GEOCHEMICAL ASSESSMENT OF THE EQUITY SILVER TAILINGS POND

MEND Project 2.11.5c

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Geochemical Assessment of the Equity Silver Tailings Pond

FINAL REPORT

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Preamble

PREAMBLE

Introduction

Finding an environmentally sound, yet cost effective, mode for disposal of sulphide-containing mine waste has been a challenge facing both the mining industry and government for many decades. Given the critical role played by oxygen in the process of acid generation, thoughts towards abatement of this problem have focused around elimination of oxygen as a reactant. Consequently, arguments for subaqueous disposal arose naturally from the premise that acid generation from sulphides could be suppressed when submerged underwater where oxygen concentrations are greatly diminished relative to the atmosphere. In other words, lowering the concentration of one of the principal reaction ingredients (oxygen) would lower the oxidation reaction rate, hence the rate of generation of acid and dissolved metals. This premise was based on the well understood chemical characteristics of natural water bodies and sediments.

While founded on sound theoretical principals, the efficacy of subaqueous disposal prior to the 1980’s was largely unproven and supported by only a few, limited scientific studies. In order to address the paucity of relevant data, a suite of projects created through the BCARD Task Force and MEND were designed, and involved fieldwork in a series of lakes where mine tailings had been deposited (Anderson and Mandy Lakes, Manitoba; Buttle and Benson Lakes, British Columbia). The program utilized a variety of state-of-the-art sampling, analytical and interpretive techniques designed to measure directly the reactivity and short and long-term chemical stability of subaqueous mine tailings deposits. Further, the questions to be answered by the project temporarily avoided the many and complex biological components, and focused on the geochemical environment. It was determined that once subaqueous tailings reactivity had been adequately assessed, and the geochemical processes delineated, the biological issues could be approached in a better-defined context and on a project-specific basis.

The results of the work supported the hypothesis: sulphide-rich mine tailings, when stored in the subaqueous environment, were largely chemically unreactive. In the few instances where release of dissolved metals were observed, natural secondary chemical processes within the sediments inhibited their release to the water column.

The following overview is intended to provide a summary of the MEND Project reports and a general description of the geochemical systems which contribute to the effectiveness of subaqueous disposal.

Background Chemistry

The instability or reactivity of metal sulphides arise from their mode of formation. Sulphides are formed in reducing environments (in the absence of oxygen). Consequently, they are unstable and susceptible to chemical reaction in the oxygen-rich environment of the earth's surface. Accordingly, the most stable environment in which to store sulphide-rich mine tailings is one devoid of oxygen - one that mimics their environment of genesis.

Subaqueous systems are an effective first approximation of a stable environment for sulphides not because they are devoid of oxygen (indeed, subaqueous environments most often have measurable concentrations of dissolved oxygen), but rather because they contain low oxygen levels even in their most saturated state. The maximum concentration of dissolved oxygen found in natural waters is approximately 25,000 times lower than that found in the atmosphere. Because the rate of sulphide oxidation is in part dependent on the concentration of oxygen, it is readily apparent that the generation of acid and dissolved metals will be dramatically minimized underwater. Further, once the small inventory of dissolved oxygen in the water is consumed, it is typically replaced very slowly by processes of molecular diffusion and small-scale turbulence; the transfer of oxygen in water is nearly 10,000 times slower than similar transfers in air. Consequently, storage under permanent water cover is perhaps the single most effective measure that may be taken to inhibit acid generation from sulphidic mine tailings.

Sediments recreate an environment stable to sulphide minerals even more effectively than a water cover, in part because of the low concentrations of dissolved oxygen but also because of a natural tendency for sediments to become chemically reducing. To understand why the sedimentary environment is an appropriate site for the storage of sulphidic mine tailings, it is first necessary to outline some of the natural chemical processes found in that environment.

Natural sediments typically contain a spectrum of components ranging from eroded rocks and soils of local origin to unique substances formed within the deposits.

