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Assessment of Biological Treatment of the Faro, Grum and Vangorda Pit Lakes

October 2004

LORAX ENVIRONMENTAL

Executive Summary

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In support of ongoing closure planning for the Anvil Range Mine site, an assessment of bio-remediation to lower zinc levels in the Grum, Vangorda and Faro Pit Lakes was conducted. The study involved a whole-lake fertilization of Grum Pit Lake including alternate manipulations in mesocosm experiments (limnocorrals). In addition, physical and geochemical conditions in both Faro and Vangorda Pit Lakes were studied to assess bioremediation in these systems as well.

A resident population of algae in Grum Pit Lake facilitated the rapid onset to a highly productive system with the addition of nutrients; neither fish fertilizer nor EDTA were required to enhance algal growth. Similar conditions do not exist for either the Vangorda or Faro Pit Lake and as a result, lake preconditioning (*i.e.,* early spring fertilization) would likely be required to realize algal growth.

The response of Zn in Grum Pit Lake to enhanced productivity was an initial transfer from the dissolved to particulate fraction followed by settlement of particulate (organic matter) out of the surface layer and into deeper waters. The growth rate of algae was more important to Zn removal than the concentration of algal cells as adsorption sites saturated quickly and became unavailable.

The quantity of Zn removed from Grum Lake surface water resulting from fertilization from late June, 2004 to the beginning of September, 2004 was sufficient to allow discharge of the upper two to three metres of lake water to the receiving environment had it been deemed necessary (i.e. surface water concentrations of Total Zn <100 μg/L). An experiment in one of the limnocorrals in which fertilization ceased at week 6 indicated that a program of pulsed eutrophication (*i.e.,* addition of nutrients followed by a period of no nutrient addition) was not capable of reducing Zn to low levels. The best mitigation results arise from sustained growth.

Both Faro and Vangorda Pit Lakes appear to host conditions suitable to bio-remediation particularly if under-ice fertilization in the early spring occurs. The added advantage of fertilization in both Vangorda and Faro Pit Lakes relates to their pre-existing stratification. Because these systems are stratified and suboxic at depth, they may produce hydrogen sulphide at depth under conditions of higher productivity and thereby draw Zn out of the lower water column through sulphide precipitation.

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1. Introduction

In support of ongoing closure planning for the Anvil Range Mine site, an assessment of the efficacy of pit lake bioremediation to lower zinc levels was conducted. Dissolved Zn has accumulated in the three pit lakes (Faro, Grum and Vangorda) due to runoff from pit walls and seepages and has reached concentrations too high to discharge water to the receiving environment.

Recent research has suggested that Zn (and other metals) sorbs to organic surfaces and that bioremediation (in the form of elevated biological productivity in surface waters) holds potential to remove Zn from the water column.

Accordingly, Lorax Environmental Services Ltd. (Lorax) was commissioned to conduct an assessment of the efficacy of lake fertilization to lower Zn levels in these pit lakes. The study involved the fertilization of the Grum Pit Lake, one of the three lakes on site. In addition, the operation and study of mesocosm experiments using limnocorrals attached to a raft moored within the lake were conducted.

This report presents the findings of this study and focuses on the feasibility of fertilization as a treatment strategy to mitigate Zn concentrations in each of the three pit lakes. Chapter 2 presents the methodologies employed within the study and Chapter 3 forwards the results. Chapter 4 discusses the applicability of whole-lake fertilization to treating each of the three Anvil Range pit lakes.

2. Methods

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2. Methods

The objective of the Grum Lake study was to define the efficacy of bioremediation through nutrient amendment to remove Zn from the water column of Grum Pit Lake (Figure 2-1). To this end, a whole-lake manipulation was performed in addition to a suite of limnocorral experiments. While the pit lake manipulation (addition of nutrients to the pit lake) was designed to directly assess the efficacy of bioremediation, the limnocorrals were to serve both as a control and as alternative manipulation strategies.

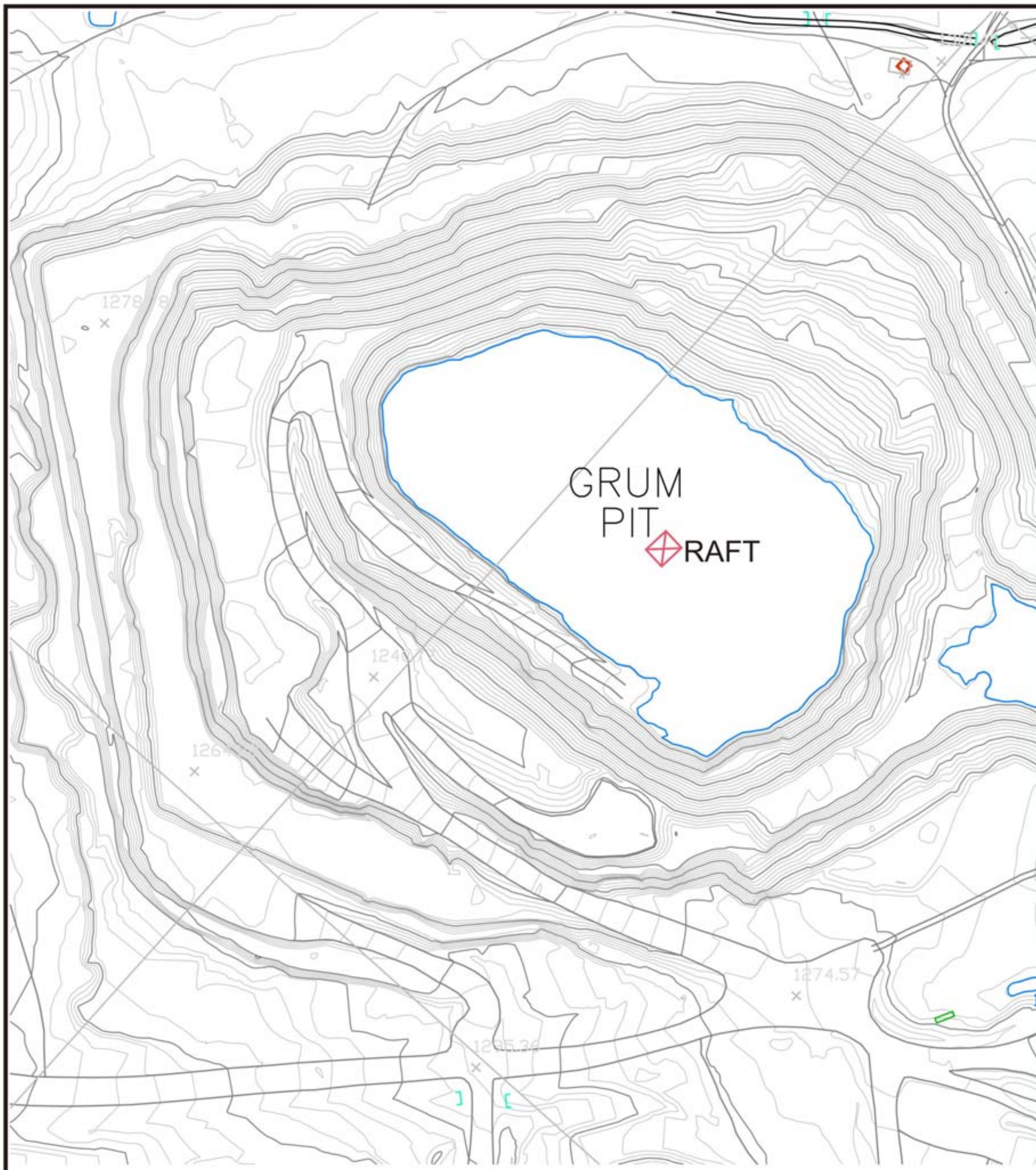
The whole-lake manipulation involved the addition of a relatively simple nutrient blend. The limnocorrals received either no additions (control), additions of nutrient plus fish fertilizer (a source of additional micronutrients) and addition of nutrients and EDTA (to mediate potential toxicity from Zn).

Fertilization and field sampling was conducted by Laberge Environmental Services. The details of these manipulations and sampling program are described below.

2.1 Nutrient Amendment Program

A variety of parameters influence the concentration of nutrient in the water column of a lake following nutrient addition, most notably the thickness of the mixed layer. Accordingly, specific concentrations within surface waters are difficult to target and as a result, nutrient additions are typically described in terms of nutrient addition per lake surface area rather than as absolute water column concentrations.

In determining the potential nutrient addition rate, data was considered from the experimental lakes work conducted in Ontario in the 1970's and 1980's (*e.g.,* Schindler, 1978; Schindler et al., 1978; Schindler et al., 1987) and was designed to force Grum Lake in hyper-eutrophia for the three-month period encompassed by the open-water experiment. Given that phosphorus is typically the ultimate limiting nutrient in such systems, the nutrient additions were based on calculated phosphorus content while ensuring that the nitrogen content of the fertilizer was sufficiently in excess (*i.e.,* in excess of the redfield ratio N:P $\approx$ 16) to prevent nitrogen limitation. The fertilizer used was a custom blend agricultural liquid fertilizer with a 29-5-0 blend of urea ammonium nitrate and ammonium phosphate. The fertilizer mixture produced a N:P ratio of 10.4:1 by weight or a molar ratio of approximately 23 thereby providing N in excess of the N:P ratio at which most phytoplankton acquire nutrients.



Grum Pit Lake and the Location of the Mooring Raft

Figure 2-1

Fertilizer was applied to Grum Lake and to the limnocorrals at the same concentration, based on an estimate lake area of 200,000 m^2 (SRK, 2004). Fertilizer was supplied in 55 gallon drums.

Three drums of fertilizer were added each week, providing a fertilization rate of 1170 mg $N/m^2/wk$ and 110 mg $P/m^2/wk$. This dose is approximately twice as high as the highest fertilization rate reported in the literature. The high concentration used was chosen to achieve the maximum phytoplankon growth over the short growing season that exists at Faro. Experiments at Equity Silver in Houston, B.C. (Crusius et al., 2001; McNee et al., 2003) had shown that similar concentrations of nutrients had produced higher phytoplankton biomass than achieved in lake fertilizations reported in the literature (*i.e.,* the experimental lakes) which typically try to achieve maximum growth rates without the commensurate build up of biomass associated with eutrophic conditions. Since eutrophication was not a concern in Grum Lake in the short term, conditions suitable for maximum biomass production were utilized.

2.2 Whole-Lake Manipulation

The whole-lake manipulation involved weekly additions of ~625 L of the nutrient mixture from the stern of a small boat. The nutrient mixture was pumped from a 55 gallon drum on board the boat into the prop wash to facilitate mixing with the lake water (Figure 2-2). Flow rates were optimized to disperse the nutrient addition as widely through the lake as possible.

While nutrient addition occurred weekly, water column sampling occurred on alternate weeks. Water column samples were collected from the moored raft at depths of 1, 3, 5, 7, 10, 20, 30 and 40 meters depth by peristaltic pump and in-line filter (where required) immediately prior to fertilization. Samples were collected for analysis of total metals, dissolved metals, nutrients and physical parameters. All samples were preserved and shipped to ALS Laboratory in Vancouver. Concurrent with the water sampling, the water column was profiled with a CTD equipped with a fluorometer. Sediment traps were deployed in the lake adjacent to the raft. Trap samples were analyzed for organic carbon, nitrogen and metals.

Figure 2-2: Weekly fertilization of Grum Lake utilizing controlled flow of fertilizer from a 55-gallon drum into a prop wash.

2.3 Limnocorrals

As explained above, the limnocorral experiments were conducted to assess the potential of alternative water column amendment should Grum Lake water be unable to sustain algal growth. Three limnocorrals were installed and maintained attached to the raft: a control, an amendment with EDTA and an amendment with fish fertilizer (Figure 2-3).

Limnocorrals are experimental water column enclosures, which are open at the top and the bottom and isolate a portion of the water column from lateral mixing within the lake. The limnocorrals used in this project were 3 m in diameter and approximately 12 m in length. They were designed to isolate the mixed surface layer, which according to data from previous years (Gartner Lee, 2003) extended into the 4 to 5 meter depth range.

The control limnocorral, which received no nutrients, served as a control for the mesocosm experiments and for the Grum Lake manipulation.

Figure 2-3: Grum Lake raft with three limnocorrals attached to periphery.

The EDTA experiment (EDTA) was conducted in the event that algae would not grow due to Zn toxicity. Prior to whole-lake manipulation, zinc concentrations in Grum Lake were on the order of 10 mg/L, well above known toxicity thresholds for a variety of phytoplankton species. It was felt that the addition of EDTA could serve to lower the free-ionic concentration of zinc in the water column and thereby mitigate or reduce any associated growth inhibition to algae. At the beginning of the limnocorral experiment Zn was added to one limnocorral in a quantity sufficient to complex an assumed inventory of dissolved Zn equivalent to a concentration of 5 mg/L in the upper 4 metres of the water column. It was assumed that the water associated with ice melt would reduce surface water Zn concentrations from 10 to approximately 5 mg/L.

The fish fertilizer treatment (Fish) was conducted in response to previous laboratory experiments (Sobelewski, 2003) that suggested that algal growth responded more rapidly in the presence of such an amendment. While the mechanism was unclear, it was thought that fish fertilizer provided either metal-complexation capacity (hence, toxicity amelioration of Zn) or a suite of micronutrients unavailable in the lake water of previous experiments. Therefore, commercial fish fertilizer was added to one of the limnocorrals at start-up at a dose of 0.5 L/m^2. This addition was designed to emulate as closely as possible the concentration of fish fertilizer used in the previous laboratory experiments.

It should be noted that the concentration of nutrients or other amendments in the field is difficult to compare directly to laboratory conditions as the absolute concentration in the field depends on the thickness of the mixed layer and effect of wind mixing to disperse the amendment into the water column.

Nutrient additions occurred in both the EDTA and Fish limnocorrals at the same surface application rate and on the same days as at Grum Lake. Accordingly, approximately 22 mL of nutrient mixture was added to each limnocorral every week. As noted, the control limnocorral received no nutrient additions.

Limnocorral sampling occurred commensurate with the Grum Lake sampling program and involved profiling of the water column with a fluorometer-equipped CTD in addition to the collection of water samples by peristaltic pump at six depths (1, 3, 5, 7, 10 and 13 metres). Samples were pumped to the surface and filtered in-line (where necessary). Samples were collected for total metals, dissolved metals, nutrients, physical parameters and chlorophyll "a" in some cases.

Sediment traps were installed at the bottom of each limnocorral and trap sediments were analyzed for dry mass, organic carbon, nitrogen and metal content.

All samples were shipped to the ALS laboratory in Vancouver.

Program Amendment

By early August, due to high productivity in the Grum whole lake, it became evident that neither the EDTA nor Fish limnocorral experiments were required. Rather than shutting them down completely, it was determined that two additional experiments could be run. To one limnocorral, nutrient additions were ceased in order to observe the effect of nutrient limitation on the removal of Zn and algae from the water column. Vangorda surface water was added to the other limnocorral in an attempt to verify that algal growth could be induced in water which was known to contain considerably higher concentrations of Zn. To facilitate this latter experiment, Vangorda water was collected in a pump truck and layered over the upper 5 metres of Grum water. It was hoped that the warm temperature of the Vangorda surface water would offset its elevated density associated with its higher TDS. This, however, proved not to be the case and over the period of one to two weeks, the Vangorda surface water sank and mixed into the Grum Lake water within the limnocorral.

2.4 Other Instrumentation

A suite of autonomous data-logging instrumentation was installed at the Grum Lake site in support of potential physical lake modelling in future. Specifically, a Hobo weather station (monitoring wind speed, direction, temperature, precipitation, insolation) was installed on the raft in Grum Lake. In order to complement the CTD data, highresolution thermal data of the lake water column were collected using a thermistor chain suspended from the raft. Thermistors were also installed in the potential inflow streams to the Grum, Faro and Vangorda feeder streams to assess the density of inflows in a "flow-through" configuration.

3. Results

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3.1 Physical and Geochemical Evolution

Grum Lake is a relatively small pit lake hosting a present day volume on the order of 2.2 million m^3 and a surface area of approximately 200,000 m^2. The maximum lake depth at the time of the study was marginally greater than 40 m.

The data suggest that Grum Lake stratifies early in the open-water season; by the end of June, 2004 (the commencement of sampling in the present study), there was not only a pronounced thermocline (a rapid change in temperature with depth) centered at approximately 2 metres depth, but a strong halocline (a rapid change in salt content or conductivity with depth) at the same location (Figures 3-1 and 3-2). As the primary source of contaminants to Grum Lake is pit wall runoff and seepage (SRK, 2004), the mechanism for formation of this open-water stratification must be related to the spring melt. It is suspected that under ice, the water column is stratified thermally with colder water adjacent to the ice overlying warmer water near the temperature of maximum density (~4 to 4.5°C). Water conductivity is likely near uniform from the previous fall turn-over event at approximately 1000 µS/cm. As the air temperature warms, melt water from the ice (having a very low conductivity) dilutes the water of the surface layer and creates a situation in which physical stability is maintained by the disparity in salinity (the content of dissolved salts) between the upper few metres and water at greater depths (Figure 3-1). The strength of the halocline and thickness of the surface mixed layer from year to year are likely a function of the degree of wind mixing that occurs commensurate with ice break up. Regardless, the halocline is sufficiently strong to prevent vertical mixing of surface water into the lake interior in the spring even when surface water warms through its temperature of maximum density (fresh water is at its most dense at 4°C).

As the surface layer continues to warm though the spring and summer, the stratification is intensified and the lake is physically stable until the fall when turn-over occurs. This tendency can be seen in the current study through the evolution of temperature and conductivity in the water column through the summer and fall (Figure 3-2).

The conductivity data (Figure 3-1) suggests that input of relatively fresh surface water contributes to the stability of the surface layer by progressively lowering the salinity and increasing the strength of the halocline. However, during the fall, the weakening thermocline promotes a thickening of the mixed layer, erosion of the halocline and a corresponding increase in conductivity (and Zn) in the mixed layer (Figure 3-1). Eventually the entire water column mixes and reoxygenates.

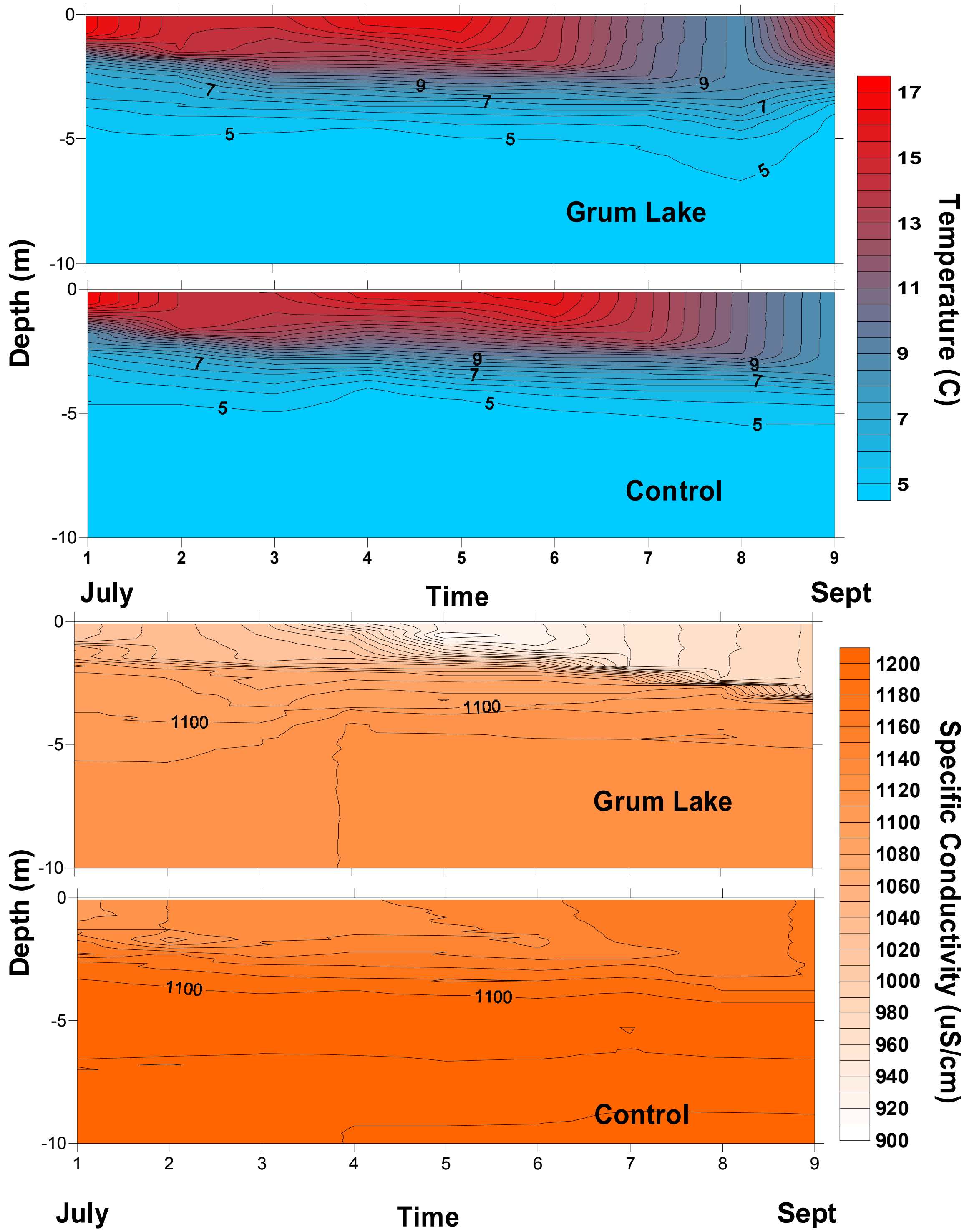

Figure 3-1: Temperature and specific conductivity with time in the surface waters of Grum Lake and the control limnocorral.

Oxygenation must occur seasonally as there is no evidence of low oxygen conditions or suboxia even though a base level of primary productivity exists within the lake (fluorescence profile in Figure 3-2; discussed in greater detail below). This notion is supported by previous data which indicate high concentrations of dissolved oxygen throughout the water column even in August after a summer's worth of primary productivity (Gartner Lee, 2003; SRK, 2004).

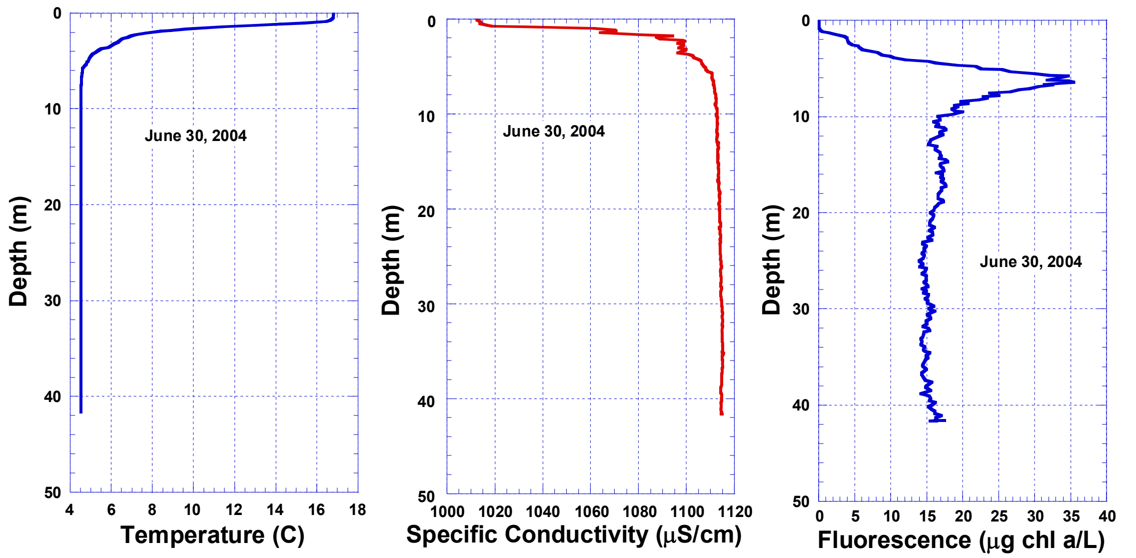

Figure 3-2: Temperature, specific conductivity, and chlorophyll in Grum Lake at the study start-up (June 30, 2004).

It is suggested that the seasonal distribution of Zn in Grum Lake follows a recurring pattern dictated largely by the processes described above. The well oxygenated water column suggests that marked lake-wide mixing occurs, most likely in the fall. Thus, during the fall and possibly in the winter (under ice), the water column hosts a near uniform distribution of Zn at a concentration near that currently observed in the deeper waters (*i.e.,* ~10 mg/L). With freshet comes an inventory of Zn from rinsing of the pit walls, but more important is the dilution of the surface layer associated with ice melt. The comparatively fresh ice melt water is devoid of Zn and reduces the mixed layer Zn concentration from ~10 mg/L to approximately 5 mg/L. Under normal conditions, this inventory is further reduced to a small degree by the base-level of productivity in the lake (described later); however, evidence of this removal is erased from the water column at fall turn-over when the lake mixes to depth.

3.2 Fertilization and Photosynthetic Biomass

3.2.1 Fertilization of Grum Lake

Fertilization of Grum Lake involved the weekly application of a mixture of liquid urea ammonium nitrate and liquid ammonium phosphate at a rate of 1170 mg N/m^2 and 110 mg P/m^2.

The aim of the fertilization program was to stimulate and sustain the growth of phytoplankton in the lake. The study was completed between June 30th and Sept. 8th, 2004.

At the start of the fertilization program there was a significant population of phytoplankton present in Grum Lake, with a maximum concentration at 6 m depth, approximately the depth of the pyconcline, and little phytoplankton at the surface (Figure 3-3). This situation is typical of a phytoplankton community whose growth has been limited. Phosphate, the nutrient that typically limits freshwater phytoplankton growth, was below detection limit at all depths on June 30th, confirming that the natural phytoplankton inhabiting Grum Lake was under phosphorus limitation . The chlorophyll profile in the control limnocorral was similar to that in Grum Lake (Figure 3-3).

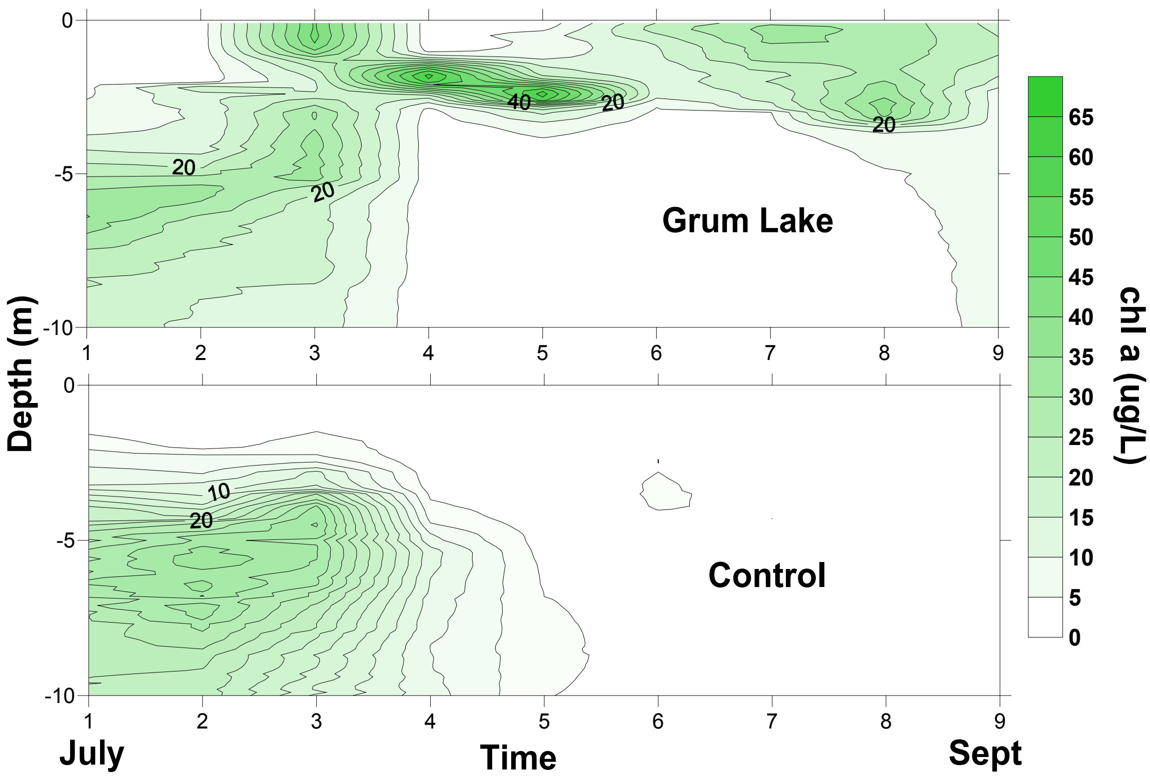

Figure 3-3: Chloropyll a concentrations with time in Grum Lake and the control limnocorral.

The pre-existence of phytoplankton at the initiation of the fertilization program allowed for a rapid response to the increased nutrient addition. Integrated chlororphyll "a" value (mass of chlororphyll "a" per unit area over a given depth interval) in the top 4 m doubled from 15 to 28 mg Chl m^{-2} one week after initial fertilization (Figure 3-4). After 2 weeks of fertilization integrated chlororphyll "a" values had increased to 110 mg Chl m^{-2} over the same 4 m depth interval. At this time there were 2 maxima of chlorophyll in the water column, one at the surface and a subsurface maximum at around 5 m depth.

Maximum concentration of chlororphyll "a" (hence phytoplankton) anywhere in the water column in Grum Lake throughout the course of the summer occurred in August when peak chlorophyll was greater than 60 µg/L at 2 m deep. At this time the concentration of phytoplankton was low in the upper metre of water, yet the integrated chlorophyll value was ~70 mg Chl m^{-2} in the upper 4 m, an intermediate value. There are two possible explanations for this behaviour.

The first possible reason for this behaviour is that these profiles were indicative of nutrient limitation in the surface water, as discussed above for initial conditions. In other words, the algal biomass remained constant within the water column (as indicated by the constant integrated chlorophyll value for the upper 4 m) but the population of algae had settled towards the base of the mixed layer (as evinced by the deepening chlorophyll maximum). Phosphate concentration at this time was above detection limit but remained low (~0.02 mg/L). Since measurements of nutrients and chlorophyll were made a week after fertilization, it is possible that nutrients were consumed in the first few days after addition and that phytoplankton sank to the pycnocline (a rapid change in density as a result of changes in temperature and/or salinity with depth) subsequent to nutrient depletion.

The second and more likely reason for the growth patterns in Grum Lake surface water relates to observations of changing watercolour by field personnel during the sampling program. During the whole lake manipulation, watercolour was observed to evolve from green to brown and back to green (K. Nordin, pers comm.). The change in colour is indicative of a shift in algal species assemblage and corresponds to three zones of increase in the integrated chlororphyll "a" values (Figure 3-4). In mid to late July, the Grum Lake surface water was noted to change to a brown colour (possibly indicative of diatom dominance); the "brown" water lasted approximately one month, corresponding to an algal crash and regrowth phase (as indicated by integrated chlororphyll "a" data; Figure 3-4). Finally, in mid/late August, Grum Lake water was noted to revert to the original green colour, corresponding to another decrease and progressive increase in integrated chlororphyll "a" (Figure 3-4). The final increase in chlororphyll "a" likely represents a species assemblage change back to the population that originally colonized the lake. It is important to note that in general, regardless of the species assemblage, the integrated chlororphyll "a" value increased with ongoing fertilization through to the end of the experiment (Figure 3-4).

In the control limnocorral, to which no nutrients were added and which was isolated from the additions to Grum Lake, the relatively high initial phytoplankton concentration that was present below 3 m gradually declined to near detection limits by mid August. This further demonstrates the dramatic effect of nutrient additions in Grum Lake to increasing primary productivity. In the control limnocorral, conditions of light and temperature were the same as in the whole lake, but the lack of nutrients prevented phytoplankton growth.

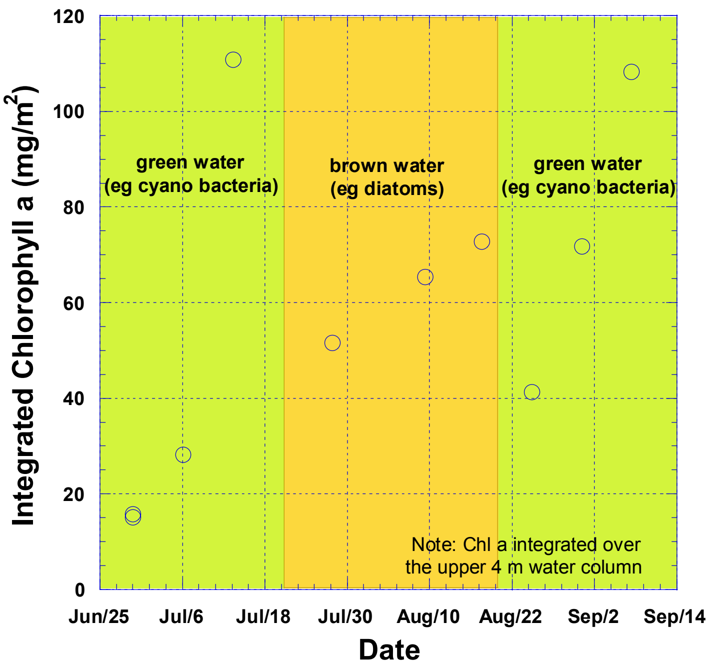

Figure 3-4: Integrated chlororphyll "a" concentration over the upper 4 metre of water column and observed colour changes of Grum Pit Lake surface water.

Despite the high fertilization rate used in this experiment, relative to concentrations reported in the literature, there was no build-up of a phosphate in the water column over the course of the experiment (Figure 3-5). There was, however, a small increase in nitrate and ammonium over the course of the experiment, but total N remained low; some inventory of the nitrate is likely associated with the nitrification of ammonium. This indicates that higher concentrations of P could be assimilated by phytoplankton and used for growth if they were made available. The N:P ratio used was apparently close to the ratio at which these elements were absorbed, but may be adjusted slightly lower in future fertilizations as evinced by the progressive build up of nitrogen species (Figure 3-5).

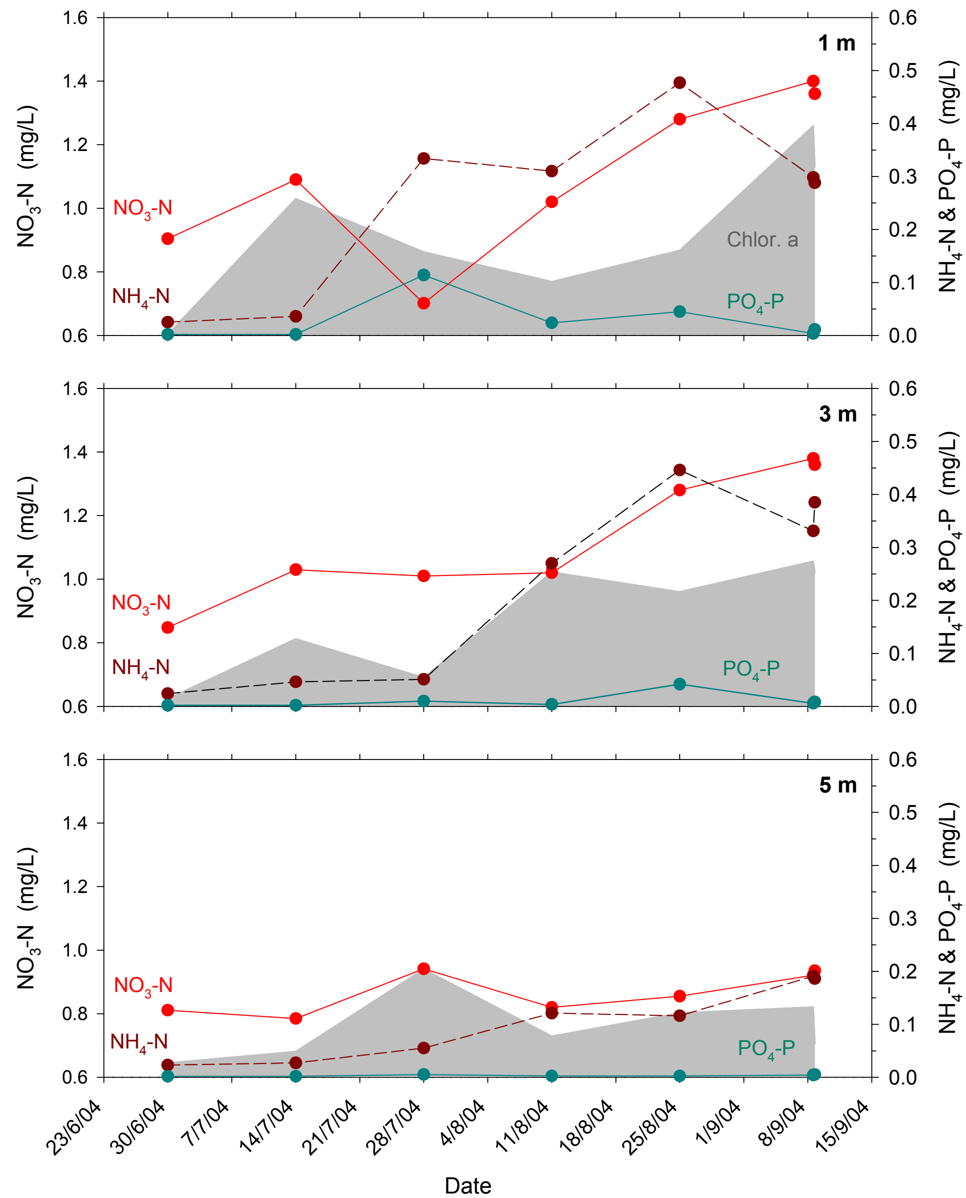

Figure 3-5: Temporal variations of nutrient concentrations in Grum Lake.

3.2.2 Limnocorrals

The chlororphyll "a" data for the Fish and EDTA limnocorrals are presented in Figure 3-6. For the first 6 weeks, these two limnocorrals were operated in their original configuration and showed no significant departures in behaviour from Grum Lake. Specifically, the baseline productivity at depth below the mixed surface layer disappeared within the first 5 to 6 weeks similar to both the control limnocorral and Grum Pit Lake (Figure 3-3). Similarly, the surface mixed waters of both the Fish and EDTA limnocorrals displayed the large increase and subsequent decline in chlororphyll "a" seen in Grum Pit Lake over the first 6 weeks.

At the 6-week mark, the Fish and EDTA limnocorrals were converted to alternate experiments as described previously. Fertilization ceased in the Fish limnocorral while the EDTA limnocorral received water from the Vangorda pit lake. The Vangorda water proved to be too dense and flowed out of the bottom of the limnocorral; however, the cessation of fertilization in the Fish limnocorral offered insight into the application of pulsed eutrophication to the Grum Pit Lake system (a situation in which productivity is increased rapidly and then nutrients additions cease, promoting rapid uptake of Zn and settlement of the associated particulate organic matter).

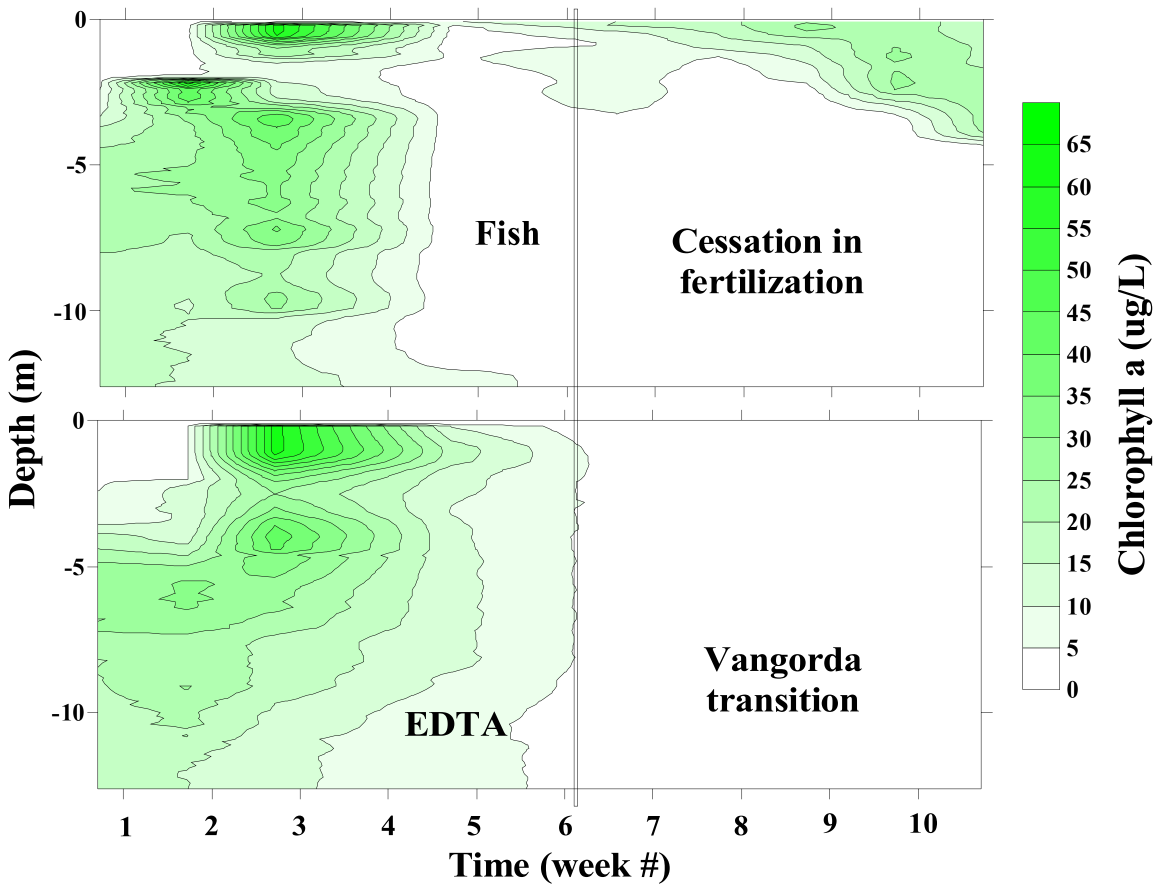

Figure 3-6: Fluorescence data from the Fish and EDTA limnocorrals; weekly fertilization ceased in Fish on August 10 while the EDTA limnocorral

The cessation of nutrient additions to the Fish limnocorral did not have the effect of immediately shutting down primary productivity. As can be seen in Figure 3-6, chlororphyll "a" concentrations remained and increased marginally in the mixed surface layer. The continued existence of measurable chlororphyll "a" in the surface layer is not unanticipated as the internal recycling of algae (an nutrient) often occurs in such systems. The progressive increase in chlorophyll towards the end of the experiment likely reflects the deepening of the mixed layer and the introduction of nutrient from water below the pre-existing thermocline.

3.3 Zn Removal

The most salient impact of elevating primary productivity in the mixed layer is on the behaviour and distribution of Zn. At the beginning of the experiment in late June, virtually 100% of the Zn in the water column was dissolved (Figure 3-7). The dissolved Zn concentration in the surface layer was ~5 mg/L, whereas the water at depth (≥5m) contained approximately 10 to 11 mg/L Zn. The reduced surface concentration was brought about by dilution with ice melt water.

Within two weeks (*i.e.,* by July 14), a substantial fraction of the Zn in the mixed layer (as represented by the 1 m depth sample) had transferred to the particulate phase (Figure 3-7). Following the initial transfer from a dissolved to particulate phase, Zn was progressively removed from the mixed surface layer by settling particulates. This notion is supported by sediment trap samples which hosted Zn concentrations in excess of 2.5 wt. % (discussed below).

The Zn removal process is best illustrated in the temporal variation of total zinc (T-Zn) and dissolved zinc (D-Zn) concentrations at different depths in the upper water column as illustrated in Figure 3-7 along with the corresponding chlororphyll "a" concentrations (gray background). Initial T-Zn and D-Zn concentrations at 1 m depth are relatively low compared to those at other depths illustrating both dilution of surface waters with ice melt water in concert with the zone of maximum algal growth. As discussed above, virtually all of the primary productivity associated with fertilization occurred in the upper mixed layer (*i.e.,* 1 to 3 metres) where nutrients were added and where light needed for photosynthesis is greatest.

Initially, a rapid increase of the chlororphyll "a" concentration occurred in the surface water. Concurrently, a large proportion of the D-Zn inventory transferred to the particulate phase, which resulted in a decrease in D-Zn but not in T-Zn. The T-Zn is not removed until particulate concentrations become greater and settling becomes significant.

During the mid phase of the experiment (*i.e.,* week 4 through 6; August), T-Zn at the 1 m interval is at its lowest concentration (<0.1 mg/L), whereas T-Zn in the 3 m layer continues to decrease (Figure 3-7).

Towards the end of August through the end of the experiment in early September (weeks 8 through 10) the T-Zn and D-Zn concentrations appear to increase slightly in both the 1 and 3 m depth intervals, due to erosion of the thermocline. By mid-late August, the thermal stratification is beginning to break down and wind mixing forces both the thermocline and haloclines deeper into the water column (Figure 3-1). An important effect of this evolution is the entrainment of water from deeper depths into the surface mixed layer. As described above, this is readily seen in the late summer/fall increase in conductivity in the mixed surface layer and is visible here as a commensurate increase in dissolved Zn in the 1 and 3 m samples through the same period of time (Figures 3-1 and 3-7).

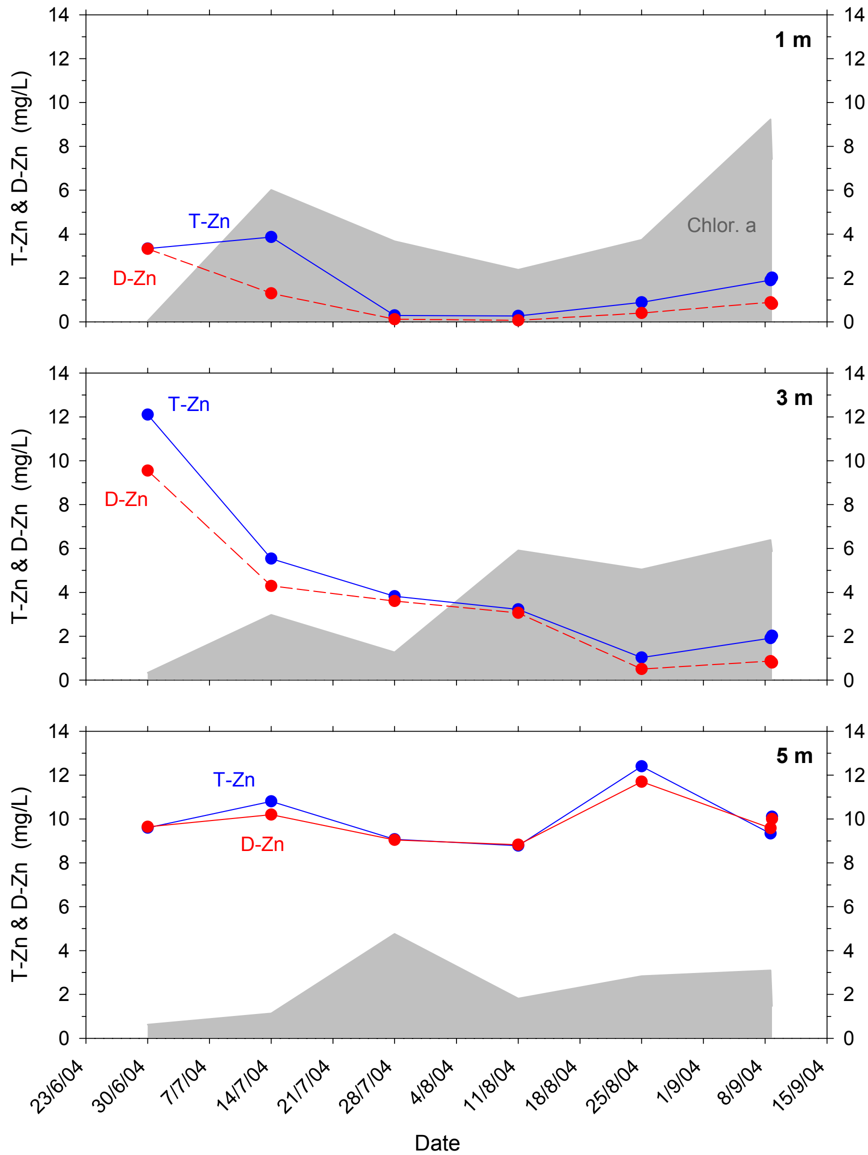

Figure 3-7: Temporal variation of T-Zn and D-Zn concentrations in Grum Lake. Note: sampling dates occur at two-week intervals.

The T-Zn concentration at 5 m depth, immediately below the thermocline, is almost entirely dissolved and remains relatively constant and high during the course of the experiment (Figure 3-7). Similarly, the T-Zn concentration in the control limnocorral (all depths) is almost entirely dissolved zinc. The T-Zn concentrations at 1 m and 3 m depth vary between 3 mg/L and 6 mg/L while concentrations at the other depths are generally around 10 mg/L supporting the notion that ice melt has contributed to dilution of the surface water Zn.

Interestingly, even though the lowest concentrations of Zn were achieved in the 1 m depth interval, the largest quantity of Zn was removed at 3 m depth (no Zn removal occurred at 5 m or greater depth). It appears as though the absolute quantity of Zn removed is proportional to the concentration where organic sorption sites are available. This notion is supported by the removal of Zn from the mixed layer during active algal growth through the duration of the experiment (Figure 3-8). Worthy of note is the base level of Zn removal in the absence of fertilization (*i.e.,* in the control limnocorral). This removal is associated with the baseline productivity in the Grum Lake surface layer and is not associated with a limnocorral artifact (*i.e.,* adsorption onto the limnocorral wall) given that removal is restricted to the mixed layer and does not occur at depth in any of the limnocorrals (Figure 3-9).

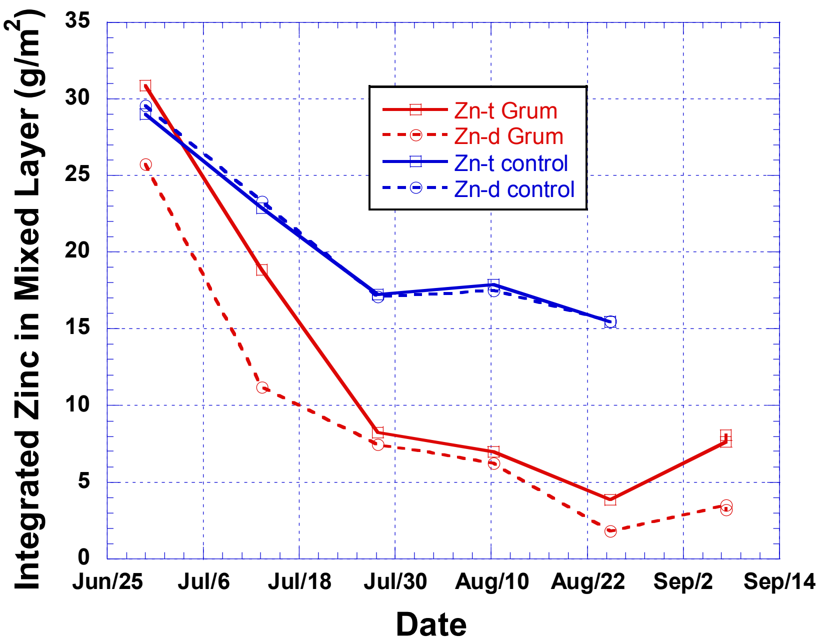

Figure 3-8: Integrated total and dissolved Zn in the mixed layer (upper 4 metres) through the duration of the experiment.

The transfer of zinc from the dissolved to the particulate phase is generally attributed to the combined effect of biological uptake (assimilation) and adsorption to cell walls. Biological uptake will be greatest during periods with increased productivity while adsorption will occur throughout the entire fertilization period unless adsorption sites at cell walls have become saturated in which case it too will be governed by growth rate.

Removal of Zn through settling particulates is supported by the sediment trap data which show high concentrations of Zn in the solid-phase of trapped material (Table 3-1). Concentrations of Zn were on the order of 2.7 wt.% in the 12 metre traps. This concentration is very high when compared with typical crustal abundances, which are 100 to 200-fold lower (Turekian and Wedepohl, 1961). While the flux of material to the

40 m traps was higher by one order of magnitude (Table 3-1), the corresponding concentration of Zn was considerably lower (*i.e.,* ~0.6 wt.%). Visual observation of the deep trap samples indicated a predominance of what appeared to be lithogenic material (*i.e.,* derived from pit walls rather than organic productivity) while the shallow trap material appeared predominantly organic in nature.

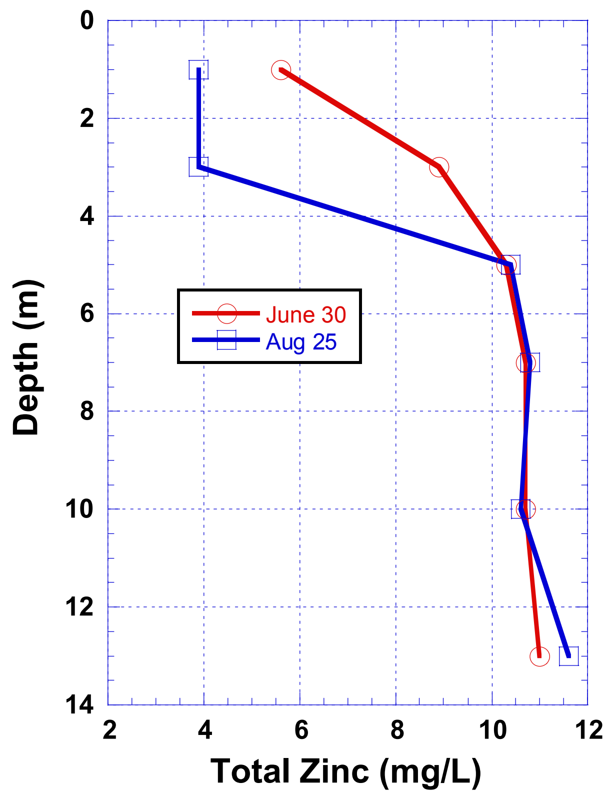

Figure 3-9: Total Zn in the control limnocorral at the beginning (June 30, 2004) and late (August 25, 2004).

Table 3-1:
Sediment Flux, Zn content and Zn Flux in Grum Lake Sediment Traps

	SedimentFlux (g/m^2/day)		Zn (wt.%)		Zn Flux (g/m^2/day)	
replicate	1	2	1	2	1	2
12 m trap	3.6	3.5	2.75	2.64	0.099	0.092
40 m trap	34.8	37.3	0.584	0.647	0.203	0.241

With the cessation of fertilization of the Fish limnocorral at approximately 6 weeks into the experiment came the opportunity to assess the impact of pulsed eutrophication on the removal of Zn. Figure 3-10 illustrates the removal of Zn from the water column. After the cessation of fertilization, there was no further reduction in Zn in the water column.

The data suggest that an inventory of algal biomass was recycled in the mixed layer but was unable to further reduce the content of Zn.

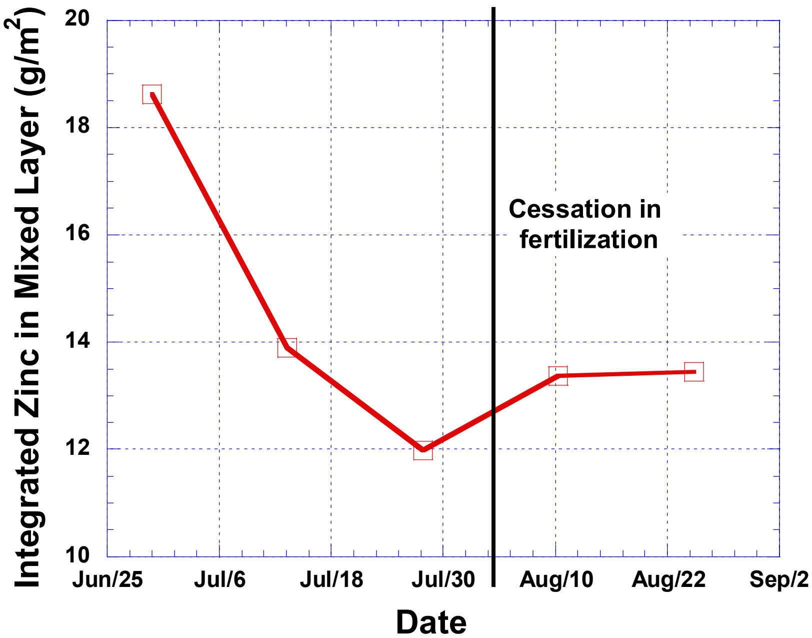

Figure 3-10: Integrated Zn in the surface mixed layer (upper 4 metres) before and after the cessation of fertilization of the Fish limnocorral

3.4 Characteristics of Faro and Vangorda Pit Lakes

Initial surveys were conducted for both the Faro and Vangorda pit lakes in order to supplement existing information on their physicochemical state and to facilitate determinations as to their potential to be bioremediated.

Vertical profiles of conductivity, temperature and fluorescence measured in the water column of each lake are presented in Figure 3-11 while profiles of dissolved oxygen (DO) and total zinc (T-Zn) are compared in Figure 3-12.

In contrast to Grum Lake, Faro and Vangorda Lakes appear to be permanently stratified. Faro Lake is characterized by two haloclines: one at 3-5 m depth and the other at approximately 15-20 m depth (Figure 3-11). The thermocline at 3-5 m depth coincides with the shallow halocline. In Vangorda Lake a strong halocline and thermocline exist at 2-3 m depth; the lower regions of the lake are compositionally homogenous. It is possible that the magnitude of the Vangorda halocline was influenced by the large addition of low conductivity water earlier in the season. Nevertheless, the associated density contrast must be a permanent feature of the lake given the existence of reducing conditions below.

Both Faro and Vangorda Lakes have suboxic bottom waters. The DO profiles (Figure 3-12) suggest that permanent stratification occurs at the lower halocline at 15-20 m depth (decoupled from the thermocline) in Faro Lake and at 2-3 m depth in Vangorda Lake (in association with the thermocline). Interestingly, the haloclines in Grum and Faro Lakes associated with the shallow thermoclines are relatively small in comparison to that of Vangorda. Presumably, the resulting pycnocline is too weak to prevent fall turn over in the mixed layer. While Grum Lake mixes top to bottom, Faro Lake turns over to its deeper halocline where the additional increase in density is a sufficient barrier to mixing thereby creating anoxic conditions below depths of 15 to 20 metres.

The DO profiles indicate that the lower water column in both Faro and Vangorda lakes is suboxic. Sampling artifacts (bottle exposed to atmosphere) resulted in the presence of measurable oxygen in the deep samples of both lakes. It is suspected that the measurement of oxygen in deep waters is erroneous given the ancillary data (*i.e.,* Fe, Mn etc), which suggest that suboxic conditions at depth prevail. Given the low levels of baseline productivity in each of these lakes, suboxia can only be achieved if the water column is permanently stratified.

The suggested permanent stratification and indeed, of the redox state, is reflected in the vertical profiles of the total zinc in both Faro and Vangorda pit lakes. Total zinc concentrations in the suboxic zone of the water column at Faro Lake are considerably lower than those in the oxic zone suggesting that some of the Zn inventory may have been removed through sulphate reduction and sulphide precipitation. The opposite applies to the Vangorda Lake where the total zinc concentrations in the suboxic zone are twice as high as those in the oxic zone. Despite the strong stratification, fully anoxic conditions do not prevail, as there is no evidence of sulphide precipitation. Worthy of note is the fact that total zinc concentrations in the water column of Vangorda Lake are one order of magnitude higher than those in either Faro or Grum Lakes.

Finally, the fluorescence data in Figure 3-11 suggest that, in contrast to Grum Lake, there is no ‘indigenous’ photosynthetic biomass present in the water column of Faro Lake and Vangorda Lake. The fluorescence measured in the water column of each lake is virtually zero.

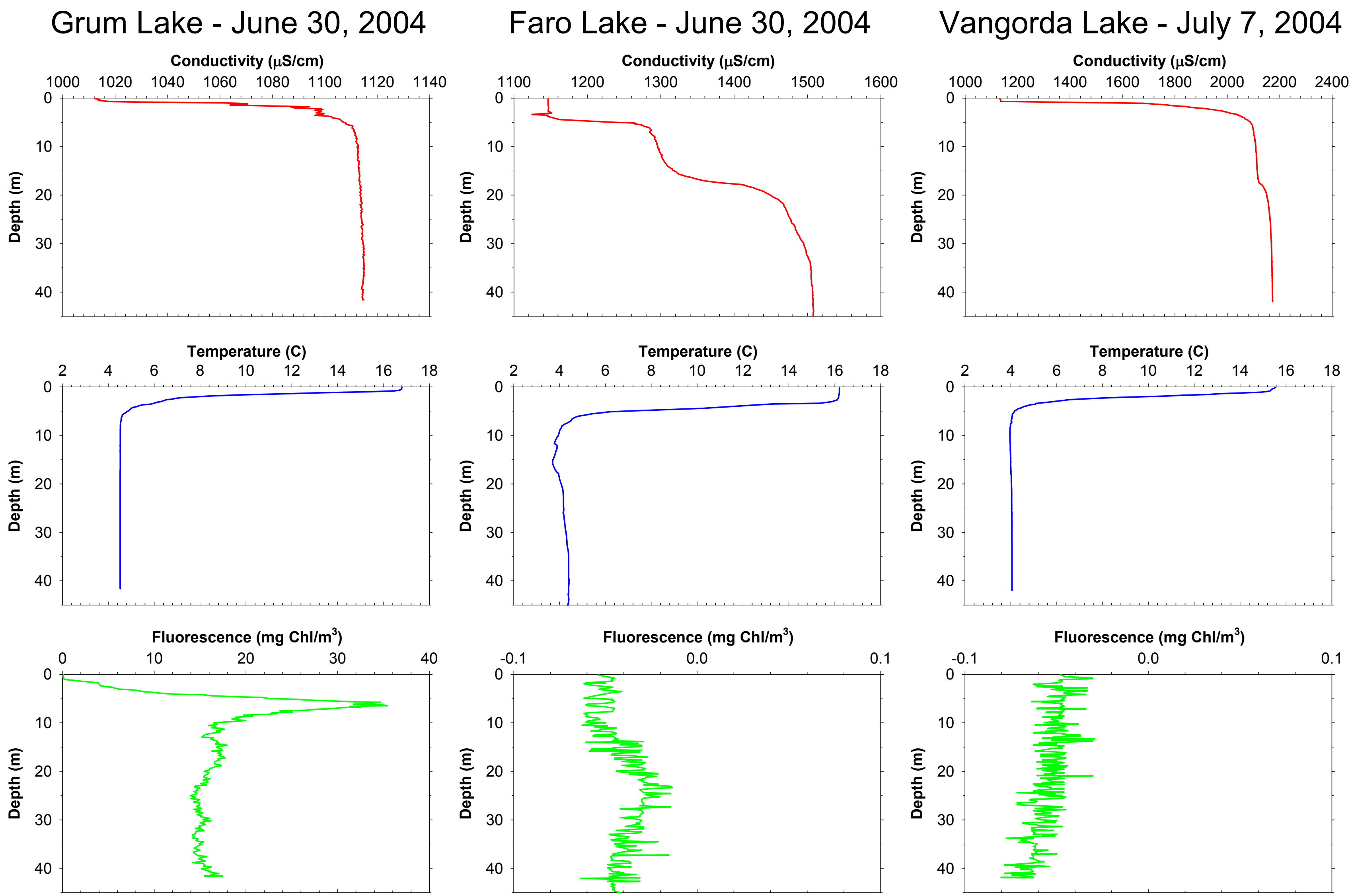

Figure 3-11: A Comparison of Water Column Characteristics of Grum, Faro and Vangorda Lakes.

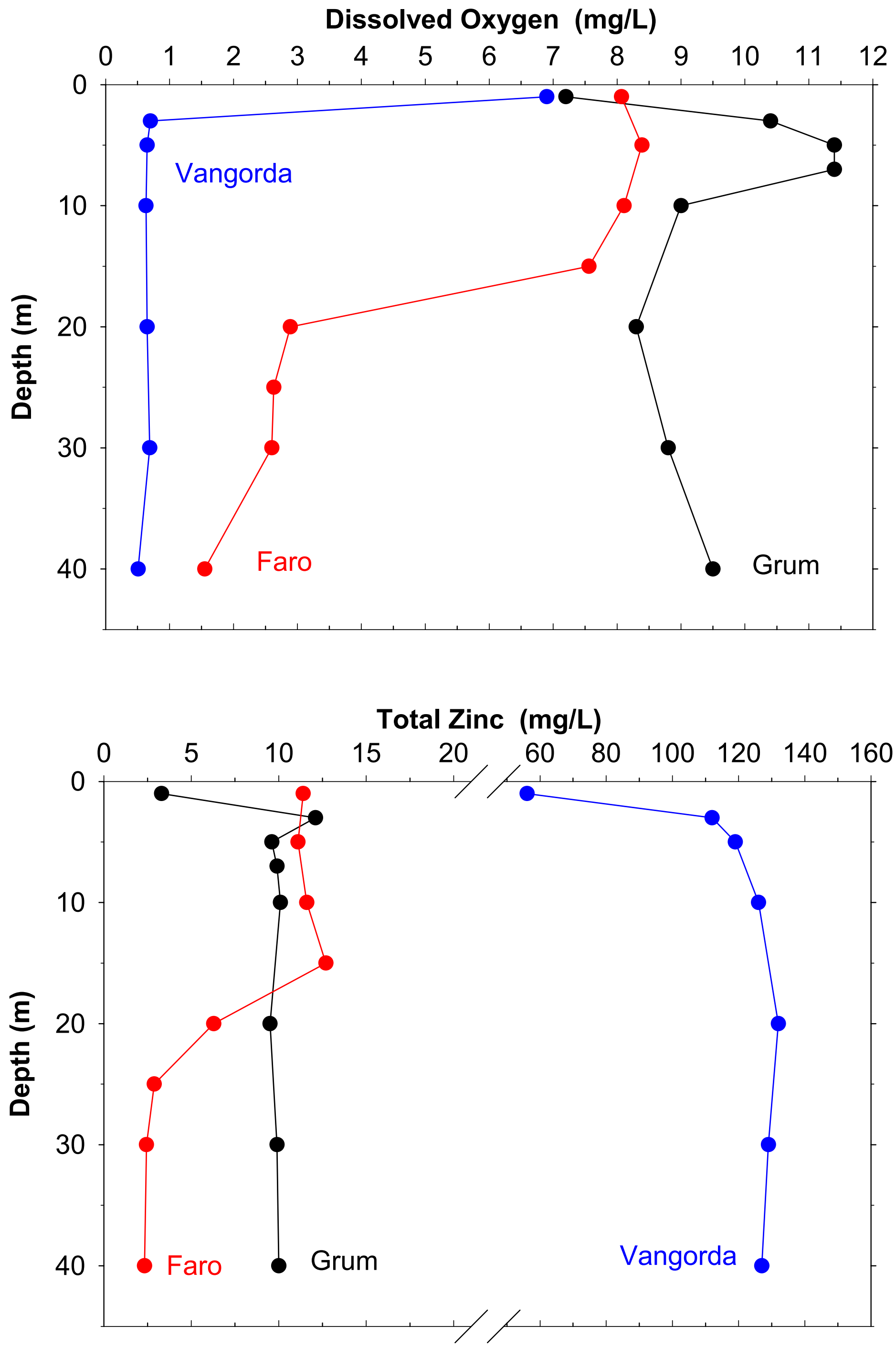

Figure 3-12: Profiles of dissolved oxygen and Total Zinc Concentrations in the Faro, Grum and Vangorda Pit Lakes.

4. Discussions

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4. Discussion

The investigation demonstrated Zn removal from the water column of Grum Pit Lake. There are two active removal mechanisms: 1) incorporation of Zn into the algal cell and, 2) uptake of dissolved Zn onto adsorption sites on cell surfaces. Both processes are followed by settlement of Zn-laden particulate organic matter out of the water column. However, the data clearly indicate that Zn uptake is restricted to surface water where algal growth occurs and not deeper in the water column despite a substantial flux of algal biomass settling through the water column. The implication is that algal cells have a finite inventory of binding sites, and even though they host enormous surface areas, the binding sites can become rapidly saturated in the presence of high concentrations of dissolved Zn. In other words, the transfer of dissolved Zn to particulate algal cells only occurs when rapid growth is underway as Zn uptake requires the formation of fresh adsorption sites. Thus, the growth rate is more important to metal removal than the abundance of algal cells. Algal abundance is more important to the creation of reducing conditions at depth in the water column and the commensurate removal of Zn through sulphide precipitation.

4.1 Comparison between Lake and Limnocorrals

The lake and the limnocorrals are well-coupled thermally and the limnocorrals do not appear to limit algal growth. The primary distinction arises in the very aspect the limnocorrals are designed to do: isolate a portion of the water column. Specifically, it was noted in Section 3.1 that the physical structure of Grum Lake evolves through the open water season through the continual addition of fresh water. In contrast, the limnocorrals isolated the surface layer at the time of their installation and as a result, conductivity remained relatively constant. The impact of dilution on the inventory of Zn is difficult to discern; however, the results show a net removal in the pit lake relative to the limnocorral.

4.2 Efficacy of Phytoremediation for Grum Lake

Grum Lake is very well poised for remediation; there is an existing standing stock of phytoplankton as evinced by the elevated fluorescence data throughout the water column and the visible presence of ice algae. Thus, there was no lag time in growth associated with nutrient addition; the lake was visibly green with a measurable increase in chlorophyll a one week after fertilization and within two weeks there was prolific algal growth. Subsequent fertilization campaigns would be expected to respond in the same rapid fashion.

It is unclear why Grum Lake is so well suited to growth of algae, however, it is suggested that the water column hosts a seasonally available and recycled inventory of nutrients. The source of this nutrient inventory is not immediately evident; however, the effectiveness of the fertilization program can in part be attributed to the strengthening of existing productivity cycles. As discussed below, this has important implications for the other two pit lakes.

An important implication of the base level of productivity in Grum Lake relates to the associated level of Zn removal which occurs in the absence of external fertilization. Evidence for such removal was seen in the control limnocorral in which Zn decreased from a starting concentration of ~5 mg/L to a final concentration approaching 3 mg/L early in the experiment. This degree of Zn removal is anticipated annually but is likely offset by Zn additions from pit wall runoff and seepage.

The chlorophyll a data from Grum Lake (Figure 3-3) mid season (where the algae display behaviour indicative of P limitation) suggest that the lake could accommodate more frequent fertilization than the weekly schedule dictated by the experiment; indeed, P concentrations were at or near detection limits throughout the experiment. More frequent additions or a continuous flow delivery system might accommodate more rapid algal growth. While the mixed layer Zn removal in Grum Lake would not necessarily be advanced by such a strategy (*i.e.,* total and dissolve Zn levels in the upper mixed layer are already very low), the higher organic flux rate could facilitate improved Zn removal at deeper depths by both providing more free adsorption sites in addition to providing a stronger driving force towards reducing conditions (and sulphide precipitation) at depth.

The current fertilization program has demonstrated that the mixed layer of Grum Lake (approximately 400,000 m^3) can be treated to the extent that release to the receiving environment could occur with minimal dilution achieving receiving water quality criteria for the protection of aquatic life.

Pulsed eutrophication (*i.e.,* addition of nutrient followed by cessation of nutrient addition) is not an effective remediation strategy for Grum Lake despite the fact that considerably quantities of Zn are removed from surface water. Rather, the most effective treatment strategy involves prolonging the algal growth season as long as practically possible.

The water column nitrogen data (nitrate, nitrite and ammonia) suggest that an alternate and more cost-effective liquid fertilizer with a lower nitrogen content could be used for future applications. A lower nitrogen mix would have the added benefit of improving surface water quality from a discharge perspective if progressive seasonal discharge of Grum Lake waters were deemed necessary.

Therefore, if the objective is to use whole-lake fertilization to treat sufficient water for annual discharge to the receiving environment, the current program would suffice. This notion is based on the observation that the upper two metres of water column (representing at least 400,000 m^3 at current size) can be treated to near-compliancy within one summer season.

Optimization of the nutrient delivery system could result in a cost effective treatment system. However, if the objective is to treat the entire water column for Zn or, to use Grum Lake as a treatment system for other site waters, a longer treatment time frame with the objective of inducing sulphate reduction at depth would be in order. Under such circumstances, engineering of the physical structure of the water column (*i.e.,* inducing salt stratification) could be beneficial in achieving this goal.

4.3 Efficacy of Phytoremediation for Faro and Vangorda Lakes

While considerably less data exists for either the Faro or Vangorda pit lakes, several generalized statements can be made regarding their amenabilities towards Zn mediation through fertilization.

Faro Lake

Unlike Grum Lake, Faro Lake does not have a population or resident algae; there is undetectable fluorescence in the water column (Figure 3-3). Accordingly, it would take considerably longer for a viable algal population to establish following the commencement of fertilization and a substantial portion of the ice-free growing season could be lost for Zn removal. However, a strategy involving the intentional maintenance of an over-wintering algal population similar to those found in Grum Lake could facilitate a rapid spring growth response. Strategic winter fertilization of the under-ice surface waters could be sufficient to foster spring growth of algae prior to ice break up such that rapid growth rates could be achieved shortly after the first open-water fertilizations. Indeed, the first nutrient addition could be dispersed on the ice surface prior to break up facilitating an early start to algal growth.

Faro Lake is considerably larger than Grum Lake and hosts a surface area three times the size (~600,000 m^2). The larger lake would require a commensurately larger nutrient load than either Grum or Vangorda Lakes.

Even though Faro Lake is stratified at depth, the upper 15 to 20 m of the water column resemble Grum Lake in that it turns over and oxygenates seasonally (Figure 3-9). In this regard, it is conceivable that in subsequent fertilization years, a resident population of algae could remain in the intermediate waters such that rapid algal growth could be realized with successive amendment seasons. Nutrient and algal biomass will be lost to the deep, stratified layer; however, this will foster more strongly reducing conditions at depth and more sulphide precipitation of Zn (and other metals) than presently occurs.

In essence, the primary limitation to fertilization of Faro pit lake is the absence of a standing crop of phytoplankton.

Vangorda Lake

Like Faro Lake, Vangorda Lake has a very small to non-existent standing crop of algae. It also has Zn concentrations more than one order of magnitude higher than either Grum or Faro Lakes. Despite these Zn concentrations, the laboratory study suggested that algae could grow in these waters (Microbial Technologies, 2004).

Vangorda Lake has extremely strong stratification due to a large salinity gradient in the 2 to 3 m depth range (the largest of the three lakes). While the magnitude of this halocline may have been increased by the unusually large quantity of water entering the system in the spring, this density feature likely exists year-round and governs the physical stability of the lake. It is the most likely driving force towards reducing conditions at depth (via the absence of atmospheric contact and reoxygenation) as there appears to be little to no productivity to drive a significant oxygen demand.

The relatively small size of Vangorda Lake makes it an appealing test case for fertilization. It would require similar or small quantities of fertilizer given its smaller surface area (120,000 m^2) and relatively thin mixed layer. Moreover, the near-suboxic conditions at depth offer the best potential for large-scale mitigation of Zn through the precipitation of ZnS. While deep waters host relatively high concentrations of Fe, ZnS precipitation can be expected to occur given the relative solubilities of ZnS and FeS (Postma, 1996).

However, like Faro Lake, Vangorda could take some time to respond to initial nutrient amendments given the absence of a microbial population. If a full-scale manipulation were to be considered, a strategy similar to that described for Faro Lake above should be considered.

A general strategy to be applied to these high latitude pit lakes where both light and nutrients limit growth would be as follows:

1. Facilitate growth of seed population of algae which can capitalize rapidly on available nutrient early in the growing season when light is plentiful. This might be accomplished through strategic fertilization/inoculations of lake surface waters through the ice in the spring once daylight hours become longer. Growth at this time will be slow due to low temperature, but the establishment of even a modest seed population will be advantageous.

2. Initiate the first fertilizations as early as possible in the growing season. The growing season is short but light conditions are not limiting. Thus, the first fertilization could be deposited directly on the ice such that the initial dose occurs at break up, a period on the lake normally difficult to access.

3. Since growth rate is important to Zn uptake, nutrient additions should be spaced as closely together as practically possible. Once established, the algae will consume nutrient rapidly and cycle between active growth and limitation if fertilization events are separated by too much time.

5. Conclusions

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5. Conclusions

Following is a suite of conclusions derived from the Grum Pit Lake fertilization program conducted during the open-water season in 2004.

- The limnocorrals used in this study represented good proxies for the physical and geochemical evolution of the Grum Pit Lake. The primary exception was related to the isolation of the surface layer from external input of surface runoff. Specifically, it became apparent that the seasonal evolution of Grum Lake surface water is influenced by fresh water input, either through seepage, precipitation or pitwall runoff.
- Amendment programs such as the addition of fish fertilizer or EDTA were not required to initiate algal growth in the Grum Pit Lake.
- Primary productivity in Grum Pit Lake responded very rapidly to fertilization due largely to the pre-existing seed population of algae in the water column. Chlorophyll a concentrations increased rapidly and the corresponding transition of dissolved Zn to the particulate fraction occurred within the first few weeks of fertilization. Subsequent settlement of Zn-laden particulate matter removed total Zn from the water column.
- Fresh algal cells were most effective in removing Zn from surface waters as settling organic matter did not appear to remove additional Zn from the water column below the thermocline. Accordingly, the growth rate of algae is more important to Zn uptake than the absolute concentration of algal cells.
- The fertilization program undertaken in Grum Pit Lake was sufficient to reduce total Zn concentrations to values that could be discharged to the receiving environment before degradation of the thermocline. The degradation of the thermocline in the fall facilitated mixing of Zn-rich water at depth into the surface layer thereby increasing the total Zn concentration.
- Despite several successions of algal populations, continued fertilization of Grum Pit Lake resulted in an overall net increase in chlorophyll a in the surface mixed layer. Accordingly, the best approach to bio-remediating Grum Lake involves initiating fertilization as early as possible in the spring to capitalize on as long a growing season as possible.
- Pulsed eutrophication is not recommended for Grum Pit Lake as the entire open-water growing period is required to maximized Zn removal.

The above points likely apply to the Faro and Vangorda Pit Lakes. Comments germane to these latter two systems are as follows:

- Seed population of algae does not appear to exist in either Faro or Vangorda Pit Lakes suggesting that algae may not be as quick to respond to nutrient additions as seen in Grum Pit Lake. However, once established, a standing crop is expected to persist through winter to allow rapid growth the following spring. Rapid growth conditions early in the year could be improved in these other pit lakes by pre-fertilizing the lake in the early spring before ice-free conditions occur. Under such conditions, remediation of both Faro and Vangorda Pit Lakes is feasible.
- Both Faro and Vangorda Pit Lakes are strongly stratified and appear to be seasonally, if not permanently, anoxic at depth. An additional benefit to fertilization of these two systems is the enhanced potential for onset to further reducing redox potential at depth and inducing sulphate reduction. Such a process would serve to further remove Zn from bottom waters in excess of the algal removal anticipated to occur in surface water.

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Appendices

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Appendix A

Date	Station	pH field	pH lab	Temp °C	Cond. µS/cm	D.O. mg/L	Secci m	Chlor a mg/m^3	TSS mg/L	Alk mg/L	NH_4-N mg/L	NO_3-N mg/L	NO_2-N mg/L	PO_4-P mg/L	T-Zn mg/L	D-Zn mg/L	P-Zn mg/L
6/30/04	GL_1	8.05		16.6	906	7.2	5	0.06	3.0	152	0.025	0.90	0.011	0.002	3.3	3.3	0.01
6/30/04	GL_3	7.56		13.2	975	10.4		0.48	3.0	168	0.024	0.85	0.002	0.002	12.1	9.6	2.55
6/30/04	GL_5	7.74		11.9	966	11.4		0.89	3.0	166	0.023	0.81	0.002	0.002	9.6	9.6	-0.04
6/30/04	GL_7	7.58		11.1	975	11.4		1.50	3.0	169	0.025	0.86	0.003	0.002	9.9	10.1	-0.25
6/30/04	GL_10	7.25		11.4	976	9.0		0.77	3.0	170	0.026	0.98	0.003	0.002	10.1	10.2	-0.10
6/30/04	GL_20	7.01		10.1	976	8.3		**0.55**	3.0	167	0.030	0.97	0.002	0.002	9.5	9.5	-0.01
6/30/04	GL_30	6.54		9.1	980	8.8			3.0	167	0.030	0.96	0.003	0.002	9.9	10.1	-0.23
6/30/04	GL_40	6.04		7.4	980	9.5			3.0	168	0.026	0.96	0.003	0.002	10.0	10.3	-0.30
7/14/04	GL_1	8.66		16.2	1169	9.7	0.5	8.60	5.8	169	0.036	1.09	0.009	0.002	3.9	1.3	2.57
7/14/04	GL_3	8.16		15.5	1189	1.9		4.25	6.8	170	0.046	1.03	0.008	0.002	5.5	4.3	1.25
7/14/04	GL_5	8.04		13.2	1304	9.8		1.62	3.0	182	0.027	0.79	0.004	0.002	10.8	10.2	0.60
7/14/04	GL_7	7.99		12.7	1324	10.8		15.70	3.0	185	0.028	0.88	0.003	0.003	11.4	11.2	0.20
7/14/04	GL_10	7.69		11.8	1364	7.8		13.50	3.0	185	0.050	0.94	0.003	0.004	11.4	10.9	0.50
7/14/04	GL_20	7.53		10.7	1414	7.5		**4.23**	3.0	186	0.025	0.95	0.003	0.002	10.5	10.5	0.00
7/14/04	GL_30	7.28		9.1	984	7.6			3.0	185	0.034	0.95	0.002	0.002	11.0	10.9	0.10
7/14/04	GL_40	7.28		8.4	986	7.3			3.0	183	0.050	0.94	0.003	0.005	11.6	11.0	0.60
7/28/04	GL_1	*8.73*		15.9	722	8.3	0.6	5.25	5.4	89	0.334	0.70	0.003	0.114	0.3	0.1	0.17
7/28/04	GL_3	*8.06*		13.6	768	8.0		1.81	3.0	159	0.051	1.01	0.007	0.010	3.8	3.6	0.22
7/28/04	GL_5	*7.80*		8.6	699	7.9		6.80	3.0	175	0.055	0.94	0.002	0.005	9.1	9.0	0.03
7/28/04	GL_7	*7.61*		8.2	688	7.8		6.80	3.0	170	0.041	0.94	0.002	0.004	8.9	9.1	-0.25
7/28/04	GL_10	*7.34*		8.0	697	7.8		2.29	3.0	168	0.576	0.94	0.003	0.005	9.4	8.9	0.43
7/28/04	GL_20	*7.44*		8.0	721	7.8		5.60	3.0	172	0.041	0.94	0.003	0.005	9.1	9.3	-0.25
7/28/04	GL_30	*7.29*		9.2	711	7.8		6.03	3.0	169	0.048	0.93	0.003	0.004	5.5	8.9	-3.39
7/28/04	GL_40	*7.28*		7.9	699	7.8		6.01	3.8	176	0.046	0.93	0.003	0.004	9.1	9.1	-0.02
8/11/04	GL_1	8.80	8.47	15.8		*7.9*	1.7	3.39	3.0	97	0.310	1.02	0.009	0.024	0.3	0.1	0.20
8/11/04	GL_3	7.96	8.24	13.2		*7.9*		8.45	6.2	146	0.270	1.02	0.009	0.004	3.2	3.1	0.16
8/11/04	GL_5	7.55	8.12	9.2		*7.3*		2.59	3.0	172	0.121	0.82	0.004	0.002	8.8	8.8	-0.05
8/11/04	GL_7	7.22	7.81	7.6		*7.0*		1.44	3.0	173	0.084	0.91	0.003	0.002	9.5	9.7	-0.23
8/11/04	GL_10	6.98	7.90	7.1		*7.4*		1.98	3.0	170	0.079	0.95	0.003	0.002	10.3	9.9	0.36
8/11/04	GL_20	7.35	7.92	10.4		*7.5*		1.71	3.0	170	0.069	0.90	0.004	0.002	10.0	9.9	0.12
8/11/04	GL_30	7.29	7.96	9.1		*7.6*		2.47	3.0	170	0.081	0.93	0.004	0.002	10.4	9.6	0.81
8/11/04	GL_40	*7.28*	7.97	*7.5*		*7.8*		1.80	3.0	172	0.088	0.88	0.005	0.002	9.3	9.4	-0.14
8/25/04	GL_1	9.03	8.50	13.3	856	7.4	0.9	5.35	6.5	115	0.477	1.28	0.013	0.045	0.9	0.4	0.49
8/25/04	GL_3	9.03	8.53	12.9	857	7.8		7.21	6.5	116	0.446	1.28	0.012	0.042	1.0	0.5	0.53
8/25/04	GL_5	7.79	7.90	13.2	987	6.7		4.05	3.0	173	0.116	0.86	0.004	0.002	12.4	11.7	0.70
8/25/04	GL_7	7.69	7.89	10.9	988	6.2		1.49	3.0	172	0.086	0.91	0.003	0.003	12.8	12.3	0.50
8/25/04	GL_10	7.69	7.91	9.3	992	7.0		1.38	3.0	170	0.083	0.92	0.003	0.003	12.2	12.2	0.00
8/25/04	GL_20	7.64	7.90	8.2	993	7.2		1.60	3.0	169	0.114	0.90	0.004	0.003	12.2	12.4	-0.20
8/25/04	GL_30	7.64	7.90	7.8	995	7.4		1.20	3.0	168	0.116	0.89	0.004	0.002	12.2	12.3	-0.10
8/25/04	GL_40	7.61	7.91	7.1	997	7.8		1.37	3.0	169	0.117	0.88	0.004	0.002	12.1	11.9	0.20
9/8/04 14:37	GL_0	8.61		8.5	990	10.0		13.70	8.0	130	0.317	1.36	0.013	0.012	1.9	0.9	1.01
9/8/04 14:37	GL_1	8.72		8.1	996	11.0	0.4	13.20	9.0	129	0.298	1.40	0.015	0.004	1.9	0.9	1.01
9/8/04 14:37	GL_2	8.69		8.3	993	10.9		17.60	7.0	129	0.333	1.36	0.013	0.035	1.9	0.8	1.10
9/8/04 14:37	GL_3	8.61		8.1	995	10.2		9.13	6.0	128	0.331	1.38	0.014	0.006	1.9	0.9	1.05
9/8/04 14:37	GL_5	7.66		7.5	1127	8.5		4.42	3.0	176	0.191	0.92	0.005	0.004	9.3	9.6	-0.24
9/8/04 14:37	GL_7	7.77		5.7	1138	7.9		0.17	3.0	174	0.104	0.94	0.004	0.004	10.0	8.9	1.12
9/8/04 14:37	GL_10	7.23		5.7	1137	8.0		1.28	3.0	171	0.105	0.94	0.004	0.004	8.6	8.9	-0.28
9/8/04 14:37	GL_20	7.85		6.8	1131	7.5		0.71	3.0	166	0.221	0.92	0.005	0.002	8.9	9.0	-0.18
9/8/04 14:37	GL_30	7.22		6.3	1140	6.7		3.32	3.0	168	0.156	0.92	0.005	0.002	9.1	9.4	-0.22
9/8/04 14:37	GL_40	*7.38*		*6.3*	*1135*	*7.3*		0.68	3.0	166	0.143	0.91	0.005	0.002	9.6	9.1	0.53
9/8/04 18:25	GL_0	8.71		8.4	993	10.9		14.20	5.0	129	0.293	1.36	0.014	0.010	2.0	0.9	1.10
9/8/04 18:25	GL_1	9.05		7.0	1000	10.4		10.60	8.5	127	0.288	1.36	0.013	0.011	2.0	0.8	1.19
9/8/04 18:25	GL_2	8.67		6.8	1000	9.6		14.70	9.5	130	0.298	1.35	0.013	0.007	2.0	0.8	1.23
9/8/04 18:25	GL_3	8.95		6.8	1001	10.1		8.39	6.5	130	0.385	1.36	0.014	0.008	2.0	0.8	1.23
9/8/04 18:25	GL_5	7.81		6.6	1113	8.5		2.10	3.0	176	0.186	0.94	0.005	0.005	10.1	10.0	0.10
9/8/04 18:25	GL_7	7.73		6.4	1133	8.4		6.45	3.0	173	0.092	0.95	0.004	0.007	10.3	10.3	0.00
9/8/04 18:25	GL_10	7.00		5.7	1138	7.8		5.36	5.0	172	0.084	0.94	0.005	0.004	10.4	10.0	0.40
9/8/04 18:25	GL_20	7.27		5.5	1141	7.4		2.72	3.0	167	0.104	0.93	0.006	0.003	10.5	10.3	0.20
9/8/04 18:25	GL_30	7.12		5.5	1142	6.9		0.84	3.0	169	0.109	0.93	0.006	0.003	10.2	10.1	0.10
9/8/04 18:25	GL_40	7.15		5.5	1144	6.8		0.96	3.0	164	0.117	0.92	0.005	0.002	9.9	9.1	0.79

Appendix B

Date	Station	pH field	pH lab	Temp °C	Cond. µS/cm	D.O. mg/L	Secci m	Chlor a mg/m^3	TSS mg/L	Alk mg/L	NH_4-N mg/L	NO_3-N mg/L	NO_2-N mg/L	PO_4-P mg/L	T-Zn mg/L	D-Zn mg/L	P-Zn mg/L
6/29/04	C_1	7.84		17.8	929	9.3	5.0	0.06	3.0	155	0.025	0.90	0.008	0.002	5.6	5.6	0.02
6/29/04	C_3	7.74		11.8	955	12.1		0.34	3.0	164	0.020	0.86	0.005	0.002	8.9	9.2	-0.32
6/29/04	C_5	7.56		9.2	976	12.9		0.47	3.0	169	0.027	0.90	0.002	0.002	10.3	11.2	-0.90
6/29/04	C_7	7.07		8.6	981	11.9		0.54	3.0	168	0.020	0.92	0.002	0.002	10.7	11.2	-0.50
6/29/04	C_10	6.63		7.5	984	10.2		0.45	3.0	169	0.021	0.97	0.002	0.002	10.7	10.3	0.40
6/29/04	C_13	6.28		6.6	985	10.1		0.53	3.0	168	0.029	0.97	0.003	0.002	11.0	11.3	-0.30
7/14/04	C_1	8.11		15.2	952	8.7	2.9	0.63	3.0	173	0.111	0.89	0.008	0.002	5.5	5.4	0.07
7/14/04	C_3	8.02		13.9	952	9.6		4.12	3.0	174	0.052	0.89	0.007	0.004	5.9	6.2	-0.29
7/14/04	C_5	7.91		8.7	981	13.4		13.20	3.0	183	0.027	0.85	0.002	0.002	10.1	10.1	0.00
7/14/04	C_7	7.49		7.7	983	11.4		12.70	3.0	187	0.027	0.87	0.003	0.002	10.1	10.2	-0.10
7/14/04	C_10	6.90		7.3	982	9.3		5.40	3.0	184	0.053	0.95	0.002	0.002	9.9	10.1	-0.22
7/14/04	C_13	6.52		6.9	990	9.4		0.71	3.0	184	0.044	0.96	0.003	0.002	10.5	10.6	-0.10
7/28/04	C_1	7.97		16.0	825	8.8	2.9	0.15	3.0	160	0.093	0.90	0.010	0.004	3.2	3.0	0.22
7/28/04	C_3	7.89		13.3	760	10.5		0.38	3.0	162	0.091	0.86	0.005	0.002	5.4	5.6	-0.14
7/28/04	C_5	7.90		9.3	708	11.7		1.17	3.0	166	0.058	0.82	0.003	0.002	8.8	8.9	-0.13
7/28/04	C_7	7.90		8.4	672	11.3		4.10	3.0	168	0.032	0.86	0.002	0.002	8.7	9.2	-0.45
7/28/04	C_10	7.82		7.7	659	9.5		7.69	3.0	167	0.042	0.96	0.002	0.003	8.9	8.9	0.01
7/28/04	C_13	7.87		7.4	678	8.9		3.51	3.4	174	0.042	0.94	0.003	0.004	9.2	8.9	0.37
8/11/04	C_1	7.83	8.07	15.3			4.0	0.61	3.0	162	0.096	0.88	0.010	0.002	3.4	3.3	0.06
8/11/04	C_3	7.57	8.08	13.3				0.91	3.0	164	0.081	0.85	0.007	0.002	5.5	5.4	0.13
8/11/04	C_5	*7.48*	8.05	9.4				0.26	3.0	171	0.099	0.80	0.002	0.002	9.6	9.5	0.02
8/11/04	C_7	7.39	8.04	7.4				1.84	3.0	168	0.064	0.86	0.002	0.002	9.8	9.8	0.01
8/11/04	C_10	7.25	7.87	7.3				1.41	3.0	170	0.064	0.94	0.002	0.002	10.1	10.3	-0.20
8/11/04	C_13	7.15	8.00	6.8				1.56	3.0	175	0.083	0.92	0.003	0.002	10.1	10.4	-0.30
8/25/04	C_1	8.26	7.86	11.5	963		4.5	0.56	3.0	160	0.099	0.89	0.010	0.002	3.9	3.8	0.02
8/25/04	C_3	8.34	7.99	12.5	961			0.45	3.0	163	0.098	0.88	0.010	0.002	3.9	3.9	-0.03
8/25/04	C_5	7.96	7.78	7.8	977			0.97	3.0	169	0.104	0.80	0.002	0.002	10.4	10.6	-0.20
8/25/04	C_7	7.76	7.78	6.4	978			0.86	3.0	174	0.098	0.86	0.002	0.002	10.8	10.7	0.10
8/25/04	C_10	7.65	7.78	6.2	992			1.16	3.0	166	0.077	0.93	0.002	0.002	10.6	10.5	0.10
8/25/04	C_13	7.66	7.84	6.1	995			0.99	3.0	170	0.089	0.91	0.003	0.003	11.6	11.5	0.10
9/8/04	C_1	8.05		7.5	1101	9.6	4.9										
9/8/04	C_3	8.14		7.5	1102	9.1											
9/8/04	C_5	7.75		6.9	1114	9.7											
9/8/04	C_7	7.21		5.5	1128	10.5											
9/8/04	C_10	6.99		5.3	1136	8.2											
9/8/04	C_13	6.90		5.2	1147	8.2											

interpolated data
detection limit
measured at 15 m depth