

# The Physical, Chemical and Biological Dynamics of Two Contrasting Pit Lakes: Implications for Pit Lake Bio-Remediation

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## Abstract

The Main Zone and Waterline pit lakes at the Equity Silver Mine near Houston, BC (Canada) are the sites of an ongoing 3-yr government- and industry-funded research program. The pits exhibit considerable contrasts in their physical, chemical and biological limnology. The Main Zone pit is deep (~120 m), maintains permanently oxygenated bottom waters, and hosts a modest level of phytoplankton productivity. In contrast, the Waterline pit is shallow (~40 m), exhibits negligible plankton productivity, and is characterized by permanent stratification and bottom water suboxia below a water depth of ~10 m. In order to assess the feasibility of various bio-remediation strategies, field-scale manipulations were conducted using limnocorrals. Two manipulation strategies were tested: 1) addition of algal nutrients (phosphate and nitrate) to Main Zone Pit surface waters; and 2) addition of nutrients (surface waters) and dissolved organic carbon (deep waters) to the Waterline Pit. Nutrient addition was conducted in order to stimulate algal production and enhance metal scavenging by biogenic particles, while dissolved organic carbon (ethanol) was added to increase oxygen demand and foster the development of sulphate reduction in pit bottom waters. In the Main Zone Pit, the stimulation of algal growth resulted in the pronounced removal of both dissolved and total metals (Zn, Cu and Cd) from surface waters, with higher rates of metal removal being observed at higher nutrient additions. Metal removal could be attributed to the scavenging of dissolved metals by biogenic particles and subsequent particle settling. A similar pattern of removal from surface waters was observed in Waterline Pit (Zn and Cd). The addition of ethanol to deep waters in Waterline Pit was effective in promoting sulphate reduction in the lower layer. The development of reducing conditions resulted in near-quantitative removal of dissolved Zn and Cd, presumably as secondary metal sulphides. Collectively, the results demonstrate that the passive forms of bioremediation tested in these pit lakes may be effective for whole pit-lake remediation.

KEY WORDS: Pit lake, Remediation, Mining

## INTRODUCTION

The Equity Silver Mine, located near Houston, B.C. (Canada), operated from 1980 through 1994. Gold- and Ag-bearing ores were extracted from three open pits as well as underground workings. Since mine closure in 1994, one of the pits (the Southern Tail Pit) has been backfilled with waste rock and tailings, while the Waterline and Main Zone pits were allowed to fill with a combination of groundwater, surface runoff and precipitation. Lakes now fill these latter two pits.

In order to further our understanding of these pit lake systems, a three-year research program was initiated by scientists at Lorax Environmental Services and the University of British Columbia, jointly sponsored by the Natural Sciences and Engineering Research Council (NSERC) of Canada and industry. The program entails characterization of the physical and chemical limnology of two pit lakes (year 1), the testing of various remediation strategies using limnocorrals (year 2), and refinement of a coupled physical-geochemical model (year 3).

The following paper presents results from years 1 and 2, which describe the physical, chemical and biological characteristics of these pits, as well as presents data for a series of field-scale water-column manipulations designed to assess the feasibility of bioremediation strategies for trace metals (Zn, Cu, Ni, As and Cd).

## **FIELD AND ANALYTICAL METHODS**

Rafts were constructed in both the MainZone and Waterline pits to serve as floating supports for limnocorrals, as well as for a sample collection for pit-lake characterization (Figure 1). Rafts were constructed from untreated timber and Styrofoam SM insulation and secured to the tops of the pit walls at four points. The rafts also housed meteorological stations that incorporated wind speed, wind direction, and temperature sensors.

Profiling of a variety of physical parameters was carried out using a Seabird CTD (Conductivity, Temperature and Depth meter). In addition to the standard sensors of conductivity, temperature and pressure (which can be converted to depth), the instrument was outfitted with a fluorometer and a transmissometer. The fluorometer measures *in situ* fluorescence, which can be correlated to the concentration of chlorophyll *a*, while the transmissometer measures light transmission, which is related to suspended matter concentration.

Pit-lake water samples were collected using a 5-L Go-Flo bottle using a hand-operated winch outfitted with a trace-metal-clean Kevlar line. Sample processing was carried out immediately after sample collection. Nutrient and metal samples were collected in acid-washed LDPE bottles. Dissolved samples were filtered through 0.45 µm acid-washed cellulose-acetate filters. Samples for chlorophyll *a* were collected by filtering 100-500 mL of water through 25 mm GFF filters. Nutrient and chlorophyll samples were kept cold in coolers during sampling and transported to the laboratory where they were frozen within 6 hours of collection. Dissolved oxygen was determined on selected samples in duplicate by the Winkler method (Parsons et al., 2001). Metal concentrations were determined by ICP-MS by the methods of Martin et al. (2001).

Limnocorrals were constructed from pieces of untinted polyethylene tarp material which were sewn along the long side to form a tube 1.8 m (i.d.) x 12 m long (Figure 1). One-cm diameter PEX-pipe support rings were inserted into 8-cm sleeves placed every 2 m along the tube to ensure the tube maintained a cylindrical shape. Floatation was provided from six 15 cm-diameter Ethafoam™ logs (90 cm long) that formed a hexagonal shape upon insertion into pre-sewn sleeves. Support rings extending 30 cm above the lake surface were constructed from two 1.8-m diameter rings (5-cm diameter polyethylene), separated by 20-cm of 15 cm-diameter Ethafoam™. Eight limnocorrals were fastened to the MainZone raft (Figure 1), while four limnocorrals were attached to each of two rafts on the Waterline Pit. Two limnocorrals were used as controls on each pit, while the remaining six were used for different water column manipulations.

The MainZone limnocorrals were sampled using an integrated water sampler (Sutherland *et al.*, 1992) that collected samples that integrated the water column from 0-1.2 m, 1.2-2.7 m, 2.7-5.7 m and 5.7 m-8.7 m. The Waterline limnocorrals were sampled using a peristaltic pump (6 mm-diameter Tygon tubing ) and were sampled at discrete depths of 0, 3, 6, 8 and 9 m. This approach minimized the introduction of dissolved O<sub>2</sub> into the deep waters. Dissolved samples were filtered using 0.45 µm cellulose acetate filters. Samples were collected for total and dissolved metals. Metal samples were acidified to pH = 2 using environmental-grade nitric acid. Total and dissolved metals (Ni, Cu, Zn, Cd) were measured via inductively-coupled mass spectrophotometry (ICP-MS) as described by Martin et al. (2001).

## **LIMNOCORRAL MANIPULATIONS**

Experimental manipulations of the water column in MainZone and Waterline pits were conducted using limnocorrals. Limnocorrals are experimental enclosures which physically isolate a column of water, and allow for the testing of multiple whole-lake treatments at comparatively-low cost (Figure 1). Two remediation pathways were tested: 1) removal of metals from surface waters via metals sorption to particles and subsequent particle settling; and 2) removal of

metals from deep waters via precipitation of sulphide minerals. Settling particles, especially organic aggregates, play a dominant role in the binding and transfer of heavy metals to lake sediments, thereby regulating the concentrations of dissolved species in surface waters (Nriagu *et al.*, 1981; Sigg, 1985; Jackson and Bistricki, 1995). Many trace metals (*e.g.* Cu, Pb, Hg, Cd, Zn) readily react with free sulphide in reducing environments to form insoluble metal sulphides. Manipulations were designed to enhance these removal.

Water column manipulation in the MainZone Pit consisted of weekly fertilization with nitrate and phosphate (at a molar ratio of 10:1), with nutrient doses similar to those described by Schindler *et al.* (1971) (Table 1). Fertilization of Main Zone Pit limnocorrals was conducted to encourage both: 1) the scavenging of dissolved metals by biogenic particles; and 2) the removal of metals via particle settling. Of the eight limnocorrals in Waterline Pit, two were used as controls (no nutrients added), three received low levels of nutrients ( $0.7 \text{ mmol P m}^{-2} \text{ wk}^{-1}$ ), while the remaining three received higher levels of nutrients ( $1.4$  to  $14 \text{ mmol P m}^{-2} \text{ wk}^{-1}$ ) (Table 1).

The manipulation of limnocorrals in Waterline Pit involved both fertilization and the addition of ethanol (Table 1). Fertilization was conducted to encourage: 1) the scavenging of dissolved metals by biogenic particles; 2) the removal of metals via particle settling; and 3) the development of reducing conditions (*i.e.*, sulphate reduction) in bottom waters associated with the breakdown (*i.e.*, oxidation) of settling organic detritus. The Waterline Pit is strongly suboxic below depths of  $\sim 5$ - $10 \text{ m}$ , and is therefore poised at the sulphate-reduction redox boundary. Hydrogen sulphide ( $\text{H}_2\text{S}$ ), which is a direct product of sulphate reduction, reacts rapidly with many trace metals to form insoluble sulphide minerals. In this manner, the effectiveness of metal sulphide removal could be assessed. Of particular interest was to monitor the response of dissolved arsenic, which is present in high concentrations in the suboxic layer.

In order to accelerate the onset of reducing conditions in the Waterline limnocorrals, dissolved organic matter (ethanol) was added

directly after one month of fertilization to two limnocorrals that had received high nutrient additions (Table 1). Specifically,  $500 \text{ mL}$  of ethanol was injected into the suboxic layer in order to stimulate sulphate reduction in the pit bottom waters. Ethanol represents a labile source of organic carbon that is readily oxidized by bacteria. Therefore, the addition of ethanol increases the oxygen demand and drives the redox regime towards more reducing conditions.

## **RESULTS AND DISCUSSION**

### **Pit Lake Characterization**

The Main Zone Pit lake is  $\sim 400 \text{ m}$  by  $800 \text{ m}$  and has a maximum water depth of  $\sim 120 \text{ m}$ . ARD neutralization sludges are discharged periodically to the surface waters of the lake ( $\sim 5 \text{ L/s}$ ). The ARD emanates as surface runoff from pyrite-rich waste dumps on the minesite. The discharge of hydroxide sludge has a pronounced effect of the physical limnology of the Main Zone pit. Specifically, the input of dense oxygen-rich effluents, and their rapid sinking, act to mix the lake water column and sustain oxygenated bottom waters throughout the year (Figure 2). The sludge inputs manifest as a plume of metal-rich particulate matter, which is evident from depths extending from  $\sim 70 \text{ m}$  to the pit bottom ( $\sim 120 \text{ m}$ ) as revealed by reduced light transmission (Figures 2). The metal-rich sludge inputs are also manifested as elevated levels of total metals (*e.g.*, Zn, Cu, Cd and As) in the pit bottom waters (Figure 3). Thermal stratification develops during the summer period in the upper  $10 \text{ m}$  of the water column in response to solar heating (Figure 2).

Main Zone surface waters are characterized by surface enrichments of dissolved metals (Zn, Cu, Cd, As) (Figure 3). The available evidence suggests that such enrichment stems from pit wall sources. Sludge inputs do not appear to result in increases in dissolved metal levels either in the surface waters or in deep waters. Evidence for this stems from two sources. First, metal concentrations in Main Zone pit surface waters are of a similar magnitude to those in the surface waters of the Waterline pit, which is immediately upstream of the Main Zone pit and has had no sludge discharged into it. Second, there is no

indication of dissolved metal enrichment in the deep waters of the Main Zone pit, despite extremely high concentrations of particulate, sludge-derived metals (Figure 3).

Dissolved metal concentrations in Main Zone surface waters are naturally attenuated over the summer season. Concentrations of dissolved Zn, Cu and Cd exhibited pronounced decreases between June and October (2001) which can not be accounted for by dilutionary influences alone (Figure 4). The data suggest that such removal can be attributed to the scavenging of dissolved metals by biogenic particles (*i.e.*, phytoplankton). Fluorescence profiles reveal the presence of a chlorophyll maximum in the upper 10 m of the water column, and indicate that the Main Zone pit hosts natural phytoplankton communities. Zinc, Cu and Cd are actively involved in phytoplankton productivity cycles via incorporation into algal cells (*i.e.*, for physiological requirements) and sorption to algal surfaces (Reynolds and Hamilton-Taylor, 1992).

The Waterline Pit lake, immediately to the north, is ~150 m wide by ~500 m long and is ~40 m deep. No sludge is discharged to the Waterline Pit. The water level in the Waterline Pit is controlled by a spillway, with surface waters overflowing into the Main Zone Pit (5-10 L/s during the summer). In contrast to the Main Zone Pit, the water column of the Waterline Pit is strongly stratified throughout the year. An oxic surface layer extends down to depths ranging seasonally from ~5 to ~10 m, below which, dissolved oxygen is undetectable (Figure 5). As observed in the Main Zone pit, thermal stratification develops during the summer period in the upper 10 m of the water column (Figure 5).

Unlike the Main Zone pit, the Waterline pit is poorly productive. Low and invariant fluorescence values throughout the water column reflect extremely-low algal biomass (Figure 5). A minor chlorophyll peak, however, can be observed between 2 and 3 m depth. Productivity in the Waterline Pit is likely limited by the availability of phosphorus (Schindler, 1971). This explanation requires that there be a source of phosphate to the Main Zone pit that is not available to the Waterline pit. One such possible

source of phosphate is the hydroxide sludge delivered to the Main Zone pit lake. The reduced light transmission in the surface mixed layer likely represents the combined influences of minor plankton biomass, and colloidal Fe(III) oxides which precipitate at the oxic/suboxic boundary and which are resuspended into the surface layer (Figure 5).

The vertical distributions of trace metals in the Waterline pit contrast greatly from the Main Zone pit. The suboxic redox regime profoundly influences the behavior of redox-sensitive elements. Dissolved Fe values, for example, increase markedly across the oxic/suboxic boundary to levels of ~40 mg/L in bottom waters (Figure 6). High levels of dissolved Fe are presumably maintained via the reductive dissolution of Fe (oxy)hydroxides. Dissolved As exhibits a similar pattern of bottom water enrichment, with values reaching ~2,000 mg/L in the deep waters (Figure 6). The data suggest As concentrations are controlled the redox cycling of Fe, and is consistent with As behaviour observed in other mining-impacted systems (Azcue *et al.*, 1994; McCreadie *et al.*, 2000; Martin and Pedersen, 2002).

The Waterline pit exhibits elevated levels of Zn, predominantly as dissolved species, throughout the water column (Figure 6). Concentrations exceed 800 µg/L in bottom waters. Copper and Cd are characterized by only minor enrichments in surface waters. Below the surface mixed-layer, levels of dissolved Cu and Cd exhibit pronounced decreases (Figure 6). The decreases likely represent the removal of Cu and Cd from solution as insoluble sulphide minerals (*i.e.*, CuS and CdS). Although free sulphide was undetectable (<32 µg/L) in the bottom waters of the Waterline pit, sulphide precipitation cannot be ruled out. Indeed, CuS (-log K = 36.1) and CdS (-log K = 27.0) are extremely insoluble, and may precipitate at free-sulphide concentrations less than the limit of analytical detection (Stumm and Morgan, 1981).

### ***Limnocorral Results***

Natural phytoplankton populations in Main Zone Pit limnocorrals responded rapidly to fertilization

with phosphate and nitrate (Figure 7). In the low-nutrient addition scenario, a chlorophyll peak in the near surface became evident within 5 days of fertilization (July 2), and after 11 days (July 8), the presence of primary producers in the uppermost 2 m was well defined. A similar pattern was observed for the med/high-nutrient case, although the magnitude of the chlorophyll peaks were more pronounced (Figure 7). The near-surface chlorophyll maxima observed in the low and med/high nutrient scenarios contrast greatly with the control, which generally exhibited fluorescence peaks <5 in the upper 2 m of the water column. The generally increasing fluorescence values with depth in the control reflect the presence of primary producers in the subsurface, primarily below water depths of 2 m (Figure 7). Collectively, the fluorescence data imply that plankton productivity in surface waters was effectively enhanced via nutrient addition.

Enhanced phytoplankton production in the low and med/high-nutrient additions had a marked effect on metal distributions in comparison to the control. Two months post-fertilization, dissolved Zn concentrations in the near surface had decreased from ~250  $\mu\text{g/L}$  (control value) to 10  $\mu\text{g/L}$  and <2  $\mu\text{g/L}$  in the low- and med/high-nutrient scenarios, respectively (Figure 8). Similarly, total Zn levels decreased from ~250  $\mu\text{g/L}$  to ~100  $\mu\text{g/L}$  in the low-nutrient case over this time period (Figure 8). The med/high-nutrient limnocorrals exhibit a higher degree of total-Zn removal, with values decreasing to ~30  $\mu\text{g/L}$  (removal of ~80% Total-Zn in comparison to the control). The removal of both dissolved and particulate Zn can be attributed to the scavenging of dissolved Zn by biogenic particles and subsequent particle settling. The higher rates of metal removal in the med/high-nutrient scenario relate to the greater concentration of particles, and associated increased particle flux to deep waters. The effectiveness of Zn removal can be related to the affinity of Zn for organic particles, in which Zn is both actively assimilated by phytoplankton and sorbed to algal surfaces (Sigg, 1985; Reynolds and Hamilton-Taylor, 1992).

A similar pattern of metal removal was observed for Cu. The stimulation of algal production

resulted in near-quantitative removal of dissolved Cu in both the low- and med/high-nutrient limnocorrals two months post-fertilization (Figure 8). Pronounced removal of particulate Cu was also evident, particularly in the med/high nutrient case. Total Cu levels for the latter decreased from ~5 to <1  $\mu\text{g/L}$  after two months of stimulated algal production (Figure 8). Like Zn, Cu strongly associates with organic matter in lacustrine settings (Reynolds and Hamilton-Taylor, 1992). Cadmium was characterized by a similar, although less pronounced, pattern of removal to Cu (Figure 8).

In contrast to the Main Zone Pit, background levels of phytoplankton production in the Waterline Pit are negligible. Fluorescence values in the control limnocorrals remained low through the pre- and post-fertilization period (Figure 9). Fluorescence profiles for August 28 and September 17 show pronounced chlorophyll production in the upper 5 m of the water column in response to nutrient addition (Figure 9). The data indicate that naturally occurring phytoplankton populations can be effectively stimulated despite elevated levels of metals in surface waters (*e.g.*,  $[\text{Zn}]_{\text{aq}} = 600 \mu\text{g/L}$ ). The addition of ethanol was effective in promoting sulphate reduction in the lower layer. Free  $\text{H}_2\text{S}$  was detected in samples collected below 5 m one month post ethanol-addition. Water samples in the anoxic zone were also shown to contain sulphate-reducing bacteria (Susan Baldwin, pers. comm.). In contrast, free  $\text{H}_2\text{S}$  remained undetectable in the controls.

The combination of fertilization and ethanol addition had a pronounced effect on metal distributions in comparison to the controls. Dissolved Zn concentrations in surface waters were reduced from ~600  $\mu\text{g/L}$  to ~150  $\mu\text{g/L}$  over the two month manipulation period (Figure 10). The removal of dissolved Zn can be attributed to the scavenging of dissolved Zn by biogenic particles and subsequent particle settling. Pronounced depletion of dissolved Zn also occurred in the anoxic zone (Figure 10). The near-quantitative removal of dissolved Zn below 5 m undoubtedly reflects the precipitation of secondary Zn-sulphides (*e.g.*, sphalerite) in the anoxic waters.

Copper profiles in Waterline limnocorrals do not reveal any evidence of metal removal, and may relate to the very low concentrations of Cu present in both the control and treatment scenarios ( $[Cu] \cong 1 \mu\text{g/L}$ ) (Figure 10). We speculate that the dissolved copper may be present in a species that is unavailable for either passive or active uptake by phytoplankton. Strong copper-binding organic ligands in solution could prevent such uptake. Conversely, Cd exhibits a similar pattern of removal as observed for Zn (Figure 10). Particle scavenging and settling mechanisms contributed to decreases in total and dissolved Cd levels in surface waters of ~50% and 70%, respectively. Enhanced removal of dissolved Cd below 5 m can be attributed to the formation of authigenic  $\text{CdS}_{(s)}$ . The decrease in dissolved Cd concentration below 5 m in the control limnocorral suggests that sulphide precipitation is also occurring in the non-manipulated water columns (Figure 10). Similar profiles of Cu in the control also support the latter inference that sulphide precipitation is occurring naturally in the Waterline bottom waters (Figure 10). Such conclusions are supported by independent profiles collected in the Waterline water column (Figure 6).

Iron and As profiles exhibit no evidence of removal from either surface waters or bottom waters (Figure 11). High Fe concentrations (~10 mg/L) in the anoxic horizons may obscure Fe removal as Fe-sulphides. The lack of arsenic removal can be explained by the relatively-high solubility of As-sulphide in comparison to other metals present (e.g., Fe, Zn). In addition to the formation of discrete sulphide phases, As can also coprecipitate with Fe monosulphides and pyrite (Huerta-Diaz *et al.*, 1998). However, such mechanisms appear to be quantitatively insignificant in both the control and manipulated water-column scenarios.

### **IMPLICATIONS FOR PIT LAKE REMEDIATION**

For the limnocorral data presented herein, modest nutrient amendments resulted in the effective removal of metals from surface waters. The removal mechanism is a two-stage process, in which metals are first sequestered to biogenic particles, followed by export from the surface

layer via particle settling. In particular, fertilization appears to have considerable benefit with respect to Zn, Cu and Cd, all of which have a strong affinity for biological particles (e.g., active cellular uptake, sorption to algal surfaces).

The increased production of  $\text{H}_2\text{S}$  in the bottom waters of Waterline Pit fostered by the addition of dissolved organic carbon (ethanol) resulted in the enhanced removal of Zn and Cd as authigenic sulphide minerals (i.e., ZnS, CdS). This passive form of bio-remediation is utilized in other forms of anaerobic wastewater treatment which utilize sulphate reducing bacteria, including bio-reactors (Zaluski *et al.*, 2000), wetlands (Sobolewski, 1999) and reactive walls (Benner, 2002).

The results from the limnocorral experiments have relevance to pit lake management at Equity and elsewhere. First, both metal sorption to particles and particle settling act to reduce the bioavailability (and hence toxicity) of metals to aquatic organisms. The export of particulates (via settling) from surface waters removes metals from the available pool, while the sorption of metals to particulates reduces their bioavailability (Campbell, 1995). Both of these processes also have relevance within the regulatory framework. Mining effluents are typically regulated with respect to both water quality (e.g., total metal levels) and toxicity (e.g., LC50 with respect to *D. magna*). The results also indicate that significant improvements to surface-water quality can be achieved within a two-month fertilization period. Similarly, the results indicate that sulphide removal mechanisms can be enhanced rapidly (e.g., within weeks) via the addition of labile organic carbon (ethanol).

In order to test the effectiveness of whole-lake bioremediation, fertilization of the entire Waterline Pit Lake has been proposed. This lake was selected for whole-lake manipulation for several reasons: 1) Waterline is poised well for metal removal from both surface (via biogenic scavenging) and deep waters (via sulphide precipitation); 2) the Main Zone pit is located downgradient of Waterline and will therefore provide an effective buffer for any nutrient inputs which may escape from Waterline surface waters; 3) unlike the Main Zone, the Waterline Pit does

not receive sludge discharges, and therefore offers a more controllable setting for experimental manipulation; 4) Waterline appears to be in steady-state, which will allow more accurate delineation and quantification of the processes governing metal behaviour; and 5) the small size of Waterline will minimize fertilizer costs and monitoring requirements.

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Table 1. Timelines for limnocorrals manipulations in Main Zone and Waterline Pits

Pit Lake	Event	Date
Main Zone	Limnocorrals installed	June 24, 2002
	Manipulations:	
	• Controls: no nutrient addition	June 27 to September 30, 2002
	• Low nutrient addition: $0.7 \text{ mmol P m}^{-2} \text{ wk}^{-1}$	June 27 to September 30, 2002
	• Medium/high nutrient addition: $1.4 \text{ mmol P m}^{-2} \text{ wk}^{-1}$ : $14 \text{ mmol P m}^{-2} \text{ wk}^{-1}$	June 27 to July 31, 2002 August 1 to September 30, 2002
Waterline	Limnocorrals installed	July 10, 2002
	Manipulations:	
	• Controls: no nutrient addition	July 12 to September 30, 2002
	• Medium nutrient addition: $1.4 \text{ mmol P m}^{-2} \text{ wk}^{-1}$	July 12 to July 31, 2002
	• High nutrient addition: $14 \text{ mmol P m}^{-2} \text{ wk}^{-1}$	August 1 to September 30, 2002
	• Ethanol addition (to two high-nutrient limnocorrals)	August 8, 2002

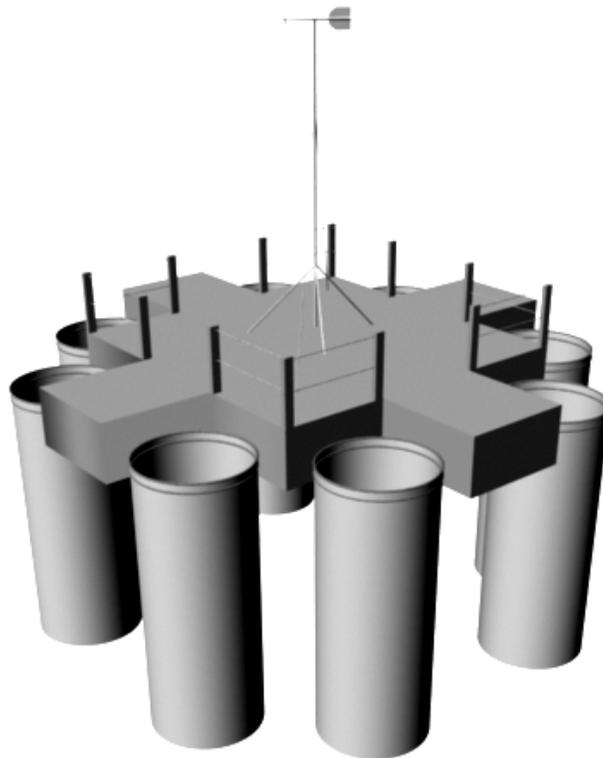


Figure 1. Schematic of floating platform and limnocorral arrangement for the Main Zone Pit.

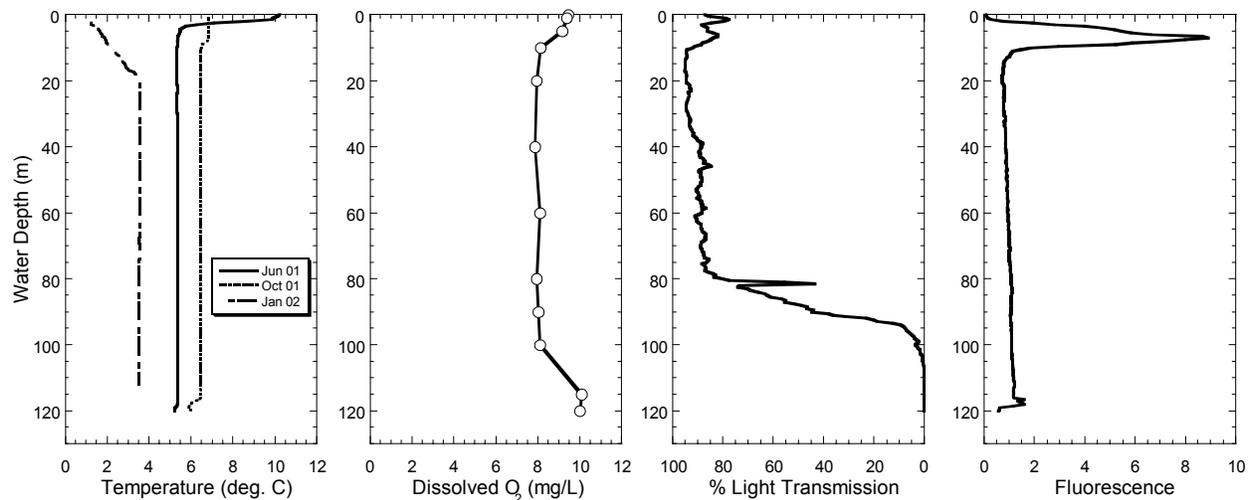


Figure 2. Depth distributions of temperature, dissolved oxygen % light transmission and fluorescence in the Main Zone Pit (June 2001). Temperature profiles for October 2001 and January 2002 are also presented.

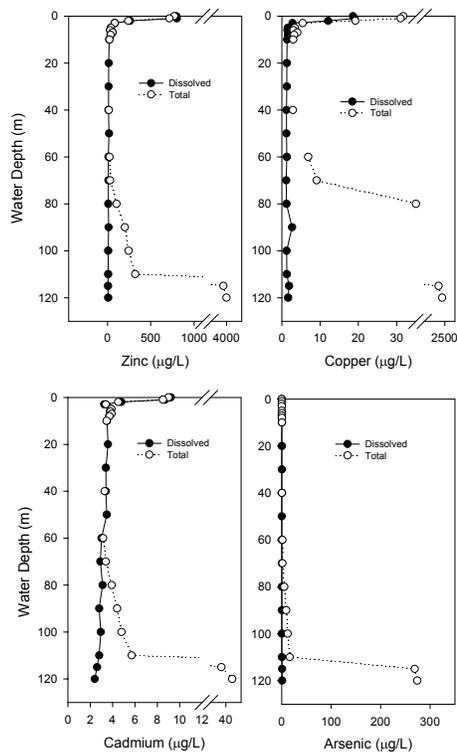


Figure 3. Water column distributions of total and dissolved Zn, Cu, Cd and As in the Main Zone Pit (June 2001).

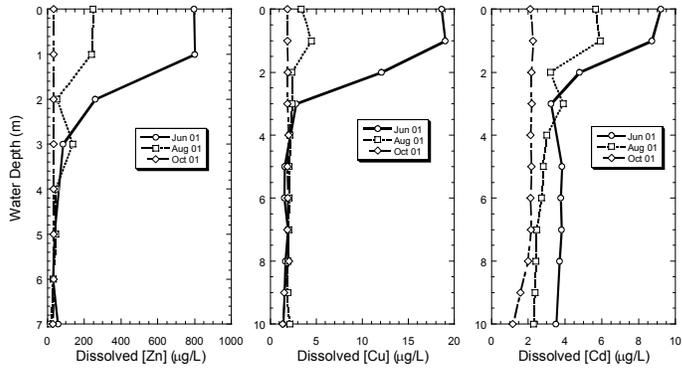


Figure 4. Depth distributions (upper 10 m of the water column) of dissolved Zn, Cu and Cd in the Waterline Pit for June, August and October (2001).

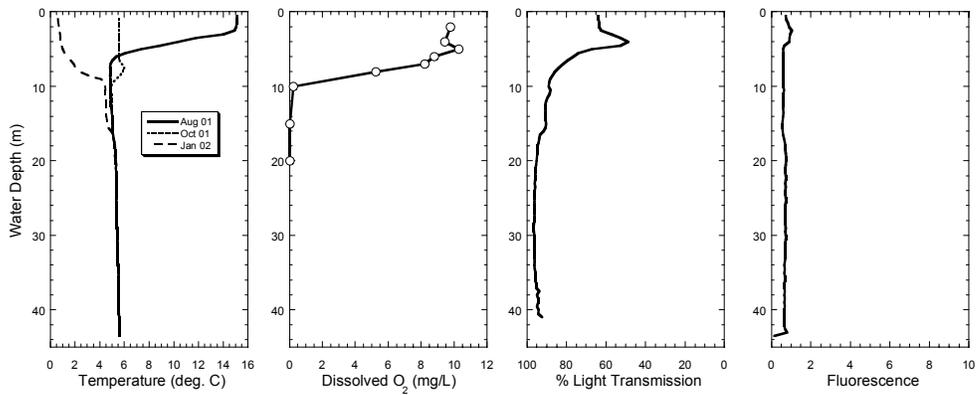


Figure 5. Depth distributions of temperature, dissolved oxygen, % light transmission and fluorescence in the Waterline Pit (August 2001). Temperature profiles for October 2001 and January 2002 are also presented.

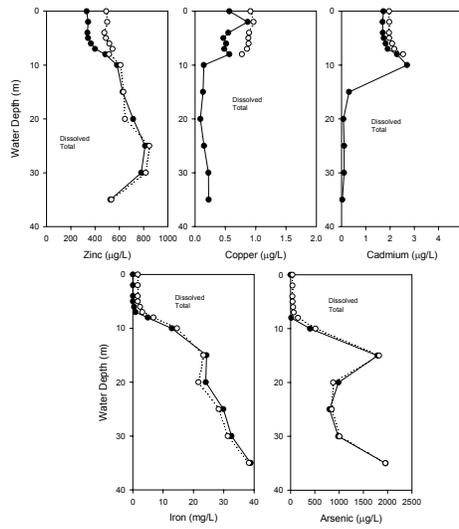


Figure 6. Water column distributions of total and dissolved Zn, Cu, Cd, Fe and As in the in the Waterline Pit (October 2001). Note: values for total Cu and Cd below 10 m were not available.

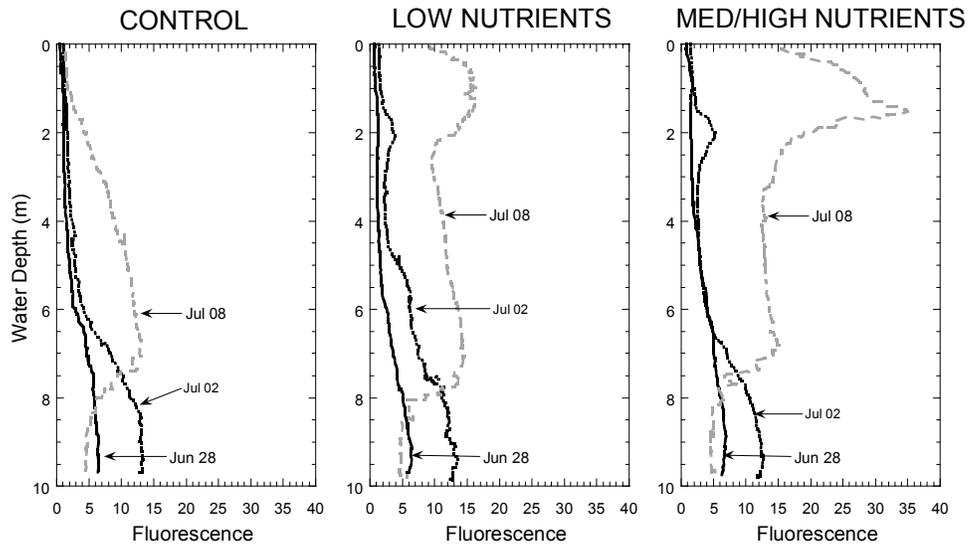


Figure 7: Limnocorrals profiles for fluorescence (a proxy for algal biomass) in the control, low-nutrient and med/high-nutrient treatments in Main Zone Pit following fertilization on June 27, 2002. Fluorescence units are roughly equivalent to  $\mu\text{g/L}$  chlorophyll.

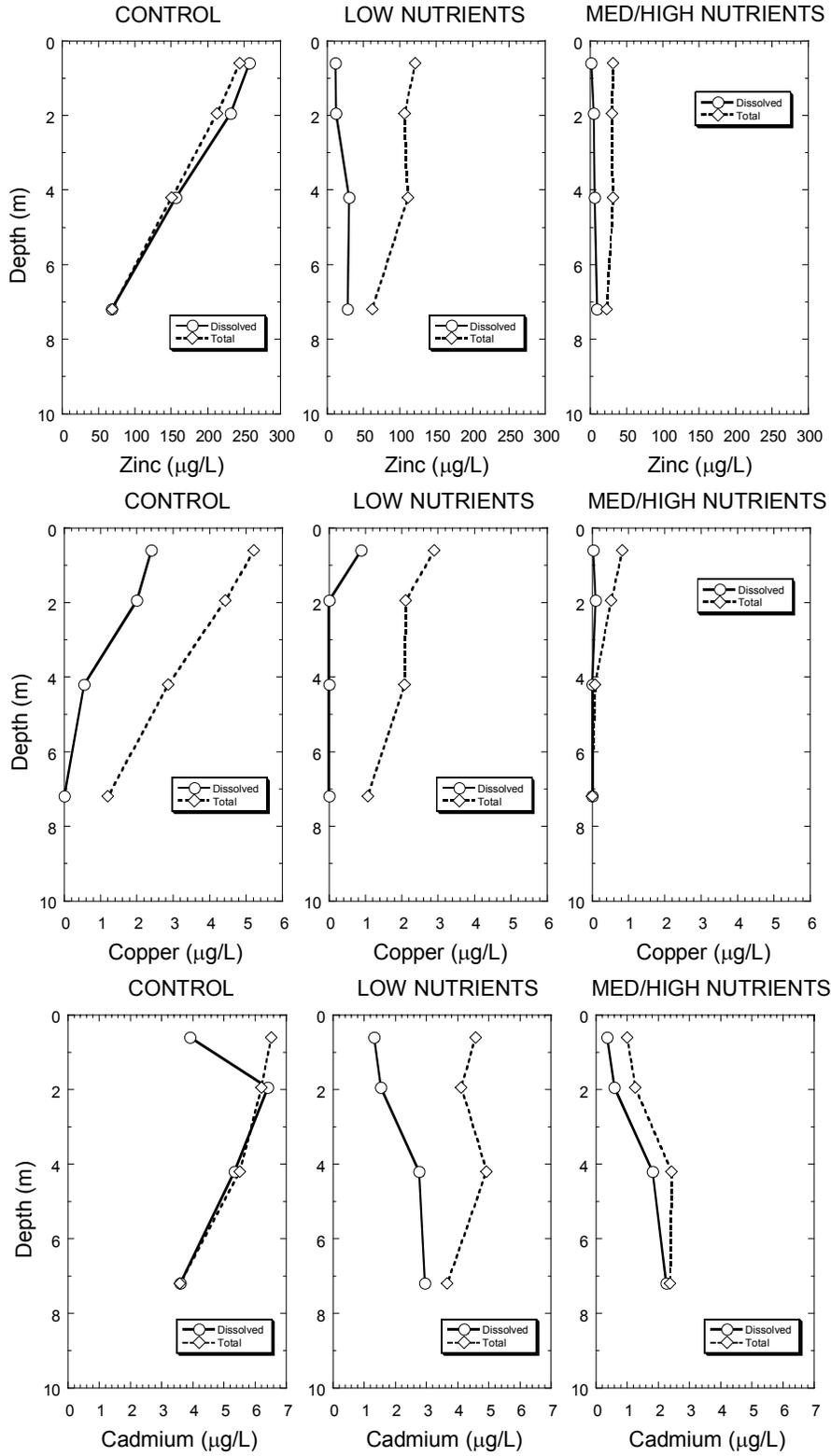


Figure 8. Limnocorrals profiles for Zn, Cu and Cd (dissolved and total) in the control, low-nutrient and med/high-nutrient treatments in Main Zone Pit two months post-fertilization.

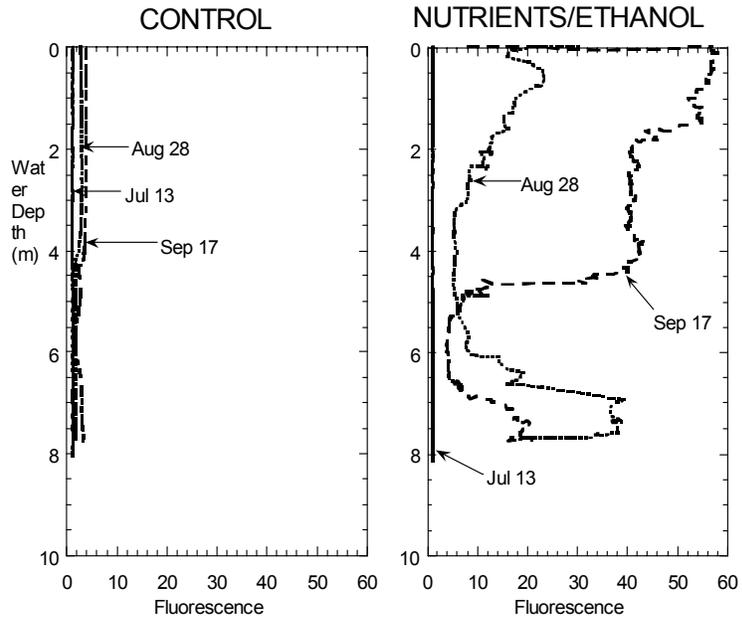


Figure 9: Limnocoralls profiles for fluorescence (a proxy for algal biomass) in the control and nutrients/ethanol treatments in Waterline Pit following fertilization on July 12, 2002. Fluorescence units are roughly equivalent to  $\mu\text{g/L}$  chlorophyll.

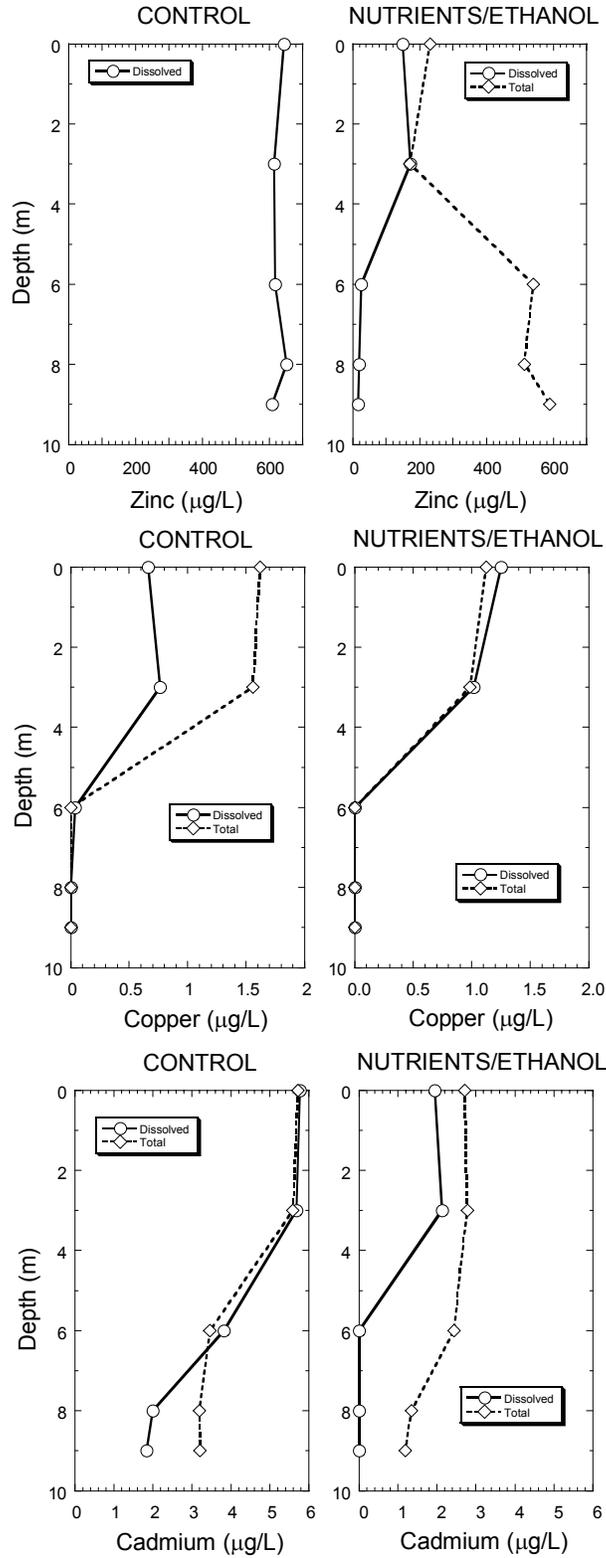


Figure 10. Limnocorrals profiles for Zn, Cu and Cd (dissolved and total) in the control and nutrients/ethanol treatments in Waterline Pit one month post-fertilization, and two months post ethanol-addition. Note, total Zn values were not available for the control limnocorral.

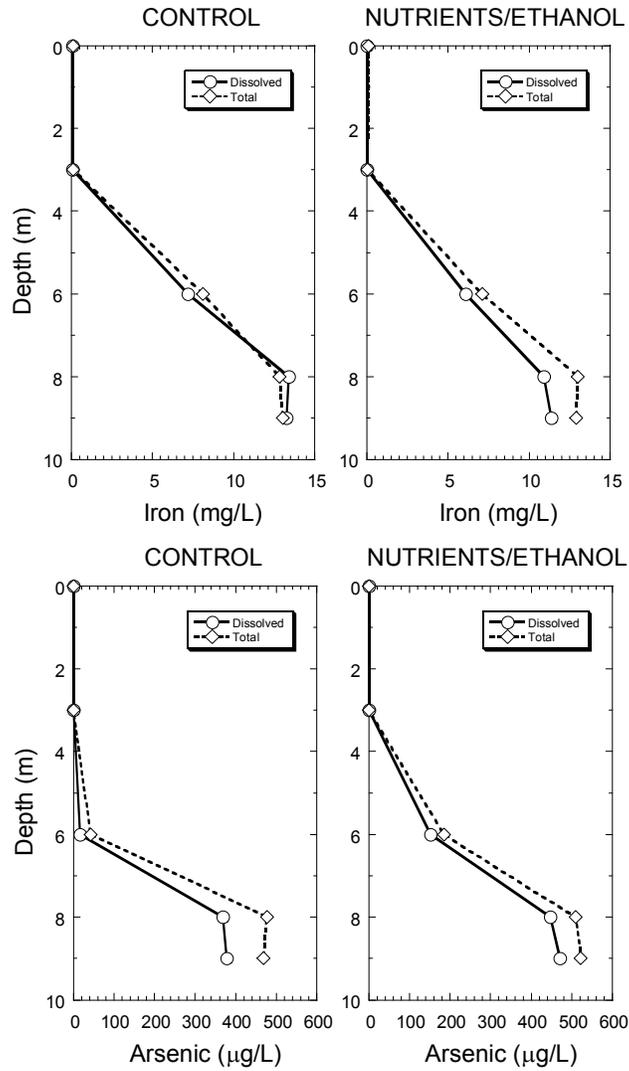


Figure 11. Limnocorrals profiles for As and Fe (dissolved and total) in the control and nutrients/ethanol treatments in Waterline Pit one month post-fertilization, and two months post ethanol-addition..