However, of all the components found in natural sediments, the remains of plants and animals (organic matter) is perhaps the most important as they are considered to be the fuel for almost all chemical reactions that occur after deposition. This is because organic matter (like sulphides) is unstable in the presence of oxygen; it has a natural tendency to decompose into its constituent elements (mostly simple molecules containing the elements carbon, nitrogen, phosphorus, sulphur and hydrogen). In other words, organic matter consumes or reacts with the oxidant oxygen to form carbon dioxide and a suite of simple, biological by-products. This reaction is accelerated by a host of bacterial species which catalyse the reaction to derive energy for their own needs. Because the concentration of oxygen in natural waters is initially low, it is often rapidly depleted within the surface layers of sediments. When oxygen is no longer available to react with the organic matter, secondary oxidants are utilized in its place by the bacterial community. They are in order of preference: nitrate, Mn-oxide, Fe-oxide, sulphate and carbon dioxide; once one secondary oxidant is consumed (*i.e.*, nitrate) the next most favoured is consumed (*i.e.*, Mn-oxide) until all are exhausted. Of particular importance is the consumption of sulphate, since the by-product of the reaction between sulphate and organic matter (in the absence of more favourable oxidants) is hydrogen sulphide, a natural analogue to metal sulphide minerals. Thus, the natural tendency in sediments is toward the creation of an environment in which sulphides form naturally, and sulphide-rich mine tailings are at their most stable in just such settings.

Methods of Examination

There are two principal ways in which to assess whether or not sulphidic mine tailings are reacting or releasing acid and metals to the subaqueous environment. The first is direct microscopic or petrographic observation of the submerged tailings particles. Thus far, in all cases where subaqueous sulphide tailings have been studied, no signs of oxidation have been observed. However, a far more sensitive, effective and elegant approach is to look for direct effects of sulphide oxidation such as a drop in pH, an increase in sulphate or the most direct indicator of all, an increase in dissolved metals. Since dissolved metals are the parameters of environmental concern and because they exist at very low concentrations naturally, measuring their distribution within sediment porewaters (the water surrounding the deposited sediment or tailings particles) yields a very sensitive indication of tailings reactivity as well as potential environmental impact.

The distribution of dissolved metals in porewaters has been determined by two proven approaches. Within the MEND projects, sampling of porewaters was accomplished utilizing the techniques of sediment coring and dialysis array (peeper). Sampling porewaters by core involves the collection of sediment with a specialized, light-weight, gravity corer. The porewaters are separated from the sediment solids by placing sequential slices of sediment into a centrifuge; the resulting fluid fraction is filtered and analysed for dissolved metals. Peepers sample porewaters much more passively. Peepers consist of an array of depressions or wells in a plexiglas plate. The wells are filled with ultra-pure water and covered with a filtration membrane. The peeper is inserted vertically into the sediments and allowed to equilibrate within the sediments for 10 to 14 days. During that period, dissolved metals move across the membrane into the sample wells while the solids are excluded. After 10 to 14 days, the water within the sample wells is chemically indistinguishable from that of the porewaters; the sample waters are removed from the wells and analysed for dissolved metals.

In order to avoid oxidizing the samples by allowing them to contact the atmosphere, all sample handling of both cores and peepers after collection is carried out in nitrogen-filled, plastic glove bags. Once the porewaters have been filtered (again, under nitrogen), they are "preserved" for subsequent analysis by the addition of a small amount of ultra-pure acid.

Chemical Manifestations of Dissolved Metals in Porewaters

Upon their formation, sediment porewaters are no more than lake water trapped between sediment particles; in the absence of chemical reactions, the composition of porewaters would be identical to the overlying lake water. If tailings are reactive and release dissolved metals to the environment, the most sensitive manifestation will be locally elevated concentrations of dissolved metals within shallow porewaters (*e.g.*, Figure 1(a)). Conversely, precipitation or consumption of dissolved metals is characterised by concentrations that decrease with depth (*e.g.*, Figure 1(b)).

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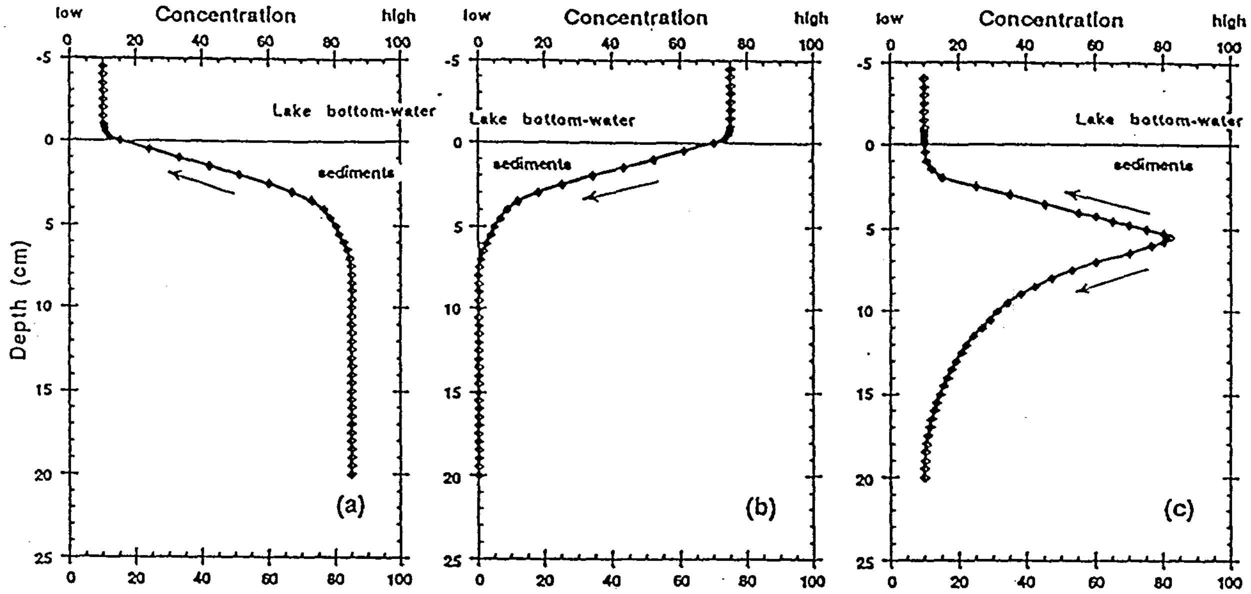

Figure 1 Three hypothetical concentration profiles for dissolved metals in the porewaters of tailings or natural sediments: (a) release of metal to pore solution. The arrow shows the gradient in concentration (from high to low) and the consequent direction of migration of dissolved metal ions; (b) consumption of dissolved metal by the deposits (*e.g.* via chemical precipitation). In this case, dissolved metals are diffusing into the lake floor; (c) subsurface release of metal to pore solution, with migration along the concentration gradients away from the zone of release, as shown by the arrows. Consumption below the peak concentration is indicated (*e.g.* via precipitation of a metal sulphide phase) as well as above the maximum which can occur when iron and/or manganese oxide particles present in the near-surface sediments adsorb upwardly migrating metal ions.

Release or consumption of dissolved metals results in the formation of adjacent zones of differing concentrations. The difference in dissolved metal concentration between a high and a low define a concentration *gradient* and results in net migration of dissolved metals from the zone of high concentration to the zone of low concentration. In sediments, this process occurs through the random motion associated with all dissolved molecules and is termed molecular diffusion. The amount of dissolved metals that migrates down a concentration gradient (from high to low concentration) is termed the flux and is proportional to the steepness of the gradient. In other words, a greater flux (*i.e.*, a greater transport of dissolved metals) occurs where a very high concentration is immediately adjacent to a very low concentration.

If a concentration gradient extends across the sediment-water interface, metals can be said to be diffusing out of or into the sediments (to or from lake water) depending on the direction of the gradient. Lower concentrations of dissolved metals in porewater relative to the overlying lake water indicates a flux of metals into the sediments from lake water (Figure 1(b)). Conversely, higher concentrations in porewaters than lake water infers a flux in the opposite direction (Figure 1(a)).

In the majority of the MEND project work undertaken thus far, metals have been observed to diffuse into the sediments from the overlying lake water. This has occurred in part because some of the lakes contained elevated concentrations of dissolved metals, but more importantly because of the natural tendency for sediments to create the environment stable to sulphides as discussed above. When sulphate is utilised as a oxidant in the decomposition of organic matter within the sediments, a natural by-product is hydrogen sulphide. Hydrogen sulphide is highly reactive with most dissolved metals (such as Cd, Cu, Hg, As, Mo, Ni, Fe, Pb, Zn and others) resulting in rapid precipitation of those metals as insoluble, solid metal sulphides. Because sulphate reduction (sulphide formation) typically occurs at shallow depths within sediments, there is a commensurate zone of localized metal consumption with the establishment of a dissolved metal concentration gradient from lake water into the sediments. The result is a flux or transport of dissolved metals into the surface sediments from the overlying lake water with the tailings acting as a sink for dissolved metals rather than a source. The concentration profile characteristic of such a case is shown in Figure 1(b).

In some instances, dissolved metals have been observed to be released from sediment solids to the porewaters. At first glance, this might suggest that the tailings are releasing dissolved metals to the overlying lake water, particularly if the concentration gradient extends to the sediment-water interface. However, there are several complicating factors that must be considered when such profiles are observed. First, several metals (such as Cd, Cu, and Zn) are released to near-surface porewaters naturally as they are often associated with organic matter - they are not tailings-derived. As the organic material decomposes or oxidizes, those associated metals are released in dissolved form and may indeed migrate back into the overlying lake water. This most commonly occurs in sediments where oxygen has not been sufficiently depleted (or more specifically, where sulphide precipitation is absent). Such release is a natural phenomenon and accounts for much of the natural cycling of certain trace metals in many natural environments. The second factor is that even though there may be some release of metals from tailings to porewaters in certain cases, a process referred to as *oxide blocking* or *oxide scavenging* can intercept much of the upward flux of those metals before the dissolved species cross the sediment-water interface into the lake water.

Such scavenging involves oxides of iron and manganese, two of the secondary oxidants discussed above. Where dissolved oxygen is present, Fe and Mn oxides exist as solids whose surfaces strongly adsorb many trace metals. When they are utilized in subsurface sediments as secondary oxidants in the absence of oxygen, they revert to dissolved Fe and Mn creating concentration gradients. As dissolved Fe and Mn diffuse upward toward the sediment-water interface, they eventually encounter dissolved oxygen and revert back to their original solid, oxide form. Iron and manganese oxides are both efficient in adsorbing a broad range of dissolved metal ions. Thus, their continuous formation in the near-surface sediments results in the establishment of an effective “blocking mechanism” that inhibits dissolved metals from entering the water column.

One final barrier to *all* metal release from tailings within lake sediments is time. The burial of tailings by natural sediments or more recently deposited tailings occurs progressively with time and has a profound effect on the ability of even the most reactive substances to affect lake water quality. As the dominant transport mechanism of dissolved metals in sediments is diffusion, and because mass transport by diffusion is effective only over short distances (*i.e.*, a few centimetres), accumulation of a relatively thin layer of sediments over an abandoned tailings deposit is sufficient to isolate tailings chemically from the water column. In this regard, subaqueous tailings disposal from a tailings reactivity stand-point is at worst a relatively short-term issue even though this “worst” condition has not as yet been observed. Nonetheless, once deposition has ceased and tailings have been buried by a few centimetres of natural sediment, they can for all intents and purposes be considered to be chemically secure for the foreseeable future.

Conclusions

This MEND project work to date has involved the study of tailings in natural lakes; little attention has been paid to the comparatively abiotic system of the man-made tailings ponds. This and future research will be directed toward such systems; however, several generalizations can be drawn from the MEND data which apply equally to both tailings ponds and natural lakes.

Firstly, the diminished concentration of oxygen dissolved in water is the single-most effective inhibitor to tailings oxidation; low concentrations of oxygen translate into low oxidation reaction rates. The presence of a permanent water cover not only minimizes the maximum concentration of oxygen to which the tailings may be exposed, but it also inhibits the rate at which that oxygen may be resupplied.

Secondly, even though tailings ponds are typically deplete in organic carbon, they still present conditions suitable to long-term storage of sulphide-rich material. Sulphide-bearing tailings themselves act as an analogue for natural sediments in that they progressively lower the concentration of oxidants, thus enhancing the potential for long-term stability.

Finally, time itself is an effective component in allowing the establishment of a physical barrier which prevents the release of metals to the overlying lake waters. The accumulation of a veneer of natural sediments (a few centimetres thick) effectively isolates the tailings. Subaqueous disposal is at worst a relative short-term risk that decreases with time to yield a stable, passive but effectively final control system.

EXECUTIVE SUMMARY

A geochemical survey was performed on the Equity Silver Tailings Pond near Huston, B.C. in the fall of 1995. Replicate peepers were used to collect pore waters from each of a shallow (~1 m) and deep site (~5 m) within the tailings pond. Ancillary solid-phase and water column data were also collected.

The distributions of most elements is indicative of small-scale, lateral inhomogeneity. While dissolved Cu is neither released nor consumed by the tailings, Sb and As display opposing fluxes. Arsenic is released from pore waters to pond waters at both sites in all replicates via dissolution of an unidentified solid phase. Conversely, Sb is consumed rapidly within the surfical deposits, presumably by adsorption to an existing solid-phase.

Direct determinations of tailings oxidation rates were calculated by measurements of dissolved oxygen from the peepers cells across the sediment-water interface. Dissolved oxygen fluxes were determined by the application of Fick's law of diffusion across the interface and also through a diffusion-consumption model applied to the dissolved oxygen data in the pore waters. The tailings oxidation rate (assuming the entire oxygen flux was consumed by tailings oxidation) was within the range of values seen for other subaqueous tailings deposits.

Table of Contents

TABLE OF CONTENTS

APPENDICES

List of Figures

Figure Page

1.0 Introduction

1.0 INTRODUCTION

Determining the reactivity of sulphide-rich mill tailings, stored subaqueously in lacustrine environments, has been the subject of increasingly detailed geochemical studies in the Subaqueous Tailings Disposal Project (MEND Project 2.11). These studies targeted two physically and biogeochemically distinct natural lakes, namely Anderson Lake and Buttle Lake. The findings from these studies have provided strong scientific support for the general tenet that potentially acid generating tailings do not undergo sufficient chemical or biochemical oxidation when stored underwater to release dissolved metals to the overlying water column at a rate which would degrade water quality to unacceptable conditions. Three primary factors, sometimes working in concert, appear to be responsible for such observations. First, low dissolved oxygen levels at the sediment-water interface diminish to anoxia at very shallow sediment depths, due to consumption of oxygen during oxidation of reduced sedimentary components. Second, the dissolved oxygen consumed is replaced by the inefficient transport mechanism of diffusion. Third, burial of tailings by natural sedimentation establishes a diffusive barrier as well as fostering anoxia in the submerged tailings.

Recognizing that lake disposal of reactive tailings is a less common management technique for preventing acid generation than disposal into a man-made tailings impoundment, the present MEND study was an attempt to extend the geochemical database to encompass the latter. Specifically, the MEND steering committee requested an evaluation of the geochemical stability of the Equity Silver Tailings Pond (herein called ESTP) sediments, the results of which form the foundation of the following report.

Highly reactive sulphide-rich mill tailings have been deposited in the ESTP throughout the life of the operation with cessation of deposition in 1994. Unlike Anderson Lake or Buttle Lake, the ESTP received comparably little organic matter inputs. However, significant quantities of relatively non-labile carbon as cyano-metal complexes was introduced to the system during operations. The geochemical conditions within the submerged tailings that evolved as a consequence of low organic matter fluxes and the presence of cyanide were a key focus of the study.

The study employed a combination of sampling methodologies: water column sampling and profiling, collection of cores, as well as the use of dialysis-membrane array-samplers (peepers). Interstitial waters from core segments was not sampled and analysed; instead, peepers alone, were used for high resolution sampling of interstitial waters.

The ESTP geochemical study, initiated in September 1995, was designed to meet the following objectives:

- assess the hydrographic and chemical status of the water column in the tailings pond;
- determine the distribution of dissolved metals, cyanide, sulphate and metabolites in interstitial waters, and to relate these to the chemical composition of the solid phases;
- to use the pore water data to provide an estimate of the flux of metals into or from the tailings sediments;
- to use the solid-phase, pore water, and water column chemical and hydrographic data to interpret controls on the chemical behaviour of the submerged tailings; and
- to compare the results obtained in this study to previous work conducted by Rescan on the stability of subaqueous tailings in natural lakes.

2.0 Scope of Work

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2.1 Background

The Equity Mine started operation in August 1980 and terminated operations in January 1994. The ore minerals in the Equity pits consisted of chalcopyrite $CuFeS_2$, tennantite $(Cu, Fe, Zn, Ag)_{12}As_4S_{13}$, and tetrahedrite $(Cu, Fe, Zn, Ag)_{12}Sb_4S_{13}$. The quantities of these materials were highest in the Southern Tail pit which was developed first and decreased for the Main Zone and Waterline pits which were mined later. Other minerals present in the Southern Tail pit were pyrite, arsenopyrite and minor quantities of galena (PbS) and sphalerite (ZnS). The Main Zone and Waterline pits contained chalcopyrite, tennantite, tetrahedrite, arsenopyrite, pyrite and pyrrhotite.

The mill started production at 5,000 tons per day and used flotation to recover sulphide minerals. In January 1985 additional grinding was commissioned and the production rate increased to 9,000 tons per day. The last stage of mining was performed as an underground mine and the production rate was approximately 1,500 tons per day over the last two years.

In January 1985 a cyanide leach plant was also added for gold recovery using CIL which ran for the rest of the mine life. A cyanide destruction system was installed using the SO_2-air process (developed by INCO) to treat tailings prior to discharging to the tailings pond.

A silver/copper concentrate was produced from mine start-up, containing chalcopyrite $CuFeS_2$, tennantite $(Cu, Fe, Zn, Ag)_{12}As_4S_{13}$, and tetrahedrite $(Cu, Fe, Zn, Ag)_{12}Sb_4S_{13}$. As the recovery from the mill circuit was approximately 90%, there were small residual quantities of these minerals in the tailings. Small quantities of arsenopyrite (0.5 to 1.0%) reported to the concentrate, but these were not leachable and hence were shipped to the smelters.

The arsenopyrite, pyrite and pyrrhotite minerals were depressed in the mill flotation circuits and these minerals reported to the tailing pond.

The neutralized sludge from the ARD treatment plant (lime addition) was co-disposed with the tailings in the tailings pond area nearest to the mill. A final layer of tailings without the sludges was deposited in this area during the last year of operation.

A leach plant started operation in October 1981, approximately one year after mine commissioning, and ran until April 1984. This plant removed arsenic and antimony from the concentrate minerals to produce a marketable product for the world smelter markets. This plant only ran for approximately 2½ years as the smelters eventually accepted the unleached concentrate products and continued use of the leach plant was not economical.

The by-products of the leach process were all solid materials and hence there was no liquid discharge from the leach plant to the tailings pond.

The sodium sulphide leach plant produced by-product calcium arsenate materials which were shipped off-site to a hazardous waste site in the U.S. A second product produced was sodium antimonate which was sold to off-site chemical markets.

Considerable quantities of sodium sulphate were also produced which were sold to the local pulp mills in Prince Rupert. A single deposit of 2,500 tons of off-grade sodium sulphate (1,000 ppm As), which could not be sold, was deposited in a till lined cell within the pond area. This cell was covered with till and then eventually flooded as the pond rose with the ongoing operations.

Tailings were discharged to the Equity Silver Tailings Pond (ESTP) via a mobile floating platform. The mine tailings were distributed around the tailings pond by periodically moving the position of the floating platform. ESTP has an area of approximately 1.2 km^2 and a maximum water depth of five metres in the central area. An emergency overflow spillway exists at the north-eastern corner of the tailings pond, which has never been used as the facility has always been a zero discharge operation. There is a paucity of historical physical and geochemical data from ESTP, and therefore little is known of the characteristics of the water column or the tailings prior to this survey.

2.2 Sampling Protocol

Geochemical data were collected from two stations in ESTP. Figure 2-1 shows ESTP and the location of the two geochemical sampling stations. The potential

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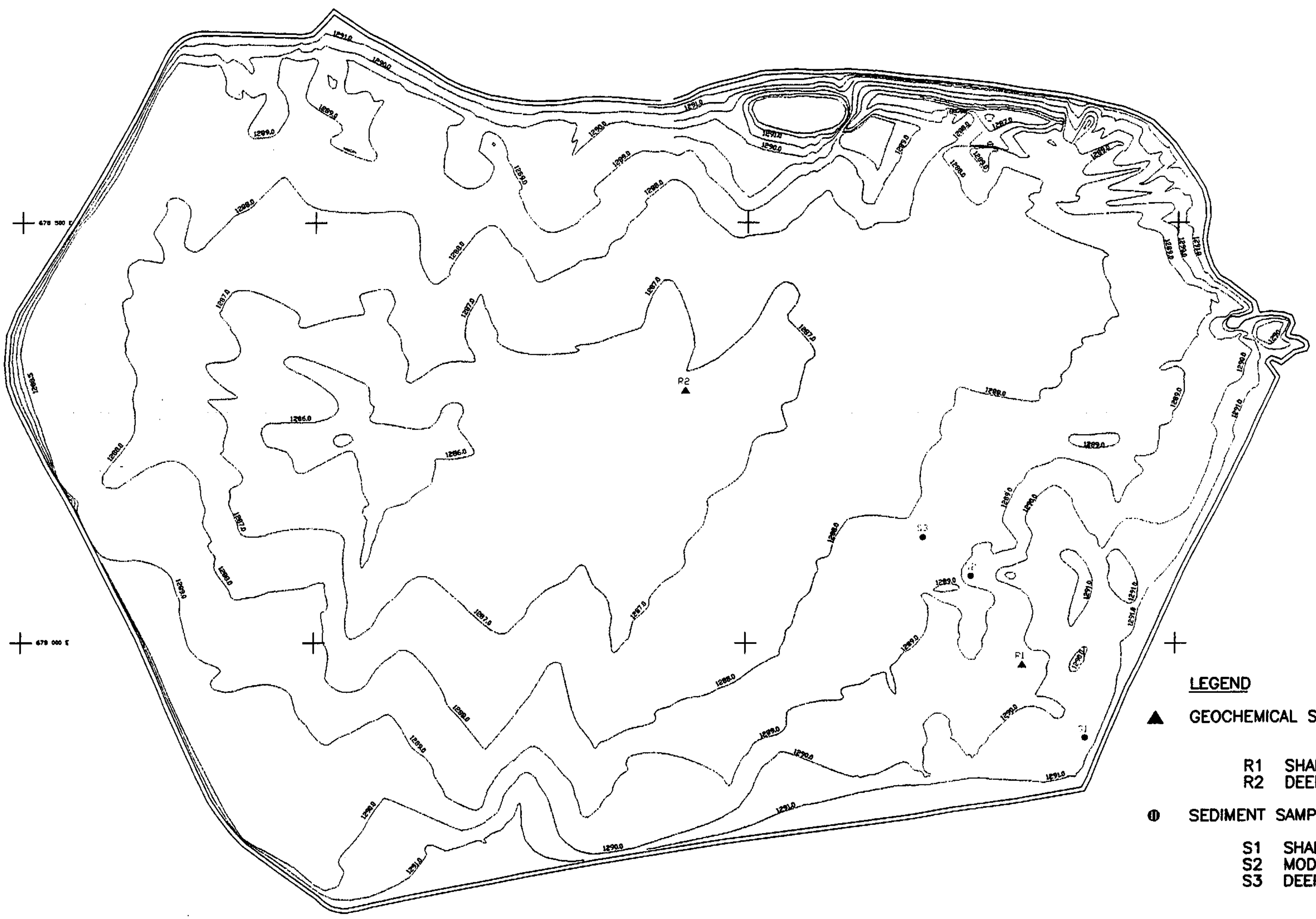

LEGEND

▲ GEOCHEMICAL SAMPLE SITES

		WATER DEPTH
R1	SHALLOW SITE	1.8m
R2	DEEP SITE	5.0m

● SEDIMENT SAMPLE SITES

S1	SHALLOW SITE	1.3m
S2	MODERATE DEPTH SITE	2.3m
S3	DEEP SITE	3.4m

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Station Location Map

Rescan

Fig. 2-1

impact of water depth on tailings reactivity was assessed by studying a shallow and a deep site in the pond. Precise station positioning was achieved through the alignment of topographical features and man-made structures around the tailings pond.

Station S (shallow site) is located towards the south-western parimeter of the pond at a water depth of approximately 1.2 m. Station D (deep site) is located in the central area of the pond at a water depth of approximately five metres. The water column, sediment-solids and interstitial-waters from the two stations were sampled. The results are used to define the nature of the geochemical environment and to assess the reactivity of the submerged tailings.

Four tandem peepers were deployed at each of the two sampling stations. The left banks from three of the peepers were sampled and analysed for metals, with the right banks providing the samples for nutrient analyses. The fourth peeper provided interstitial water samples for total cyanide analysis. One sediment core was collected at each of the two sites for solid phase analyses. A total of five water samples were collected from various depths at both sampling stations.

The geochemical survey of the tailings pond was conducted in August 1995. Specifically, peeper installation occurred during the week of August 14 and peeper retrieval, coring, water column sampling and hydrographic measurements occurred during the week of August 28, 1995. Details of this program are described below.

2.2.1 Water Quality Sampling

The maximum water depth in ESTP is five metres, which suggests that turbulent mixing throughout the water column is likely. The presence of strong chemical or physical vertical gradients in the water column is therefore very unlikely. Where gradients are potentially strongest (*i.e.*, the sediment-water interface), water column sampling was accomplished using the exposed portions of the peepers (see Section 2.2.3). However, three water column samples were collected at station D (at water depths of 3.5, 1.5 and 0 m), and two samples were collected at Station S (at water depths of 1.5 and 0 m).

The water-column was sampled using a 1 L acid-washed Go-Flo bottle, which was rigorously cleaned and acid-washed prior to field use. The bottle was first cleaned thoroughly in Vancouver by washing with a mild detergent followed by several rinses with distilled water. The interior of the bottle was then exposed to low strength (1% v/v) ultrapure Seastar HCl followed by several rinses with dilute (0.1% v/v) HCl, separated by many rinses with copious amounts of distilled, deionized water (DDW). The Go-Flo bottle was stored in clean plastic until deployment.

Immediately prior to sampling, Go-Flo bottles were rinsed with DDW. Sampling involved attaching a clean Go-Flo bottle to either a stainless steel hydrowire weighted by resin-coated ballast. Once lowered to the appropriate depth, the bottles were tripped by a stainless steel messenger.

Because the water-column in ESTP is oxic, sub-sampling of water was not conducted under a nitrogen atmosphere to avoid oxidative artifacts. However, care was taken to collect uncontaminated trace metal sub-samples, using acid-washed tubing to draw samples in concert with the implementation of general trace metal protocol (*i.e.*, Nriagu *et al*. 1993).

Unfiltered water samples were collected for total metals, total cyanide (CN) and physical parameters while filtered water samples (filtered with 45 mm, 0.45 µm mixed cellulose acetate filters) were apportioned to two fractions:

1. trace metals (Sb, As, Cd, Cu, Fe, Pb, Mn and Zn), preserved by acidification to pH 2 with ultra-pure $HN0_3$; and
2. the anions nitrate, phosphate, sulphate and chloride, preserved frozen.

2.2.2 Interstitial Water Sampling

Dialysis-membrane array-samplers (peepers) were utilized to sample waters at high resolution both within the sediments and across the sediment-water interface. A tandem peeper consists of two vertical banks of sample wells machined into an plexiglas plate. In principle, a semi-permeable membrane traps de-oxygenated, distilled deionized water within the peeper-cavities, while allowing diffusion of dissolved species across its surface. When in contact with sediments, the entrapped peeper-water comes into chemical equilibrium with adjacent interstitial water such that, after approximately two weeks, the waters are chemically indistinguishable.

Each peeper is approximately one metre in length having two vertical columns of 61 wells (70 mm x 8 mm x 14 mm deep) machined into its surface; sample wells are located every 12.6 mm. The spatial resolution in the central section of the peeper is 6.3 mm which is obtained by offsetting a series of smaller wells (32 mm x 8 mm x 14 mm).

Rescan peepers were assembled for deployment under clean-room conditions at the University of British Columbia (UBC), prior to shipment to ESTP. Peeper preparation involved placing the peepers in a nitrogen atmosphere for 30 days. This was done in response to a recent study (Carignan *et al.* 1994), which showed that Plexiglas from which the Rescan peepers are made, can absorb up to 1.6% vol/vol of oxygen, which is then lost slowly (half-life of 5.7 d) once exposed to an anoxic environment. Trace amounts of oxygen in the lattice of the peepers may therefore result in precipitation of iron oxide in the peeper sample wells, which may in turn result in an overestimation of dissolved iron in interstitial waters. The 30-day nitrogen treatment of the peepers purged any lattice-bound oxygen, eliminating oxidation artifacts in sample wells.

Immediately following the 30-day de-oxygenation period, peepers were immersed in a tank of de-oxygenated, distilled, deionized water (DDDW), where bubbles were dislodged. A 0.45 µm polysulfone Gelman depth filter covered all wells simultaneously. An acrylic face plate attached with several nylon screws serves to hold the filter in place. All peeper components were cleaned with a mild detergent and rinsed with copious amounts of distilled water prior to acid-washing. Components were then acid washed in dilute ultrapure HNO_3 (0.1% v/v) followed by several 24 hour soaks in DDW to remove any residual acid. The assembled peepers were stored in sealed acrylic boxes containing DDDW bubbled with nitrogen until deployment by diver insertion.

Four tandem peepers were deployed at each of the two stations. Moorings anchored by 30 kg weights and surface floats marked the station locations. Peepers were tethered to the moorings for easy location and retrieval by divers two weeks after deployment.

Peepers were lowered vertically into the sediment with the aid of weighted aluminum benthic-lander frames. The peepers were allowed to slowly penetrate the pond sediments until the sediment-water interface eclipsed the high-resolution portion of the sample wells. The positioning of each peeper in its lander stabilized this configuration. Each peeper was logged for placement of the sediment-water interface, attached to a marking float via a slack line and left to equilibrate for 14 days. This deployment configuration allowed for high resolution sampling in the upper 60 cm of interstitial waters, and across the sediment-water interface, extending approximately 30 cm into the bottom waters, thereby integrating interstitial waters and water column samples.

Peepers were retrieved by divers and were accompanied (within 24 hours) by collection of cores at the same sites. Peeper retrieval involved *in situ* logging of the sediment-water interface. From the boat, the selected peepers were raised to just below the surface, agitated to remove adhering particulate matter, taken out of the lake and immediately inserted in their nitrogen-flushed storage boxes for transport to the field-laboratory where they were transferred to a N_2-filled glove bag. