 2002 and June 21, 2002, but the distributions of the two metals during this period are not closely correlated. This would suggest that either the input waters were not consistent in relative concentrations of Cd and Zn over time as the inferred intrusion progressed or that the metals behaved differently in situ. The concentrations of dissolved Zn do not decline to the same degree as those for Zn over the summer of 2002 suggesting that, relative to the starting concentrations of these elements, unlike Cd, Zn is not controlled by fractionation to the particulate phase.

4.2.6 Removal of metals from Layer 3 (17 m to 20.5 m depth).

The most obvious feature of the hypolimnion of the WLP is the marked “removal” of several metals in Layer 3 (17 m to 20.5 m). To shed more detailed light on this, the most comprehensive sampling session during the study was conducted at the end of the project on June 13, 03. The resulting data were used for intensive equilibrium and mass balance modeling of both in-situ authigenesis (manipulation of pe / alkalinity / pH regime) as well as to explore the possible mixing of groundwater with WLP waters at the top of Layer 4. The conceptual model that best matches the field data and modeling results invokes the intrusion of waters from the bottom portion of Adit 1, particularly during the freshet. As discussed below these waters appear to be lower in metal concentration and possibly more alkaline than those of the bulk pit lake.
hypolimnion. Sulphate-rich ARD waters generated within the upper reaches of Adit 1 may sink to the bottom of the adit and flow out and down the pit wall as a density current. Evidence for this is available from the conductivity and temperature profiles (e.g. Figure 4.2.11).

An increase in conductivity was seen in Layer 3 between March and June 2002 and January and March 2003, while temperature increased in Layer 3 between January and March in both 2002 and 2003 despite the cooling of Layer 2 waters over the winter period. Both indicators imply inflow of water from Adit 1.

Measurements made on piezometer samples from the Equity site (PDC - Equity Division, 2003) indicate that the local groundwaters contain considerable alkalinity (100 to 500 mg/L CaCO₃ equiv.). The mixing of the WLP water at 22 m depth with such alkaline groundwaters was modeled using PHREEQC (Parkhurst and Appelo, 2003) by virtually mixing two distinct solutions while precipitating specified solids. The chemical parameters chosen for the groundwater endmember were those of piezometer sample RH82-06-01 (PDC - Equity Division, 2003), which contained moderate to high alkalinity (417 mg/L). This exercise revealed that calcite, siderite and rhodochrosite were over-saturated at 22 m in the WLP. The pre-mixing degree of saturation was held constant in the calculations, causing the removal of solutes from solution as their respective solids precipitated. However, the removal of Mn through such virtual precipitation proved to be less important than dilution by groundwater in diminishing the Mn concentration (Figure 4.2.7), implying that the influence of the added alkalinity is minor, at best. Since the declines in Zn, Co and Ni contents in Layer 3 are essentially of the same order as Mn, it follows that dilution is likely to be a major factor in altering the distributions of a number of elements dissolved in Layer 3.

The added volume required by the model to account of the metal concentrations amounts to 35 % of the total volume of the layer. The added “groundwater” would of course have to have the same density as that of Layer 3 for the intrusion to be stable. Given that the layer actually warmed slightly during the peak of the intrusions in June 02 (Figure 2.5.10, page 41), stability was likely imparted by the high dissolved sulphate content in the influx. No decrease in sulphate was seen at 20 m depth over this time period, which is consistent with this suggestion. A further implication of the modeling results is that the inflowing “groundwater” is depleted in dissolved metals (but not sulphate) relative to the host lake waters. Direct measurements of the composition of the inflow would be needed to confirm this counterintuitive implication. Such data were not collected during the course of this study.
Finally, the manganese data can be used to infer that sulphate reduction (sulphide production) is unlikely to be a source of metal removal in Layer 3. Dissolved Mn is removed to the same degree as Zn, but MnS (alabandite) is much more soluble than ZnS, and would not precipitate. Thus, the decline in the Zn concentration—which remains high at 420 ppb—cannot be attributed to sulphide precipitation.

Cadmium, Uranium and, Molybdenum – The data are inconclusive as to whether the low concentrations of Cd in Layer 3 represent adsorption to Fe-oxyhydroxides or precipitation of CdS. Both the shape of the Cd profile below Layer 3 in June 03, together with a significant particulate Cd fraction in the water column, support either suggestion (Figure 3.2.8, page 99, June 13, 2003). While, as suggested above, Mn indicates that some dilution of the WLP metal concentrations occurs in this Layer, Cd is removed to a greater degree than most metals, indicating that low levels of sulphide generation may be occurring this Layer. In contrast, Ba, U and Mo concentrations did not change across Layer 3 nor were particulate phases present in this Layer for these metals. Both dissolved U and dissolved Mo roughly were correlated with conductivity, increasing in a near linear fashion from the top of Layer 3 to the bottom of the pit lake. Geochemical modeling indicated that there are no solid phases in the speciation databases that should control these elements as a function of sulphate concentrations. A conservative behavior for Mo for example, is implied by the similarity increases in Mo content and conductivity in the hypolimnnion below 15 m between March 21, 02 and June 21, 02. The consistent ratio of U and Mo to conductivity suggests that uranium is similarly conservative at the concentration levels observed in the pit.

4.2.7 The increase in Fe and As with depth below 20 m (Layers 4 to 6).

The increases in Fe and As with depth below 20 m occur at different rates with Fe (both total and dissolved) rapidly increasing in concentration at the interface between Layer 3 and 4 and As contents rising rapidly below 26 m depth. The fact that the “chemocline” for As between the epilimnnion and the hypolimnnion was routinely deeper than that for Fe by a metre or more suggests that As was preferentially removed from the water column in the zone of Fe-oxyhydroxide formation. The removal of As from Layer 4 can be attributed to adsorption onto Fe-oxyhydroxides settling from the epilimnnion and Layer 2. Such uptake is a well known geochemical phenomenon in other settings (Carlson et al., 2002; Kim et al., 2003). In support of this, the flux of Fe to the sediments recorded in sediment traps at 30 m depth was three times that
recorded at 3 m depth (Aug 16, 02 to June 13, 03) reflecting precipitation of the majority of the Fe-oxyhydroxides in the 4 to 9 m depth interval, below the 3 m trap at the chemocline. Settling of these precipitates to 30 m, as indicated by the trap data, confirms that a scavenging phase for As does pass through Layer 4.

Fe in the hypolimnion below 25 m may have been supplied by the historic input of ARD waters, intrusion of ARD waters and/or efflux from the sediments through dissolution of Fe containing solids. The rough correlation of Fe with conductivity at depth supports the input of Fe with sulphate from ARD, although the concentration of sulphate is much too high, relative to Fe, to be attributed to direct input of Fe and sulphate from pyrite oxidation. If all sulphate is assumed to come from pyrite oxidation then up to 90% of the Fe must have been removed from the waters present in the WLP. Fe also correlates with alkalinity and the control of Fe by siderite (for alkalinity) and (H, K, Na)-jarosite (for conductivity / sulphate) are both possible in the WLP hypolimnion. The dissolution of jarosite minerals in the sediments is not likely to be responsible for the correlation of Fe and conductivity due the much greater molar ratio of sulphate to Fe (15:1) in the water column in comparison to jarosite (2:3). The desorption of As from Fe-oxyhydroxides due to increased competition with surface sites from sulphate in the bottom waters is unlikely to be a major mechanism in the release of As from the sediments. While the dissolved sulphate concentration doubles with between the epilimnion and the sediments (35 m water), this anion has considerably less affinity for Fe-oxyhydroxides than As. A study of the effect of sulphate on the desorption kinetics of As on Goethite found that after 5 months less than 2.5% of As had desorbed in the presence of a range of sulphate concentrations (O'Reilly et al., 2001).

Although analysis of WLP sediments by x-ray diffraction did not provide proof of a crystalline phase precipitating from the water column (Figure 4.2.12), goethite was found in the limnocorral experiments in sediment traps deployed at 8 m depth (Figure 3.3.7, page 113).

4.2.8 Processes and controls in Layer 4 (20.5 m to 28 m).

The concentrations of many metals peak within Layer 4 at 25 m depth. Figure 4.2.13 displays the profiles of total Mn, Fe, Co, Ni, Zn, As, Cd, conductivity and alkalinity with the scales for each parameter matched to Layer 2 concentrations. This shows that Mn, Zn, Ni, Co, and to some extent As are similarly distributed in Layer 4 and the epilimnion. A conceptual model that explains this pattern is outlined below. If the change in metal concentrations across
the epilimnetic chemocline is controlled by the relative affinity for each metal for adsorption to Fe-oxyhydroxides (Figures 4.2.10, 4.2.13), then a similar pattern of metal release should occur as the pH drops and the Fe-oxyhydroxides become less stable. This supposition implies that metals least adsorbed should also be the weakest adsorbed. Metals (metalloids) such as arsenic, with strong affinities to Fe-oxyhydroxides, should not be as easily desorbed under the stronger reducing conditions at depth, and they should readily adsorb in the shallower layers where Fe-oxyhydroxides are precipitating. The lower rate of dissolved As increase with depth in comparison to Ni, Mn and Co in Layer 4 is consistent with this suggestion.

4.2.9 Processes and controls in Layers 5 (28 m to 30.5 m) and 6 (30.5 m to the bottom).

The largest increase in conductivity observed in the sampling program occurred in Layer 5 between March 02 and June 02. There is no adit adjacent to Layer 5 that could nicely explain the step in conductivity at this point. Inspection of the conductivity profiles suggests that the source of the higher conductivity could be water from Adit 1 that flowed down the face of the pit wall as a density current. This would also be consistent with the similarity in metal ratios for Co, Ni, As, Cd and Zn though Layers 3 (adit 1) and 4. The ratios of Mn, Ni, Co, and Zn to each other are similar in Layer 5 to those in Layer 3, the proposed source waters.

Fe and As distributions in Layer 5 appear decoupled from the distributions of Mn, Zn, Co, Ni and Cd. Arsenic concentrations increase rapidly from the top of Layer 5 (28 m depth) though to the pit lake boundary Layer (37 m depth) as a near constant rate of 124 ppb per m (r² = 1.00, n = 5). This implies that Fe-oxyhydroxide reduction is occurring and is releasing significant concentrations of As to solution. A diffusion rate cannot be calculated for As from the sediments despite the uniform increase with decreasing depth due unknown eddy / molecular diffusion coefficients in the open water column.

The concentration of dissolved Fe increased by 25% in Layer 6 (35 m depth) between Oct 1, 01 and Jan 25, 02 but declined by June 21, 02, presumably due to precipitation. The presence of nitrate, with a small peak at 35 m depth on Jan 21, 02 implies that sulphate reduction was not occurring over the winter at this depth. The Fe release to solution during the winter thus reflected a declining pH, poised between about 6 and -2. Subsequent precipitation, inferred from the diminishing dissolved Fe content, can be attributed to control by an Fe-solid phase, possibly Jarosite (predicted to be saturated above a pH of 2)(Figure 4.2.5).
The extremely similar profiles for Co and Ni throughout the WLP hypolimnion suggest that these two metals have a similar control on their distribution in the pit lake. Laboratory studies have found that both metals have similar affinities for adsorption to Fe-oxyhydroxides (Jeon et al., 2003). Though both these elements decrease in concentration from Layer 4 to Layer 6, it is unlikely that this is due to the increasing sulphate concentrations with depth and hence an increased sorption of these metals to Fe-oxyhydroxides (Swelund et al., 2003) as this phase appears to undergo dissolution at these depths in the WLP.

Dissolved and total Sb concentrations consistently increased slightly from 30 m to 35 m depth. This behavior was not seen in Cd and suggests that a source of Sb existed at the bottom of the pit lake. Though little information could be found in the literature, the rapid removal of Sb from below the chemocline in Layer 2 may be due to the reduction of Sb(V) to Sb(III) and the formation of a more readily scavenged Sb species. If this is the mechanism for Sb scavenging at the chemocline, the reverse may be operating in the sediments where Sb(III) is being oxidized, possibly by Fe-oxyhydroxides (Belzile et al., 2001), and re-released into the water column.

In summary, the peak in Mn, Co, Ni and Zn concentrations at 25 m depth is more likely to be due to a greater input of these metals to that horizon rather than removal in deeper waters. For Fe and As, the increase in dissolved concentrations over the same depth range appears to be due to the dissolution of Fe-oxyhydroxides. The fractionation and removal of dissolved Cd from the deep hypolimnion implies removal as CdS, and thus moderate levels of sulphate reduction. Influxes of “ground water” appear to be a mixture of alkaline natural groundwater and ARD waters from the old underground mine workings. These intrusions play a major role in the geochemical cycle of the WLP.
Figure 4.2.1: Waterline Pit Lake Major Elements – 3 Oct 03.

Figure 4.2.2: Dissolved Oxygen vs Dissolved Fe in the WLP. Stoichiometric trend lines shown for various Fe-oxyhydroxide solids (reacting 350 umol Fe).
**Figure 4.2.3:** Conservation of Fe$_{\text{dis}}$ and D.O. during mixing between the epilimnion and hypolimnion. For the right-hand graphs, changes in conductivity were taken as conservative mixing with the data points representing the excess or deficit of Fe and D.O. if D.O was supplied solely from 0 m and Fe solely from the hypolimnion.
Figure 4.2.4: Changes in the depth and conductivity of the WLP epilimnion – June 01 to June 03. The epilimnion depth is taken at the mid point of the pycnocline between the epilimnion and Layer 2. The conductivity values are from 2 m depth (mid epilimnion).

Figure 4.2.5: Saturation index for selected minerals as a function of pe. Matrix is WLP 35 m waters (13 June 03). Calculations using PHREEQC. The pe range of Fe(II) and S(II) are also indicated.
Figure 4.2.6: Generalized O-N-H system as a function of pe. Calculations using Hydra / Medusa speciation software (Puigdomenech, 2003).

Figure 4.2.7: Calculation of the effects on Mn(II) and Fe(II) of mixing “natural” groundwater with WLP waters at 22 m depth (June 13, 03). Rhodochrosite (MnCO₃), Siderite (FeCO₃) and Calcite (CaCO₃) mineral phases were precipitated (held at same saturation index as currently exists in WLP at 22 m depth). Groundwater chemistry taken from Equity piezometer RH82-06-01 ((PDC - Equity Division, 2003). Calculations using PHREEQC / minteq database / “MIX” function. Example of input file given in appendix D.1
Figure 4.2.8: Schematic representation of the possible hydrologic relationships between the old underground mine workings and the WLP.

Figure 4.2.9: A schematic representation of the inflow of groundwater from Adit 1 to the WLP.
Figure 4.2.10: Change in dissolved metal concentrations across the chemocline. Values represent 2 m dissolved concentrations (epilimnion) divided by 10 m dissolved concentrations (Layer 2).

Figure 4.2.11: Evolution of conductivity in Layer 2 – March 21, 02 to Aug 1, 02. Arrowed date labels display the depth of a “secondary” increase in conductivity in this layer as it moves up the layer over time.
Figure 4.2.12: An X-Ray Diffraction spectrograph for sediments collected at 30 m depth in the WLP (Aug 16, 02 to June 13, 03). Note than none of the spectra patterns match the solids shown to any great degree, the bulk of the material appeared to be XRD amorphous.
Figure 4.2.13: Waterline Pit metal profiles (multiple metals) with Layer 2 concentrations aligned to conductivity. June 13, 2003.
4.3 Waterline Pit Lake Limnocorral Experiments

As outlined in section 4.2, the Waterline pit lake contains several metals and metalloids at concentrations of environmental and drinking water concern. This section discusses the results obtained in experiments designed to test selected biologically mediated remediation options for these waters. The experimental design and results can be found in section 3.3. A comprehensive set of figures for metals and physical parameters (temperature, conductivity, fluorescence, transmissivity) in each limnocorral can be found in Appendix B (pages 214-262). These figures are arranged by limnocorral code number (WLL-9 to WLL-16) and sampling date.

4.3.1 Biological response.

Despite elevated metal concentrations and an oligotrophic status prior to nutrient additions, relatively small additions of nutrients produced significant algal blooms and biomass (Chl. \( a > 80 \, \mu g \, L^{-1} \) and POC > 2 mg L\(^{-1}\)) in both the medium and high nutrient limnocorral units. POC values were twice to five times greater in the hypolimnia of the nutrient-addition corrals than in the controls. Given that POC concentrations were 10 to 30 times greater in the epilimnia of the nutrient corrals compared to the controls, this would suggest limited export. The ratio of POC to DOC was high in comparison to normal eutrophic lakes (Thurman, 1985), possibly due to the lack of significant algal activity prior to nutrient additions. DOC is often generated through "sloppy eating" activities of zooplankton and through algal excretion and decay. Scavenging of DOC by iron oxides (Hamilton-Taylor et al., 1996; Rose and Waite, 2002) and increased coagulation and precipitation of DOC due to the elevated ionic strength of the pit water are further mechanisms of DOC removal from the epilimnion (Wall and Choppin, 2003). DOC and POC values in high nutrient corrals were both within the range attributed to eutrophic lakes. Control limnocorral units contained concentrations of both DOC and POC typical of oligotrophic lakes (Thurman, 1985).

The chlorophyll concentrations obtained in the limnocorral units were of the same order as those obtained in nutrient addition experiments in otherwise natural lakes (Schindler, 1974) and other polluted eutrophic lakes (Olila and Reddy, 1997; Weithoff et al., 2000; Xue et al., 1995). This would suggest that the toxicological effect of elevated metals and sulphate in the pit waters did not inhibit algal growth significantly. The literature shows that water quality will typically influence the species composition of the lake but that nutrient status will determine the total
biomass. Even in lakes of extremely poor water quality, significant algal biomass may be present if nutrients are available (Kalin et al., 2001; Nixdorf and Kapfer, 1998).

The much larger chlorophyll concentrations in the Waterline limnocorrals are a little perplexing when compared to those in the Mainzone pit, as the higher metal levels in Waterline would be expected to reduce the resident algal biomass. Several factors may contribute to the larger observed chlorophyll concentrations in Waterline. First, there may be more chlorophyll per unit carbon in Waterline algae due to different species and stress status. Second, the abundance of metals may meet a high demand for micronutrients. Third, the apparent lack of zooplankton (none were observed) and thus grazing may play a role. Finally, photo-inhibition and reduced nutrient mixing may have reduced the bloom intensity in the Mainzone limnocorrals due to a shallower first pycnocline (epilimnion) than in the Waterline. The available data do not allow the relative weights to be assigned to these possibilities, but the lack of grazing can realistically be viewed as a major influence on the standing stock of POC.

The Waterline limnocorrals differed biologically from the Main Zone corrals in one other important way. Fluorescence peaks below the chemocline of the high nutrient addition limnocorrals (WLL-9, 12, 13 and 16) indicated the presence of phototrophic bacteria. These bacteria are prevalent in anoxic and sulphidic environments, where they exist close to the chemocline above or at the point of sulphide generation (Karr et al., 2003; Peduzzi et al., 2003; Rodrigo et al., 2001). Phototrophic bacteria can often provide a significant carbon pool for oxidation by sulphate reducers (Kosolapov et al., 2003). The intensity of the anoxic bloom is most likely reduced by shading from the significant epilimnetic bloom in the limnocorrals (Duval and Ludlam, 2001; Rodrigo et al., 2001). This observation is supported by the fluorescence pattern from corrals without a hypolimnetic fluorescence peak. These showed a sharp decline in fluorescence at the chemocline. In contrast the anoxic fluorescence signal attributed to the phototrophs tended to extend into the chemocline and merge with that of the oxic bloom. Similar distribution of phototrophic bacteria over the whole chemocline and into the oxic zone has been demonstrated in other lakes (Del Don et al., 2001; Tonolla et al., 2003).

The development of this phototrophic bacterial bloom in the anoxic zone was unexpected. The fact that this bloom occurred in all of the high nutrient addition limnocorrals (four of them) and none of the medium nutrient corrals (two) or controls (two), suggests that the blooms may have been triggered by the mixing of surface-added excess nutrients through the chemocline into the anoxic zone. The export of organic carbon from the epilimnion may also be a key factor in initiating the anoxic blooms. Many phototrophic bacterial species are mixotrophic
due to the restricted supply of inorganic carbon in some anoxic environments and so may utilize organic carbon sources.

One of the objectives of the Waterline Limnocorral study was to induce production of organic carbon and the export of that carbon to the hypolimnion. In that context, the presence of phototrophic bacteria as a carbon source offers advantages over epilimnetic algal biomass. First, the export of carbon from epilimnetic blooms will be restricted by turbulent mixing within the epilimnion and the density change at the chemocline (pycnocline). It is well documented that, in general, a relatively small fraction of biomass produced in surface water is transported to depth (Harvey et al., 1995; Libes, 1992). This is due to in situ mineralization, typically aerobic, of this organic matter and density driven restriction in particle transport to depth. In contrast, anoxic phototrophic bacterial blooms that sit at the base of the epilimnion would serve as an ideal in-situ carbon source. Highly labile bacterial detritus settling below the chemoline would be mineralized using oxidants other than dissolved oxygen, and this would enhance the reduction of secondary oxidants such as nitrate and iron oxides, leading eventually to sulphate reduction.

The decline of the blooms during early and mid August in WLL-16 and WLL-12 respectively may have been due to a deepening of the redoxcline around these dates and nutrient depletion related to scavenging by Fe oxyhydroxides. Fe oxyhydroxides are known to scavenge phosphate and their generation within the corrals may have induced some level of nutrient stress (Ding et al., 2000; Gunnars et al., 2002; Ler and Stanforth, 2003). Unfortunately phosphate data are not available, but indirect evidence for scavenging is provided by the decline in As concentration at 6 m depth over the period of the waning bloom, which is attributed to uptake by oxidized iron phases. This is supported by the broadened optical backscatter peaks during this time that suggests an enhanced particulate concentration. This likely was produced by increased mixing of oxygen-bearing epilimnetic waters with Fe-rich waters from the underlying anoxic hypolimnion as the redoxcline deepened.

4.3.2 Physical response.

In general the physical response of the limnocorral approximated that of the bulk Waterline Pit lake, with one significant difference the reduced mixing / deepening of the chemocline that occurred in late summer / fall in the corrals. The influence of salinity stratification can be seen in the chemocline response to lower temperatures in the epilimnion
between Sept 17, and Oct 11, 2002. Between these dates the epilimnion temperature dropped below that of the hypolimnion but no deepening of the chemocline was observed. If temperature was predominantly determining the density profile then colder water would sink, deepening the chemocline and increasing the salinity in the epilimnion. Neither of these occurred. As salinity determines the stratification regime of the limnocorral and temperature profiles appear to match those of the bulk pit lake, the difference between the profiles of S inside and outside the corrals (Figure 4.3.4 B.) are expected to decouple the temperature from the chemocline slightly within them. The two orders of magnitude more rapid diffusion of heat than salt can cause double diffusion where heat transfers into the adjacent density layer faster than the salt (Stevens and Lawrence, 1998). This phenomenon would decrease the stability of the shallower chemocline in the corrals where warmer pit lake water was sitting outside but horizontally adjacent to the limnocorral chemocline and diffusing heat into it.

4.2.2.3 Chemical response

**Biologically mediated chemistry.** A key objective of the Waterline limnocorral experiment was to induce biological sulphide generation and the subsequent formation and precipitation of metal sulphide phases. For most of the experiment, the formation of these phases and of dissolved sulphide could only be confirmed in the corrals to which ethanol as added at depth. Somewhere between 22 and 42 days was required for the production of detectable levels of dissolved sulphide within the hypolimnia of these corrals. This was much slower than the time required for significant algal biomass to form (1 week) in the epilimnion and phototrophic bacteria (2 weeks) to grow in the hypolimnion. This probably reflects the reduction of more thermodynamically favorable oxidants prior to sulphate reduction. Nitrate, MnO₅, FeO(OH)ₓ, arsenate and some high oxidation state metal ions are all likely to be reduced prior to sulphate (Fredrickson et al., 2000; Libes, 1992; Oremland et al., 2000). The higher concentrations of sulphide found near the chemocline, where the temperature is several degrees warmer, could be an indication of thermal inhibition at depth, because bacteria are known to be particularly sensitive to water temperature (Cole and Pace, 1995; Hulshoff Pol et al., 1998). This same pattern could also be produced through nutrient limitation, however. Unlike natural organic matter, ethanol would not provide phosphate and nitrate upon mineralization of the carbon, and sulphate reducing bacteria require phosphate for their energy transfer systems (Hamilton, 1998).
Inorganic Chemical Response (Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Cd, Sb, Ba and U).

The following discussion of the behavior of selected metals and metalloids in the Waterline limnocorrals is given in mass order from Mn through to U. These parameters are presented in the same order in graphical form in Appendix B (Figures B.1 to B.48).

Manganese. For the majority of the experiment there did not appear to be any major change in the Mn concentrations at any depth that could be directly attributable to experimental manipulations. The position of the redoxcline appeared to be the most significant factor in determining Mn concentrations with higher concentrations being found in the hypolimnion. The chemocline for Mn appeared on several occasions to be higher in the water column than that for Fe (e.g. Figure B.45, 6 m). This would be expected due to the slower oxidation kinetics of Mn in comparison to Fe (Davidson, 1992), which would maintain higher dissolved Mn concentrations in the newly oxygenated portion of the hypolimnion during chemocline deepening. Mn would be thermodynamically expected to be present as MnO$_2$ and other Mn-oxyhydroxides in the oxic epilimnion (Davidson, 1992; Elbaz-Poulichet et al., 1997). As in the Waterline Pit, Mn is almost entirely in the dissolved fraction and significant formation of insoluble Mn oxides was not seen throughout the summer / fall.

The lack of Mn removal or fractionation throughout the summer suggests that no fractionation to the algal biomass occurred during the peak of the summer blooms. Thus, adsorption to algal cells appears to have been of minor influence on the removal of Mn. In contrast to the summer Mn behaviour, significant dissolved manganese was removed from the epilimnion during the winter in all nutrient addition limnocorrals. While the mechanism for this Mn removal is not known, bacterial mediation of Mn(II) oxidation is the most likely explanation (Chapnick et al., 1982; Villalobos et al., 2003). Numerous reasons behind the winter oxidation, as opposed to during the summer algal blooms, could be invoked though these would be largely speculation. Decreased metal concentrations in these limnocorrals leading to decreased bacterial inhibition / reaction competition is a candidate. It is interesting that Mn removal in the Main Zone pit lake, also presumably as Mn-oxyhydroxides, occurs during the winter.

Iron. The primary control on Fe concentrations in the epilimnion of the limnocorrals was the oxygen concentration of the water. In the anoxic hypolimnion Fe can be expected to be almost
entirely in the Fe(II) oxidation state, present as hydrated ionic species. Upon contact with dissolved oxygen this species will rapidly oxidize to Fe(III) and form insoluble Fe-oxyhydroxides (Davidson, 1985; Rose and Waite, 2002). The half life of Fe(II) under the conditions of the Waterline Pit epilimnion would be expected to be on the order of several minutes (Emmenegger et al., 1998). Precipitated hydroxides form colloids and coagulate to form flocs, which then precipitate, removing Fe from the water column (Davidson, 1992). This cycling of Fe between dissolved and solid phases often produces a peak in Fe at the redoxcline, but no such peak was seen in the limnocorral or in the pit lake itself. This would suggest that the mixing and particulate Fe production rate was less than the settling rate, reducing the buildup of Fe at the redoxcline in the open lake. Such settling was clearly in evidence—sediment trap data from the lake show that a significant rain of Fe-oxyhydroxides occurred all the way to the deepest sediments (the deepest trap was 10 m above the bottom at 30 m). The primary iron species were oxyhydroxides as opposed to sulphides; this was confirmed by visual inspection of the WL Pit sediments.

No distinct pattern of Fe flux to the sediments could be seen between the different experimental manipulations, with contrasts between limnocorral lying within the large error associated with the sediment trap method. The presence of a large pool of particulate Fe (presumably amorphous FeS) in WLL-12 to which ethanol was added should have been reflected by an increased settling flux of Fe in this limnocorral though no clear increase in Fe flux over the controls was observed.

Black flocs were conspicuous in the WLL-12 hypolimnion from September to the end of the experiment. The size of the black flocs were quite large and easily visible to the eye. The crystalline form of FeS (mackinawite) is reportedly very fine grained under natural conditions and can often pass through a 0.1 µm filter (Morse and Arakaki, 1993). This would suggest that the primary form of the particulate Fe was amorphous FeS or possibly a combination of pyrrhotite, greigite and pyrite. Both amorphous FeS and mackinawite are only semi-stable and are likely to transform to these other FeS and FeS_x minerals over time. Despite the presence of these flocs, dissolved Fe concentrations remained elevated and it appears that the large loss of dissolved Fe in the late fall in WLL-12 was not through the generation of FeS or FeS_2 but of Fe-oxyhydroxides with chemocline deepening.
Figure 4.3.1: Total Iron in the Waterline Limnocorral (3m) and Waterline Pit (2m) Epilimnion for June 02 to March 03. Note the Waterline Limnocorral's Y axis is on the left and the Waterline Pit Y axis is on the right. Error Bars represent 1 standard deviation (n = 3).
**Cobalt.** Evidence from this limnocorral experiment suggests that Co distributions are controlled by three distinct mechanisms. In the control limnocorals, where biological activity is extremely low, the concentration of Co in the epilimnion appears to be governed by the redox conditions with removal of Co (along with Mn), to a pseudo-equilibrium concentration of ~15 ppb upon oxygenation of hypolimnetic waters. The higher Co concentrations in the hypolimnion are typical of anoxic lakes (Achterberg et al., 1997). In the nutrient addition limnocorals, the generation of Mn particulate phases in the epilimnion and apparent co-adsorption / precipitation of Co to hypolimnion occurred during the winter months, in the absence of significant algal activity. Co is extremely strongly adsorbed to hydrous manganese oxides (Murray et al., 1968; Tonkin et al., 2004). Mn-oxidizing bacteria possibly facilitate this sequestration together with precipitation of Mn encrusted bacteria (Jackson et al., 1999; Taillefert et al., 2002). The third mechanism of Co removal from the ethanol addition limnocorals was through the generation of Co sulphide mineral phases or co-precipitation of Co with other metal sulphide minerals (Figure 4.3.3).

The deepening of the chemocline in late fall (Sept to Oct) in the controls saw the removal of Co in the newly oxygenated portion of the hypolimnion to levels consistent with the epilimnion. There was no congruent increase in epilimnetic Co concentrations to support mixing of hypolimnetic Co into the epilimnion. Later data show a peak of Co at the chemocline in the nutrient addition limnocorals, which would indicate the Co is precipitated and re-released to the dissolved phase in the hypolimnion. The significant difference between the controls and the nutrient addition limnocorals is that the controls appeared to maintain a reasonably stable epilimnetic Co concentration throughout the course of the experiment. Interestingly, no fractionation occurred to the algal biomass during the large algal bloom, suggesting little active uptake by the phytoplankton.

The ratio of cobalt to Mn, Fe and organic carbon in the limnocorral sediment traps adds further weight to the suggestion that Co associates with Mn. Fluxes of Co to the sediment traps in the controls and medium nutrient limnocorals (likely to have the least carbon export and least hypolimnetic Mn-reduction) correlated extremely well with Mn ($r^2 = 98.6$; Figure 4.3.2(c)). In contrast, solid Fe phases did not appear to play a significant factor in Co distribution. This is supported by the presence of elevated Co above the point of Fe removal during the deepening of the chemocline in late fall. While Fe was removed from the water column upon the introduction
of epilimnetic dissolved oxygen, Co was not removed along with the Fe, but instead established a profile similar to that of Mn.

The sharp winter decrease in Co in the hypolimnion of WLL-12, to which ethanol had been added, can be attributed to the formation of insoluble sulphides and consequent precipitation. On Jan 24, 2003 the dissolved Co minimum was located at 8 m, the same depth as the ethanol additions and, at that time, the peak in dissolved sulphide concentrations.

**Nickel.** The dissolved Ni concentration in the epilimnion stayed at ~40 ppb for the length of the experiment, despite a deepening of the chemocline and mixing with higher hypolimnetic Ni concentrations. This suggests that Ni was transported to the hypolimnion as the chemocline deepened, as implied by the higher hypolimnetic Ni concentrations during the fall / winter. This same pattern was seen for Fe, As, Mn, and Co.

The increase in particulate Fe-oxyhydroxides in the late fall did not lower the dissolved Ni content below the ~40 ppb level in the epilimnion. If adsorption to Fe-oxyhydroxides influenced Ni removal a decline in dissolved Ni should have been seen. It is concluded that Fe-oxyhydroxides are not important for Ni transport and removal in the control limnocorral. This is confirmed by the Waterline pit data that show a significant deepening of the chemocline between Aug 27, 2002 and Sept 17, 2002, with Fe-oxyhydroxides producing a large drop in transmissivity. During this time period Ni concentrations increased slightly in the epilimnion of the Waterline pit despite the considerable presence of the Fe-oxyhydroxide phase.

In contrast to Fe, cycling of Ni with Mn and Co is predicted from the relative adsorption affinities of Co and Ni for Mn. Ni has a significant (though considerably lower) affinity for Mn-oxide adsorption than Co (Murray et al., 1968; Tonkin et al., 2004). Nickel concentrations were higher than Co at the start of the experiment in both the epilimnion and the hypolimnion, by approximately 25 ppb in both instances. However, despite the differences in affinity for MnO2, the elements were removed from solution in roughly equimolar quantities, implying that similar adsorption kinetics were involved for both elements.

In the ethanol added limnocorral Ni was removed to the particulate phase at depth in a manner consistent with the solubility of its sulphide mineral phase. Ni precipitation followed that of Cd and Zn and preceded Co removal (Figs. 4.3.3, B.24 to B.27), as would be predicted by the various solubilities of their sulphide mineral phases (Morse and Arakaki, 1993). Speciation calculations (PHREEQC, wateq4f) indicate that both Ni and Co sulphide minerals were over-saturated. Thus, co-precipitation with FeS is not needed theoretically to explain the removal of
these metals from the dissolved phase. Under the conditions of these limnocorral experiments, sulphate reduction occurred gradually over time and would be more likely to form the less soluble NiS species before FeS.

Calculations were undertaken using the adsorption constant for Ni on FeS as given in Morse and Arakaki (1993) and assuming that all particulate Fe was FeS in the hypolimnion of WLL-12 during the winter sampling sessions. The adsorption constants ($K'$) from the WLL-12 data at 8 m ($1.04 \times 10^{-5}$) and 9 m ($1.98 \times 10^{-5}$) on 24th January 03 match those of Morse and Arakaki extremely well ($1.10 \times 10^{-5}$ in seawater at 25 °C and $1.94 \times 10^{-5}$ in dilute solution at 5 °C). The conditional adsorption constant ($K'_{FeS:Ni}$) for the WLL-12 hypolimnion could be expected to be between these two figures due to the higher ionic strength (compared to the dilute solution) and the colder temperature (compared to the seawater value).

**Copper.** The analytical data for copper were considered unreliable for this set of experiments due to intermittent contamination and anomalous results within the low concentrations experienced in the Waterline Pit. In general Cu was found to be elevated in the epilimnion and below detection limits in the hypolimnion. The considerable particulate Cu fraction in the hypolimnion suggests that there is partitioning of Cu to some solid phase, most likely organic matter or Fe-oxyhydroxides (Morel and Hudson, 1985; Swelund and Webster, 2000; Tessier et al., 1996; Xue et al., 1995). Given that biological activity in the Waterline pit is generally low and significant Fe-oxyhydroxides are present, it is proposed that oxyhydroxides act as a scavenging phase for Cu in both the control limnocorral and the Waterline pit itself. Further, Cu forms one of the least soluble of the transition metal sulphide minerals and as such is likely to be removed quickly from the deep water column during sulphate reduction (through reaction with dissolved sulphide) (Morse and Arakaki, 1993).

**Zinc.** Particulate and dissolved zinc data yield evidence for three mechanisms that removed the metal from the Waterline pit and limnocorral. The first is the co-cycling of Zn with Fe-oxyhydroxides. Zn was partitioned to the solid phase when Fe-oxyhydroxides precipitated when the chemocline deepened in the late fall. Precipitation of Fe oxyhydroxide species was inferred from thermodynamic considerations, the loss of Fe from the water column, visual observation and the reduction of transmissivity. The second mechanism mirrored that of the Mainzone limnocorral—dissolved Zn was adsorbed to the algal biomass formed upon the addition of nutrients. Although this could not be observed directly, the fractionation of Zn to the solid phase
occurred concurrently with the growth of the algal blooms in the epilimnion. It did not occur where algal biomass was not present. The adsorption of Zn to algal matter is well documented and is postulated as a significant control of dissolved Zn concentrations in lake systems (Achterberg et al., 1997; Reynolds and Hamilton-Taylor, 1992; Xue et al., 1997). The third mechanism was the formation of ZnS or co-precipitation of Zn with other metal sulphide minerals (e.g. FeS, FeS₂) due to bacterial sulphate reduction. Zinc readily precipitates as sphalerite (ZnS), which is sparingly soluble and, in the presence of significant dissolved sulphide (HS⁻, H₂S), typically forms after CuS and CdS (Stumm and Morgan, 1981).

The production of free dissolved sulphides in the high nutrient, non-ethanol addition limnocorral was much slower and of a much lower magnitude than that of the ethanol addition limnocorral. In WLL-9 between January and March 2003, there was a reduction of around 40% in dissolved Zn content at 9 m depth. There was also a considerable fraction of particulate Zn (~20 %, 90 ppb) on March 18, 2003 at this depth. This coincided with the first detection of dissolved sulphide in WLL-9 at the same depth (3.9 μm). The congruent removal of dissolved Cd to below detection limit levels (< 0.1 ppb) supports the precipitation of sulphide minerals as the removal mechanism for Zn at this horizon.

Although the Zn flux to the sediment traps reflected the degree of Zn removal from the water column of the respective limnocorral, care has to be taken in the interpretation of the flux values. In several sediment traps sulphide could be detected by smell upon trap retrieval but it was never detected in the water column (e.g. WLL-10, WLL-13). Such sulphide generation would have been fueled by the oxidation of organic matter and as such would have been greater in the nutrient-addition limnocorral. Thus, sulphide mineral phases may have formed in situ in the traps and the trap contents may therefore not fully represent precipitation of particulates in the water column.

**Arsenic.** The Waterline limnocorral experiment was conducted with the aim of proving the viability of sulphide mineral precipitation as a metal removal mechanism from the Waterline pit lake. Arsenic is perhaps the metal (metalloid) of greatest environmental concern in the lake. With concentrations reaching up to 2400 ppb in the deepest sections of the pit, the escape of this water to the environment would exceed environmental discharge regulations and could cause significant harm to aquatic life (Harvey et al., 2002; Knauer et al., 1999; USEPA, 2002).

Two main geochemical factors can be expected to influence the arsenic distribution in the lake. First, As is strongly adsorbed to, and cycles with Fe-oxyhydroxides, and this will affect its
distribution primarily in the upper water column. At depth, the As distribution is likely to reflect the release of the element from the sediments upon the reductive dissolution of the oxyhydroxide adsorbant. Second, arsenic readily reacts with sulphide to precipitate a suite of minerals, including arsenopyrite, realgar and orpiment, but these are more soluble than Cd, Cu, Zn and particularly Fe sulphide species. At first glance, both of these factors should preclude significant depletion of dissolved sulphide in the Waterline lake water column. However, arsenic adsorbs relatively strongly to mackinawite and amorphous FeS however (Bostick et al., 2003b; Huerta-Diaz et al., 1997); it follows that the large pool of ferrous Fe present in the hypolimnion of the limnocorals should increase the importance of FeS amorphous phases in the adsorption and co-precipitation of As beyond simple discrete mineral solubilities.

As removal was seen in the hypolimnion of the ethanol limnocorals (e.g. Figures B.17 and B.18, pages 231-232), but this was also true for the non-sulfidic corals (controls and other nutrient addition limnocorals). A complication in such comparisons is that there was likely a significant flux of Fe oxyhydroxides through the hypolimnion of all the limnocorals during the deepening of the chemocline. These would quickly have scavenged dissolved As and removed it from solution. At the same time, the reducing conditions of the hypolimnion would have favored the release of adsorbed As from its Fe-oxyhydroxide host, further complicating interpretation of the As profile for a given depth range (Harvey et al., 2002). Comparison of the epilimnion and hypolimnion samples taken outside the limnocorals during the late fall chemocline-deepening event show a marked decrease in the ratio of Fe_{particulate} to As_{particulate} (from 48 to 26) in the deeper samples (8 and 9 m). This would suggest that the Fe-oxyhydroxides present in the epilimnion are not saturated with respect to adsorbed As, with adsorption being limited by the total loading of As mixed into the epilimnion along with the ferrous Fe.

Consideration of the above factors collectively does not allow a definitive conclusion to be drawn. As clearly cycles with Fe, and probably co-precipitates with sulphide phases, but the net balance between addition to the deep waters from dissolving oxyhydroxides and consumption by readsoption or sulphide precipitation cannot be resolved with the current data set.

**Molybdenum.** Mo has a strong affinity for adsorption onto Mn-oxyhydroxides (Achterberg et al., 1997; Crusius et al., 1996; Kuhn et al., 2003; Magyar and Sigg, 1993; Muller et al., 2002) and a relatively lesser attraction for adsorption to Fe-oxyhydroxides (Bostick et al., 2003a). Biological uptake in aquatic systems is minor because the element typically occurs as the
relatively refractory oxyanion MoO$_{4}^{2-}$; indeed, no fractionation of Mo occurred during the height of the algal blooms in the Waterline limnocoral experiment, reinforcing the biological unavailability of the molybdate ion. Like other metals, Mo reacts with sulphide but in a complicated set of reactions that see several soluble thiomolybdate species being formed as S replaces O in the molybdate (MoO$_{4}^{2-}$) species (Correns et al., 1978; Helz et al., 1996). In the presence of FeS, these culminate in the precipitation of MoS$_{3}$ (Correns et al., 1978) after (Bertine, 1972). The formation of MoS$_{3}$ is only favorable under low pH through the reaction of protons with MoS$_{4}^{2-}$. Theoretically, this species is unlikely to be stable at the circum neutral pH of the Waterline pit waters (Helz et al., 1996).

No thermodynamic stability constants were available for Mo in the standard thermodynamic databases and as such this element was not included in speciation calculations. However, the formation of particulate Mo in the presence of sulphide in both ethanol-added limnocorals suggests that either co-precipitation of Mo with other sulphide minerals or precipitation as a discrete sulphide phase did in fact occur. Helz et al (1996) introduced the concept of a geochemical "switch" in regards to the geochemical behavior of Mo where, at a critical HS$^{-}$ concentration, the formation of particle reactive thiomolybdate (MoO$_{x}$S$_{(4-x)}$) occurs and Mo is scavenged by FeS or humic phases. In WLL-12, Mo fractionated to a solid phase prior to the obvious FeS formation (Figure B.25) but well after almost all Zn had formed a solid phase (likely sphalerite). This implies that a discrete MoS$_{x}$ phase may have precipitated in the deep waters of the corral.

**Cadmium.** The geochemistry of Cd in the Waterline limnocorals is perhaps the most complicated of the metals studied in this experiment. Iron cycling appears to have a moderate influence on the formation of particulate Cd. Although Cd is known to adsorb to Fe-oxyhydroxides (Dong et al., 2000), organic matter and Mn-oxyhydroxides are stronger scavenging phases (Dong et al., 2003; Tessier et al., 1993). Nevertheless, in both the Waterline pit and in some limnocorals, a peak in Cd coincides with an increase in dissolved Fe at the chemocline. The Cd peak is entirely in the dissolved fraction, implying that Cd is released from the Fe-oxyhydroxides rapidly upon entering the chemocline / hypolimnion. However, the formation of particulate Mn and subsequent removal of Mn during the late fall / winter in the nutrient addition limnocorals also appeared to remove Cd from the epilimnion.

Biological uptake also played a role. In the presence of the summer algal blooms in the nutrient addition limnocorals, Cd was rapidly partitioned to the particulate phase, presumably
the algal biomass. Up to half of the dissolved fraction was removed during the bloom (WLL-16, Sept 17, 2002). A final influence on Cd speciation was the formation of sulphides. Cd is one of the least soluble sulphide minerals (Huerta-Diaz et al., 1997) and, as would be expected, particulate phase Cd formed rapidly in the ethanol addition limnocorals, even before the presence of detectable dissolved sulphide (Figs. 4.3.3 and B.23). Particulate Cd appeared in the hypolimnion within three weeks of the ethanol additions in WLL-12 and WLL-16.

**Antimony.** The sharp decline in Sb concentrations below the chemocline in the control limnocorals and in the Waterline pit lake itself remains enigmatic. Two distinct removal mechanisms were present for Sb in the experimental manipulations. The formation of particulate Sb in the epilimnion and at the chemocline of the nutrient addition limnocorals during the late fall and winter, concurrently with the removal of Mn and the fractionation of other metals, suggests that Mn-oxyhydroxides play an important role in the scavenging and transport of Sb in these limnocorals. The presence of a particulate Sb peak at the chemocline of WLL-10 during January 03 (together with other Mn-oxyhydroxide scavenged metals (e.g. Co and Mn)) following a large flux of Mn from the water column, support Mn scavenging for Sb. Experimental evidence has shown that Sb has a greater adsorptive affinity for Mn-oxides than Fe-oxides and Al-oxides and that Mn oxides have a greater capacity than these other phases (Thanabalasingam and Pickering, 1990). In contrast to the effect of manganese cycling, Sb was not significantly influenced by the algal blooms in the nutrient addition limnocorals. No evidence of biouptake was observed.

Particulate Sb appeared to form in the early stages of sulphide generation in the hypolimnion of the ethanol (Figs. 4.3.3, B.23 and B.24) and high nutrient addition limnocorals. This could be attributed to the precipitation of stibnite, which has a pK (pK~28) (Helz et al., 2002) that is lower than that for most other metal sulphides including Cu, Cd and Zn (Huerta-Diaz et al., 1997). Similarly, Sb is removed from the hypolimnion of the Waterline pit itself, in the absence of detectable free sulphide, but in the same manner as Cd. Again, precipitation of a sparingly soluble sulphide phase is the leading candidate to explain the observed removal.

4.3.3 Waterline Limnocorral Experiment Conclusions
The experimental manipulations generated three distinct biologically-mediated metal removal mechanisms. The addition of nutrients to the epilimnia of the limnocorals generated large algal blooms with chlorophyll concentrations reaching levels seen in eutrophic lakes (Thurman, 1985). The presence of this algal biomass caused Zn, Cd and possibly Cu to partition rapidly to the solid phase, presumably though adsorption to, or uptake into, the algal matter. The higher POC and DOC concentrations in the epilimnia of the nutrient addition limnocorals appear to have facilitated the production of Mn-oxyhydroxides in the epilimnia during the ice over period. Bacterial Mn(II) oxidation (Chapnick et al., 1982) is a likely candidate for the removal of Mn from the epilimnion waters in this case.

The removal of Mn from the epilimnion coincided with the removal of several metals (Co, Ni, Mo, Sb, Ba) that had previously maintained reasonably stable concentrations throughout the algal blooms. Thus, the promotion of Mn(II) oxidation during the winter months is a possible remediation measure for those metals not removed through adsorption to the algal biomass. The formation of metal sulphides offered a third mechanism for the removal of metals. The introduction of ethanol as a labile reduced carbon source into the hypolimnion of the waterline limnocorals generated significant dissolved sulphide (>2300 μmol). The export of organic carbon from the algal blooms in the epilimnion of the nutrient addition limnocorals also showed evidence of enhancing sulphide production but to a lesser degree and at a slower rate. Several metals were removed from the hypolimnia to differing degrees in the presence of dissolved sulphide (Cd, Zn, Mo, Sb, Ni, Fe and Co). The degree of metal removal was related to the solubility of the respective metal sulphide mineral (Cd, Zn, Mo), the starting concentrations of the metal ions (Fe) and/or the affinity for incorporation into host metal sulphide phases (Ni, As).

A note on the presence of phototrophic bacteria in the hypolimnion of the nutrient addition limnocorals should be made. These bacteria oxidize dissolved sulphide to sulphate as an energy source and are an indication of the presence of dissolved sulphide in the water column. Although these bacteria represented a significant (reduced carbon) biomass in the limnocorals where they occurred, they may have hindered the ultimate goal of metal sulphide precipitation through hydrogen sulphide oxidation. Ultimately it is likely that this biomass would be oxidized under anoxic conditions and, possibly using sulphate as an electron acceptor, replacing much of the dissolved sulphide consumed.

The mixed success in metal removal is illustrated at the end of the experiment in Figure 4.3.2 (a). Here the epilimnetic removal of Cd was significant though less so for the elements Co,
Ni and U. Hypolimnetic (below 6m) removal for all the metals shown was enhanced under the sulfidic conditions of WLL-12. Figure 4.3.3 is a timeline of dissolved metal concentrations at 8 m depth in WLL-12. This figure displays the removal of sulphide forming minerals in rough agreement with their respective solubilities.
Figure 4.3.2: (A). Dissolved metals and sulphide in WLL-11 (Control) and WLL-12 (High Nutrient and Ethanol), March 18, 03. (B). Correlation between Optical Backscatter and Total “dissolvable” sulphides in WLL-12. (C). Cobalt and Manganese in WLL sediment traps.
**Figure 4.3.3:** Timeline of dissolved Co, Ni, Zn, Cd, Sb and H$_2$S concentrations in WLL-12 (ethanol addition) at 8 m depth.
5 Conclusions

This research has highlighted physical and biogeochemical processes and controls that influence the distributions and behaviours of metals in two mine pit lakes at Equity Silver Mine, Houston, British Columbia. The Main Zone pit lake is oxic year-round, has relatively low concentrations of dissolved metals and is mesotrophic. The Waterline pit lake is meromictic, anoxic at depth, contains elevated concentrations of several metals (Fe, As, Zn) in the hypolimnion and displays evidence of low rates of sulphate reduction in the deep waters. The juxtaposition of these two lakes provides a useful illustration of the management strategies available for circum neutral pit lakes. As discussed further below (section 5.1), a desirable range of both pH and pe can be obtained in pit lakes to minimise the concentrations of environmentally harmful solutes, particularly metals.

The biogeochemistry of the Main Zone pit lake is dominated by the disposal of ARD treatment (lime neutralization) sludge into the basin during most of the year. This sludge provides mixing energy, moderate amounts of dissolved oxygen, alkalinity and a scavenging phase for metals. Despite the large volumes of particulate Fe pumped into the pit each season with the sludge, dissolved Fe is below detection limit (5 to 10 ppb) in the water column. Sulphate is the major anion in the Main Zone pit and its concentration is apparently controlled by the precipitation of gypsum. Mn is the only major trace metal identified as being released into the pit through sludge deposition with maximum values of 2200 ppb at the end of the sludge pumping season (fall). Mn is removed from the water column over the winter period in the absence of sludge deposition, possibly as Mn-oxyhydroxides.

The physical structure of the Waterline pit is marked by a series of density stratifications maintained by haloclines. In the geochemical context, the most significant of these haloclines forms the boundary between the epilimnion and the hypolimnion. The depth of the epilimnion varies seasonally, being shallowest (~ 3.5 m) in the early summer as intrusive freshet waters (intruding at 15 – 20 m depth) lifts the chemocline from beneath. The maintenance of the upper halocline (chemocline) restricts the transport of dissolved oxygen from the epilimnion to the hypolimnion and promotes anoxia at depth. While the drivers of the oxygen demand at depth have not been defined, they are likely to be organic carbon mineralization and Fe(II) oxidation. An increase in dissolved Fe and As with depth almost certainly reflects dissolution of Fe-oxyhydroxide minerals and the release of As scavenged to the surface of this solid phase. The
contrasting distributions of Cu, Cd and Sb are marked by depletion at depth which appears to be due to low rates of sulphate reduction and associated precipitation of particulate sulphide phases. Free dissolved sulphide was below detection limits (0.5 μMol) however.

To assess the possibility of manipulating the lakes to remove the high dissolved metal inventories from the surface waters, which are those waters that run off to ambient drainage in the region, a series of experiments were conducted in limnocorals moored in both lakes. Nutrients were added repeatedly at different levels (control, low, intermediate, and high) and the evolution of biomass (chl a) and dissolved, suspended particulate and settling particles was monitored over the course of one full year. An additional carbon source (ethanol) was added at depth in two of the Waterline limnocorals in an effort to relieve apparent carbon limitation to bacterial growth and stimulate sulphate reduction. In the Waterline Pit, this work showed that Cu, Zn, and Cd can be removed through adsorption to / uptake by algal biomass in the oxic epilimnion while Co, Ni, Zn, Cd, Mo and Sb can be removed as sulphide mineral phases in the presence of ethanol induced sulphate reduction. In the Mainzone Pit, the limnocorral experiments similarly showed that metals can be removed with relatively high efficiency and vectored to depth in sinking biodetritus. These results collectively demonstrate the feasibility of removal of metals from pit lake waters via algal scavenging and biologically induced sulphate reduction, at least in naturally anoxic pit lakes.

5.1 Implications for the design of pit lake closure plans and their perpetual management.

The post-mining physical, hydrologic and chemical characteristics of mine pit lakes have, in the past, been largely a function of the economics of ore body extraction rather than design. Waste rock is typically deposited as close as possible to the open pit to reduce transport costs. Where feasible, waste rock from adjacent mining operations has also been placed (backfilled) into the open pits themselves [PDC - Equity Division, 2003 #759]. The presence of waste rock in the catchment as well as exposed mine pit walls and bench rubble increases the probability of flow of ARD into a pit lake. To avoid perpetual “active” management of the water quality in the decommissioned pit closure plans must account for the mass balances between acid-base and redox reactions in the water body.

The use of ARD mitigation technologies such as dump covers, aqueous disposal, co-disposal (with tailings), acid base accounting, wetland treatment, pump and treat (lime
neutralization, bioreactors, industrial alkaline waste, etc), reactive barriers and surfactants [Patterson, 1987 #838][Alcantara, 2004 #754][Greenway, 1996 #237][Benner, 1999 #33][Doye, 2003 #155] provides some hope for reducing the acid loadings to mine pit lakes. A complication in the active treatment technologies for ARD is that the process can often proceed for decades or even centuries [Pereira, 1995 #462][Nagorski, 2002 #873][Anderson, 2004 #872]. Tighter legislation, environmental bonds and public expectations are fast placing the economic costs of long-term management of ARD into the balance sheets of operating and future mines. Passive treatment and mitigation technologies provide the only real alternative for mines containing significant sulphide mineralization. The work presented in this thesis suggests that pit lakes have significant potential to act as passive treatment basins. For example, within quantifiable geochemical limits, ARD added at depth in a pit lake like the Waterline would be “naturally” neutralized by existing (or artificially augmented) alkalinity, and metals could be removed via sulphide precipitation. This would especially be the case were whole-lake manipulation to be undertaken that would enhance sulphate reduction rates in the deep waters.

The research presented here demonstrates that “final” water quality within MPLs is a function of both physical and chemical processes. The physical controls on lake mixing such as surface area to depth ratios, density stratification (via freshwater capping, thermocline development, groundwater intrusions, and saline-ARD intrusions), wind sheltering from high pit walls and surface inflows (density currents) all alter the residence times and supply rates of aqueous reactants. Perhaps the most significant of these is dissolved oxygen. The propensity for mine pit lakes to stratify due to the often elevated solute concentrations in comparison to natural surface waters leads to the restricted supply of oxygen to the hypolimnion. Where the reducing conditions (electron pressure / pe) of the hypolimnion are between that of Fe/Mn-oxyhydroxide dissolution and sulphide precipitation, significant concentrations of dissolved metals can accumulate.

Due to the stability of the dissolved phase of many metals within the pe window between +6 to −1 (from Fe-oxyhydroxide dissolution to sulphate reduction) it is desirable for the water column pe to be outside this range. Effectively MPLs should be managed to maintain either oxic or sulphate reducing conditions within the water column. The contact of the surface (epilimnion) of the pit lake with the atmosphere necessitates that oxic conditions persist in the upper water column. For sulphate reducing conditions to be maintained in the hypolimnion the supply of labile reduced species (predominantly organic carbon) must outpace that of oxidized species (dissolved oxygen, nitrate, nitrite, Mn/Fe-oxyhydroxides, arsenate). Thus, the design of mine pit
lakes must assess the most supportable redox regime (oxic or sulphate reducing) within the physical and chemical characteristics of the pit.

The Waterline pit lake represents a system poised at the upper boundary of sulphate reduction. There is evidence that this lake supports low rates of sulphide mineral production, and this appears capable of removing only the most insoluble sulphide minerals (Cu, Cd, Sb). However, the limnocorral experiments have shown that it is possible to increase the sulphate reduction rate in these waters to facilitate the removal of other metals (Zn, Ni, Co). Thermodynamic calculations indicate that with continued sulphate reduction Fe and As would also precipitate as sulphide minerals (Figure 4.2.5, page 162).

While the striking difference in hypolimnetic water quality between the Main Zone and Waterline pit lakes highlights the need for management of the redox conditions within the water column, acid-base conditions are of equal importance in the geochemistry of many mine pit lakes. The Equity lakes are held at circum neutral pH by the neutralization capacity in the local host rock and in associated groundwaters. In MPLs where the influx of acidity (ARD) is greater than the buffering capacity of the local geology and natural water inputs, acid conditions develop. While at circum neutral pH oxygenated decant waters are often low in metals due to the formation of insoluble metal oxyhydroxides and scavenging, at low pH even well oxygenated surface waters can contain elevated metal concentrations. The pH of a MPL will be dependant on the balance between neutralization and acid forming reactions in the catchment and water column. Where significant ARD drains to the MPL the pH can drop to below 3. This is not currently the case for the Equity site lakes, nor is such a scenario likely to develop there. Nevertheless, this concern could well be real for other sites.

The above discussion highlights the fact that closure planning for mine pit lakes must focus on both redox and acid-base balances over time. As with redox conditions there are two basic strategies for water quality management of waters receiving significant volumes of ARD: (1) sufficient acid neutralization capacity can be present in the system to maintain circum neutral pH and, (2) sufficient sulphate reduction capacity can be present to remove metals as sulphides and raise pH. It is obviously preferable to source alkalinity from natural flows and waste rock than to provide “artificial” alkalinity in the form of added base reactants such as lime / limestone where continued treatment is required. It may indeed be preferable to divert surface waters into the mine pit lakes to provide significant neutralization capacity through volume and dilution.

Although sulphate reduction strategies are more applicable to active treatment of poor quality waters (see section 5.2), it is feasible to put in place plans to induce sulphate reducing
conditions upon lake closure. As shown by the limnocorral work of this project, small additions of nutrients on a seasonal basis to promote algal growth (with surface metal removal, section 4.3) and organic carbon export to the hypolimnion would require minimal long-term cost for the mining company and may be practical in the absence of "walk away" engineering options.

5.2 Implications for the rehabilitation of pit lakes with poor water quality.

The addition of nutrients to the surface waters of mine pit lakes can provide an effective and relatively cheap metal remediation option. In general, the Redfield ratio of 106:16:1 (C:N:P) applies for the bulk composition of algal matter (Libes, 1992; Morel and Hudson, 1985). As most inland waters are phosphorus limited (Schindler, 1974), a small addition of phosphorus can generate large returns in organic carbon production (>100x). Ethanol is a very labile form of organic carbon and will generate rapid sulfate reduction in anoxic systems, as shown by the Waterline limnocorral experiments. A drawback to such additions is that a comparatively large amount of ethanol must be added, depending on the amount of metal sulfide to be precipitated. Two moles of carbon are required per mole of \( \text{H}_2\text{S} \) produced by sulfate reduction. Most metals require 1 (e.g. \( \text{CdS} \)) or 2 (e.g. \( \text{FeS}_2 \)) moles of sulfide per mole of metal to generate sulfide minerals.

The addition of nutrients has the drawback that much of the organic carbon produced may be oxidized in the epilimnion by oxygen (Eadie, 1997). Furthermore, the algal matter exported to the hypolimnion is likely to be much less labile than ethanol. This would have the effect of slowing the sulfate reduction rate and the total moles of sulfide produced per mole of carbon exported. A further complication in the use of nutrient additions is that nitrate is both a nutrient and a strong oxidizing agent. The mixing of nitrate into the hypolimnion or nitrate export with organic matter can have the effect of raising the \( \text{pH} \) of the system and inhibiting sulfate reduction. Thus, the scale and timing of nutrient additions needs to be very carefully planned.

In the treatment of Mine Pit lakes with large Fe and Mn-oxyhydroxide components in the sediments, much of the carbon exported to the sediments in particulate form (e.g. algal) may be oxidized using these solid phases as electron acceptors. Although simultaneous Fe-oxyhydroxide and sulfate reduction has been recorded in sediments (Motelica-Heino et al., 2003), these oxyhydroxides may have the effect of both oxidizing organic matter and any dissolved sulfide produced (Cantrell et al., 2003). Those metal sulfide minerals of relatively high solubility (e.g.
CoS, NiS) may be oxidized rapidly upon precipitating into Fe-oxyhydroxide sediments, re-releasing metals and sulfate into the bottom waters.

The use of adsorption of metals to algal matter as a mechanism for removing metals from the hypolimnion must be used with forethought to the ultimate redox conditions of the sediments. Adsorbed metals are readily released into porewaters and diffuse above the sediment-water interface upon the oxidation of their host organic matter or in response to the lowering of the ambient pe / pH conditions (Zhang et al., 1999). In the presence of a strong pycnocline, as is the case of the Waterline pit, or rapidly accumulating non-organic sediments, as with the Main Zone pit, exported organic matter and metals are less likely to be re-released to the epilimnion.

Sufficiently strong oxidant demand, coupled with restricted oxygen supply, is required to initiate bacterial sulfate reduction. In this case metals are likely to be released from the host algal material and, for certain metals, re-precipitated as sulfide minerals. However, care must also be taken in oligotrophic lakes, as is the case with many mine pit lakes, that a nutrient-generated algal flux to the sediments does not produce sulfate reduction and sulfide minerals that will ultimately become re-oxidized during mixing events (sediment flushing) or sediment re-suspension (Schippers and Jorgensen, 2002; Zhang et al., 1999). Turnover of the water column must be avoided, for H2S is highly toxic to biota that presumably would inhabit the epilimnia of stratified lakes.

The use of Fe and Mn-oxyhydroxides as scavenging phases for metal removal is useful for oxygenated waters only. Both of these metal oxide solid phases are readily reduced under anoxic conditions where suitable electron donors are available (e.g. organic matter or sulfide). In meromictic lakes with an anoxic monimolimnion, the combination of algal or Fe / Mn-oxyhydroxide metal scavenging from the epilimnion and the formation of metal sulfide minerals at depth may provide a cheap and sustainable metal remediation option. But site-specific complications can confound this potentially ideal solution. In the catchment distribution at Equity, for example, where overflow from the Waterline lake runs into the Main Zone, some fraction of artificial nutrient additions to the former could make their way into the latter, increasing phytoplankton production. Given that the Main Zone pit lake contains the vast bulk of its metal inventory as hydroxide sludge in the sediments, which is most stable under oxic conditions, enhanced settling of algal matter to the sediments and the subsequent increase in oxygen demand would be a concern. Thus, in such a setting, careful management of P concentrations would be required to maintain dissolved P at the level where full utilization is
achieved in the fertilized basin. Ideally, P export from such a basin should be zero. This would require skilled management, but it is a feasible objective.

In summary, this work has shown that manipulation of minesite pit lakes to yield reductions in dissolved metals in surface waters can be achieved through careful additions of nutrients to the epilimnion. Further, this research has shown that "permanent" sequestration of metals to underlying sediments can be induced by adding a labile carbon source to deep waters, where carbon limitation constrains bacterial metabolism. It is concluded that the approach pioneered here has significant beneficial implications for the long-term environmental health of pit lakes.
6 References


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Appendix A: Methods

A.1 Chemistry Sampling and Analysis.

Sampling Locations. Sampling for chemistry, CTD profiles, thermistor chain profiles and the weather station was located at the deepest point of both the Waterline (~40m) and Mainzone Pit Lakes (~120m). The initial sampling in the Mainzone Pit (June 01) was undertaken from a small boat with subsequent sampling (August 01 to June 03) undertaken from a raft specially built and permanently moored for the purpose. Waterline Pit sampling was conducted by small boat for the initial year of sampling (June 01 to June 02) after which (June 02 to June 03) a sampling raft was moored similar to the Mainzone Pit. During winter ice-over sampling was undertaken through augured ice holes located within the general area (~30m) of the rafts or boat sampling locations. Care was taken not to disturb the water column during ice auguring. GPS was used to keep track of sampling locations for repeatability between sampling dates. See Figure (2.2) for sampling sites.

Metals. Water samples for metals were collected via hand (for surface and tributary samples), 5 and 8L Niskin / GoFlo bottles or Tygon tubing and peristaltic pump. A fourth method using an "integrated sampler" was used for the Mainzone Pit Limnocorral experiment, this is described in section 4.3.2. All sampling equipment was washed in 2% Environmental Grade HCl (Anachemia) and rinsed with de-ionized, distilled water (DDW, Barnstead NANOpure II) prior to field deployment. Acid washed Nalgene LDPE 8ml and 15ml screw cap bottles were used for sample storage. Samples for Total Metals were taken directly from the sampling apparatus unfiltered. Samples for "Dissolved Metals" were passed through an acid washed 0.45\mu m filter (either cellulose acetate or polycarbonate). Filtering was done with either a Nalgene 250ml Vacuum Filter Holder (Niskin samples), an in-line filter holder (peristaltic pump samples) or syringe filters (some surface and tributary samples). All syringe filters were acid washed and DDW rinsed prior to use. Metal samples were acidified to approximately 1.25% HNO3 using Environmental Grade acid (Anachemia). Selected samples were chosen for "size fractionated metals" analysis and were passed through 20\mu m, 2\mu m, 0.22\mu m (Osmonics Inc., polycarbonate) or 0.1\mu m (Millex-W.PVDF Durapore) filters.
All metal samples were analyzed by either Graphite Furnace Atomic Adsorption Spectrophotometry (GFAAS - Varian Spectra AA 300 with Zeeman background correction), quadrupole ICP-MS (VG Plasma Quad) or High Resolution ICP-MS (ThermoFinnigan - Element 2). GFAAS was used only for Fe and Mn in samples prior to March 02 and for comparison with the ICP-MS data for Zn and Cu (selected samples only). The majority of metals data from samples prior to March 02 were analyzed using the VG Plasma Quad. All metals for samples post March 02 were analyzed using the Element 2 HR-ICP-MS. The internal standard method was used to reduce the effects of differing instrument response to sample matrix changes and instrument drift.

**GF-AAS Procedure:** A graphite platform tube was used for analysis of all metals (Fe, Mn, Zn and Cu), together with modified drying and ashing temperatures to compensate for the lower heat conductance of the platform (in comparison to partitioned graphite tubes). Analytical grade Argon was used as a cooling gas with a typical program reducing flow to 0.1 l/min during detection steps. Sample volumes were 24μl as measured by a piston autosampler.

**VG Plasma Quad procedure:** All environmental samples were diluted (if required) using 1% HNO$_3$ in DDW. A 5 point polynomial calibration curve ($y = a_0 + a_1x + a_2x^2$, $y =$ counts per second, $x =$ ppb) ranging from 0.4 to 50ppb for the metals Cr, Co, Ni, Cu, Zn, As, Mo, Ag, Cd, Sn, Sb, Ba, Pb and U was used. For the vast majority of the samples Cr, Ag, Sn and Pb were below detection limit and this data is not presented. A regression coefficient ($r^2$) value of 1.000 was normally obtained for standard curves. Curves with an $r^2$ value of less than ~0.996 were re-run until a satisfactory curve was obtained. Instrument drift and matrix response variations were compensated for using internal standard normalization with an interpolated mass response between Scandium (Sc45), Indium (In115) and Rhenium (Re187) together with Blank subtraction. 10 samples were run between laboratory blanks. Standard reference materials (Environment Canada TM-02, TM-11 and SLRS-2), through the run standards and repeat analyses were used for quality assurance. Acceptable analysis were within the stated 95% confidence limit or 5% RPD respectively.

Instrument parameters were optimized at the start of each run to maximize sensitivity. A 100μL "loop" injection system was used together with argon gas (ICP-grade) nebulization.
Element 2 analytical procedure: Multi-metal standard solutions were made up into 1.25% HNO₃ using analytical grade commercial standards (1000ppb) for the generation of standard curves. The Element 2 has a greater range than the VG PQ due to the ability to operate simultaneously in both analogue and pulse counting mode. The response of this instrument is also reputedly linear over it's operational range. For this reason, 6 point standard curves ranging over several orders of magnitude were used for elements with a comparable range in the samples (i.e. Fe, Mn, Zn, As). In most cases small deviations from a linear response were found between the lowest and the higher calibration points. For these elements the analysis sequence was evaluated twice using calibrations curves with the highest or lowest points removed respectively. Data points that fell within the range of the revised curves were used as final results. This procedure was found to generate better reference material results and repeatability between analysis dates.

The acid concentration of the sample matrix was found to be a critical factor in the Element 2 response. All standards, reference materials and samples were made up in 1.25% HNO₃ to facilitate some degree of matrix matching. Extensive trials of a suite of internal standard elements were undertaken to match the instrument response (standard curve slope) between the aqueous matrix of the standards and various sample matrices. Standard additions of concentrated multi-metal standards were used to determine instrument response in sample matrices. It appeared that the matrix driven - response suppression was a function of both the first ionization potential (FIP) of the element and it's mass charge ratio to differing degrees. Those elements with the highest FIP were suppressed most by the high sulfate matrix of the samples (and possibly other constituents such as organics).

One standard reference material (TM-25.2, TM-11) and one "reference", filtered sample from (W-5, W-25, M10%) was analyzed in every set of 12 samples (on average). The standard reference material and "reference" sample were chosen for comparability to the samples being run. The reference materials were used for the measurement of accuracy and the between-run consistency of the instrument.
Figure A.1: TM-25.2 Certified Reference Material (NWRI, 2001). Percentage Deviation of Measured Values from Certified Values. Horizontal bars represent Certified 95% confidence limits. Vertical bars represent measured 95% confidence limits. n = 122.

Chlorophyll. Samples for chlorophyll analysis were passed through a Glass Fibre Filter (GFF-F Advantec MFS Inc. Borosilicate microfibre GF 75, 25mmØ, nominal 1µm pore size) or polycarbonate filters of 20µm, 2µm and 0.22µm pore size (for size fractionated samples, Osmonics Inc., Poretics, 47mmØ). Filters were then placed in aluminum foil and frozen until analysis. Frozen filters were placed in 90% acetone (8-9ml) for 24 hours prior to the acetone elutant being transferred to a fresh boric glass test tube for measurement of fluorescence. Two to three drops of 10% HCl was added to the acetone elutant after the first fluorescence measurement (Fo) and a second reading was taken of the acidified elutant (Fa). This acidification step is taken to calculate the phaeophytin (dead chlorophyll) component of the original reading [Parsons, 1984 #540]. This data was used in part to calibrate the fluorometer onboard the SBE19 CTD. As the field fluorometer reads total fluorescence it is often better calibrated to Chl a + phaeophytin rather than Chl a alone. Chlorophyll was calculated from fluorescence by the following formula (taken from Parsons et al, 1984 and instrument calibration):
\[
\text{Chl } a. = 1.79 \times 1.28 (F_0 - F_a) \times (v/V)
\]

where \(v\) is the volume of acetone elutant, \(V\) the volume of sample filtered, \(F_0\) the fluorometer reading prior to acidification and \(F_a\) the reading after acidification.

**Currents.** An Aanderaa Instruments (Norway) RCM-7 and RCM-9 doppler current sensor were deployed within the Mainzone Pit to measure current speed and direction together with optical back-scatter (RCM-9 only), temperature, conductivity and pressure. The pressure sensors were calibrated to a metered block, measured rope and the SBE19 pressure sensor for inter-comparability. Attempts to calibrate both instruments were made by comparing the output of each to each other, by placing the RCM-9 in a flume (UBC-fluid dynamics) and by towing both instruments with a boat at low speed measuring distance and time. These calibration steps were all contained error due to operational uncertainties (such as estimates of boat speed and interference with the Doppler mechanism by flume walls) though provided an indication of the instrument accuracy.

**Freeze Core:** One sediment freeze core was taken in the Mainzone Pit in March 02. This method uses a dry ice / ethanol slurry inside a rectangular aluminum tube to freeze sediments to the outer face of the tube upon deployment. This technique is suitable for unconsolidated / soft sediments that are difficult to core through more traditional grab, gravity or box core techniques. Mr J. Crusius (USGS, Woods Hole, MA) supervised the freeze coring. Sub-samples were taken from the core at selected distances (relative depth in sediments was unknown due to over-penetration of the core into the sediments) using a plastic spatula. These samples were then freeze-dried, weighed and digested. The density of the material in the ice core was measured through measuring the dimensions of a frozen piece of ice core (sediment) and comparing the volume to the dry weight. This technique was not considered accurate due to the possible density changes in the material upon freezing though a rough indication of the sediment density could be obtained.

**Inorganic Carbon:** Electrochemical titration of the acidity produced during the production of CO\(_2\) from carbonates was used to determine inorganic Carbon in sediment samples using a UIC Inc. CM5014 CO\(_2\) Coulometer [UIC Inc., 1999 #541]. Blanks were run using empty test tubes with all data being blank subtracted. Reagent grade CaC\(_2\)O\(_3\) was used as a standard. Acceptable
measurements were 12% Carbon +/- 0.5% with sample repeats within 0.05% Carbon. A sample weight of between 30 to 70mg was used.

**Organic Carbon:** Dissolved Organic Carbon (DOC) was measured in filtered (0.45μm), acidified (H₃PO₄) water samples. A Tekmar-Dohrmann Phoenix 8000 UV-Persulfate Oxidation TOC analyzer was used for detection of DOC. Total Organic Carbon and total nitrogen in sediment trap and freeze core samples was analyzed on a Carbo Erba NA 1500 CNS analyzer. Sediment preparation and analysis was carried as per [Verardo, 1990 #571]. Sulfur was not obtained due to possible interferences of the sulfur spectra with the other analytes.

**Oxygen (Dissolved):** Samples were taken directly from Niskin bottles or from the peristaltic pump through tygon tubing placed at the bottom of 125ml Erlenmeyers / BOD bottles. Care was taken to eliminate air bubbles from samples. Sample bottles were rinsed twice and allowed to overflow three times the bottle volume before preservation reagents were added. 1ml of Manganeseous chloride and 1ml of Sodium hydroxide / sodium iodide solution were added as preservatives to each sample. Samples were titrated as per the Winkler method with Sodium thiosulfate [EPA, 1996 #321]. All samples were kept in the dark and analyzed within 48 hours of collection. The method detection limit was 0.05 ml/L, and precision was 0.02 ml/L. Accuracy of this method is somewhat hard to estimate and is tied to repeat analysis of potassium iodate standard solution. Typical replicate standard determinations were within 5% RPD or 0.05 ml/L.

**Sediment Traps:** sediment trap apparatus were specifically designed for the project with the need for frequent sampling and ease of handling in mind. These traps were smaller than typical marine traps and held removable trap tubes for ease of replacement. Lake turbulence was expected to be low given the small surface area to depth ratio typical of mine pit lakes, this allowed for smaller traps to be used. Traps were deployed in duplicate at all locations and depths. Upon careful retrieval, trap tubes were left to settle and the supernatant decanted until a volume less than 500ml was remaining. The remaining trap contents were agitated vigorously to unsettle the particulates and poured into 500ml plastic wide mouth tubs. These tubs were promptly frozen to preserve organic carbon by inhibition of bacterial respiration. One unforeseen effect of freezing was the formation of gypsum in the tubs as solutes were concentrated during the freezing process, analogous to the rejection of salts during sea ice formation.
Samples were thawed, centrifuged and further decanted until containing less than 5ml of water. This fraction was then freeze dried for four to five days until completely dry. Samples were weighed, ground to a homogeneous consistency and sub sampled for metal / sulfur, total carbon / nitrogen, inorganic carbon and XRD analysis.

**Sulfate:** Both turbidimetric and ion chromatographic techniques were used for the measurement of sulfate. The turbidimetric method listed in “Standard Methods for the Examination of Water and Wastewater – 4500 $\text{SO}_4^{2-}$” was used for sulfate determination in selected samples [Greenberg, 1992 #572]. This method deploys the generation of barium sulfate (barite) particulates and measurement of the absorbance at 420nm using a spectrophotometer (Bausch and Lomb, Spectronic 21 with Tungsten lamp). Raw sulfur counts were also obtained for aqueous samples after March 03 and all sediment trap samples using ICP-MS (ThermoFinnigan, Element 2). These raw counts were normalized to Indium (internal standard) and a standard curve calculated from known sulfate concentrations in three reference materials analyzed during each ICP-MS run. This produced a rough three-point standard curve, though total sulfur numbers generated this way are regarded as indicative only and not absolute concentrations. Sulfate in oxic systems is largely conservative and as such a good indicator of acid rock drainage inputs.

**Sulfides:** Hydrogen sulfide was measured after preservation as Zinc Sulfide (sphalerite). Excess zinc acetate was added to sample bottles prior to sampling as a preservative. Dissolved sulfide samples were passed through a 0.45 μm filter. Total sulfide samples were unfiltered and may contain mineral metal-sulfide species that could be recorded as free sulfide. The spectrophotometric method outlined in [Parsons, 1984 #540] (after [Cline, 1969 #585]), a variation on the methylene blue method of detection at 670nm, was used for analysis. The 6N hydrochloric acid matrix of the reagents used in this method is assumed to quantitatively convert the ZnS produced during sample preservation to Zn$^{2+}$ and H$_2$S. The detection limit for concentrated samples was ~1 μM.

**Total Suspended Sediments:** 500ml of sample was filtered through a 0.45μm filter in the field. Filters were then dried at 103 °C for at least one hour, left to cool in a desiccant chamber and weighed until a constant weight was obtained [Greenberg, 1992 #572]. A batch (approx. 10) of unused filters was dried and weighed to obtain blank values for subtraction from the sample weights. Unfortunately this method is not as rigorous as individually weighing filters before
sampling and after sampling though requires much less sampling effort. In samples with low suspended solids the variance in the filter weights can be equal to or greater than the sample weight. This data is also considered indicative only for lower values.

**X-ray Diffraction:** A Phillips PW 1729/1710 XRD was used to generate powder x-ray diffraction histograms using a copper source (CuKα). Selected sediment samples were ground in a marble mortar and pestle to a powder consistency and spread thinly on quartz disks using acetone. θ values from 4 to 44 were scanned in steps of 0.40. The output files were matched to standard mineral X-ray diffraction patterns using the MacDiff software [Petschick, 2003 #542].
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Appendix B. Waterline Limnocorral Experiment Figures.
Figure B.1: WLL-9 (High Nut, Seds): 13 July 02
Figure B.3: WLL-9 (High Nut., Seds): 28 Aug 02

- **Ba**
- **Zn**
- **Mn**
- **As**
- **Fe**
- **Mo**
- **Co**
- **Cd**
- **Ni**
- **Cu**

Additional graphs include:
- **Cond**
- **SO₄**
- **Trans Temp**
- **Flour OBS**
Figure B.5: ML-9 (High Nut: Seed): 11 Oct 02
Figure B.6: WELL-9 (High Nut. Sed.): 24 Jan 03
Figure B.7: WIL-9 (High Nut. Seeds): 18 Mar 03
Figure B.8: WLL-10 (Medium Nut, Sed) 13 July 02
Figure B.9: WLL-10 (Medium Nut, Seeds): 6 Aug 02
Figure B.10: WLL-10 (Medium Nut, Seds): 28 Aug 02

- Total Metal
- < 0.45um Metalls (Dissolved)
Figure B.11: WLL-10 (Medium Nut, Sedds.): 17 Sep 02
Figure B.14: Will-11 (Control, Seeds): 13 July 02
Figure B.15: WILL-11 (control, Seeds): 6 Aug 02
Figure B.19: WLL-11 (control & seeds): 24 Jan 03
Figure B.20: WLL-11 (Control, Seds): 18 Mar 03

Depths (m) for various elements:
- Ba
- Zn
- Mn
- U
- As
- Fe
- Mo
- Co
- Ni
- Cd
- Sb
- Cu

Conductivity (Cond) and sulfate (SO₄) levels are also shown.
Figure B.21: WLL-12 (High Nut, Ethanol, Seeds): 13 July 02
Figure B.24: WLL-12 (High Nut, Ethanol, Seds.): 17 Sep 02

- Depth (m) for various elements including Ba, Zn, Mn, Fe, As, Mo, Co, Ni, Cd, Sb, Cu.
- Cond pS/cm with 500-1000, 1500-2000 pS/cm values.
- Temp °C with values 2, 4, 6, 8, 10, 12, 14.
- OBS with values 0.0, 0.2, 0.4, 0.6, 0.8, 1.0.

...<0.45 μm Metals, Total Metal...
Figure B.25: WIL-12 (High Nut. Ethanol. Seeds): 11 Oct 02
Figure B.26: WLL-12 (High Nut, Ethanol, Seds): 24 Jan 03
Figure B.29: WML-13 (High Nut. Seeds): 7 Aug 02
Figure B.31: WLL-13 (High Nut. No Seeds): 18 Mar 03
Figure B.33: WIL-14 (Medium Nut, No Seeds): 7 Aug 02
Figure B.34: WILL-14 (Medium Nut, No Seeds); 28 Aug 02
Figure B.35: WLL-14 (Medium Nurt. No Seeds): 12 Mar 03
Figure B.36: WLL-15 (Control, No Seeds): 13 July 02
Figure B.37: WLL-15 (Control, No Seeds): 7 Aug 02
Figure B.39: WIL-15 (Control, No Seeds): 18 Mar 03
Figure B.40: WLL-16 (High Nut. Ethanol, No Seeds): 13 July 02
Figure B.42: WILL-16 (High Nut, Ethanol, NO Seeds): 28 Aug 02
Figure B.43: WL-L-16 (High Nut., Ethanol, No Seeds): 17 Sep 02

- OBS
- Flour
- Temp
- Cond
- SO_4
- u
- Ba
- Zn
- Cu
- Ni
- Fe
- Mn

Legend:
- Total Metal
- > 0.45 um Materials
- ...
Figure B.44: WLL-16 (High Nut, Ethanol, No Seeds): 11 Oct 02
Figure B.46: WL-S (South Rat, Waterline Pit): 13 Jul 02
Figure B.48: WL-S (South Ratl Waterline Pit): 17 Sep 02
Appendix C – Example PHREEQC input files.
Appendix C-1: Example of PHREEQC input file used for calculation of groundwater mixing with Waterline Pit lake waters at 22 m depth (June 13, 03).

SOLUTION_MASTER_SPECIES
SOLUTION_SPECIES
TITLE WL 25m groundwater alkalinity mix
SOLUTION 1 WL 25m 13 June 03
  temp  5.0
  pH   7.5
  redox pe
  pe   3
  units ppm
  density 1.002
  As  0.830
  Sb  0.0005
  Ca  321
  Mg  40.7
  Na  26.6
  Sr  10.96
  K   3.2
  Fe  30.275
  Mn  3.347
  Si  5.17
  S(6) 524
  P   0.0002
  U   1.52 ppb
  O(0) 0 ppm
  Co  0.0405
  Mo  0.00628
  Ba  0.0123
  Ni  0.0554
  Cu  0.001
  Zn  0.830
  C(4) 0
  Alkalinity 147 as Ca0.5(CO3)0.5
  -water 1 # kg
SAVE SOLUTION 1
END
TITLE groundwater from Equity
Solution 2 groundwater
  units ppm
  pH   7.36
  pe   10
  S(6) 116
  Alkalinity 417 as Ca0.5(CO3)0.5
  -water 1 # kg
END
Title Mixing of GW with WLP
Mix 1
  1  0.6
  2  0.4
EQUILIBRIUM_PHASES
  Rhodochrosite 0.09
  Calcite 0.34
  Siderite 1
SELECTED_OUTPUT
  -file 25mGW1.txt
  -reset false
USER_PUNCH
  -head Rhodo Calcite Siderite Mn(2) Fe(2) Fe(3)
10 PUNCH SI("Rhodochrosite"), SI("Calcite"), SI("Siderite"), TOT("Mn(2)"), TOT("Fe(2)"), TOT("Fe(3)")
END
Appendix C-2: Example of PHREEQC input file used for calculation of speciation for Waterline Pit lake waters at 35 m depth (June 13, 03). (pe is set in this example).

SOLUTION_MASTER_SPECIES
SOLUTION_SPECIES
TITLE Waterline 35m June 13.
SOLUTION 1 Wateline 35m June 13
  temp  5.5
  pH    7.5
  redox pe
  pe    3.0
  units ppm
  density 1.002
  As   1.6
  Sb   0.0007
  Ca   400
  Mg   56
  Na   50
  Sr   12
  K    4.5
  Fe   42
  Mn   4
  Si   5
  S(6) 356
  N(-3) 1.9 as NH4
  U    1.8 ppb
  O(0) 0 ppm
  Cd   0.00002
  Co   0.030
  Mo   0.0074
  Ba   0.012
  Ni   0.042
  Cu   0.0001
  Zn   0.4
  Alkalinity 180 as Ca\(\cdot\)5\(\cdot\)CO\(\cdot\)5
  -water 1 # kg
SOLUTION_MASTER_SPECIES
  U    U+4 0 238.029 238.029
  U(4) U+4 0 238.029
  U(5) UO2+ 0 238.029
  U(6) UO2+2 0 238.029
SOLUTION_SPECIES
  #primary master species for U
  #is also secondary master species for U(4)
  U+4 = U+4
    log_k 0.0
  U+4 + 4 H2O = U(OH)4 + 4 H+
    log_k -8.538
    delta_h 24.760 kcal
  U+4 + 5 H2O = U(OH)5- + 5 H+
    log_k -13.147
    delta_h 27.580 kcal
  #secondary master species for U(5)
  U+4 + 2 H2O = UO2+ + 4 H+ + e-
    log_k -6.432
    delta_h 31.130 kcal
  #secondary master species for U(6)
  U+4 + 2 H2O = UO2+2 + 4 H+ + 2 e-
    log_k -9.217
\[
\begin{align*}
\text{delta}_h & \quad 34.430 \text{ kcal} \\
\text{UO}_2^+ + & + H_2O = \text{UO}_2\text{OH}^+ + H^+ \\
\log_k & \quad -5.782 \\
\text{delta}_h & \quad 11.015 \text{ kcal} \\
2\text{UO}_2^+ + & + 2H_2O = (\text{UO}_2)^2(\text{OH})_2^2 + 2H^+ \\
\log_k & \quad -5.626 \\
\text{delta}_h & \quad -36.04 \text{ kcal} \\
3\text{UO}_2^+ + & + 5H_2O = (\text{UO}_2)^3(\text{OH})_5^5 + 5H^+ \\
\log_k & \quad -15.641 \\
\text{delta}_h & \quad -44.27 \text{ kcal} \\
\text{UO}_2^+ + & + \text{CO}_3^{-2} = \text{UO}_2\text{CO}_3 \\
\log_k & \quad 10.064 \\
\text{delta}_h & \quad 0.84 \text{ kcal} \\
\text{UO}_2^+ + & + 2\text{CO}_3^{-2} = \text{UO}_2(\text{CO}_3)^2^{-2} \\
\log_k & \quad 16.977 \\
\text{delta}_h & \quad 3.48 \text{ kcal} \\
\text{UO}_2^+ + & + 3\text{CO}_3^{-2} = \text{UO}_2(\text{CO}_3)^3^{-4} \\
\log_k & \quad 21.397 \\
\text{delta}_h & \quad -8.78 \text{ kcal}
\end{align*}
\]

**PHASES**

Uraninite

\[
\begin{align*}
\text{UO}_2 + & + 4H^+ = 2H_2O + U^{+4} \\
\log_k & \quad -3.49 \\
\text{delta}_h & \quad -18.63 \text{ kcal}
\end{align*}
\]

**EQUILIBRIUM PHASES 1**

END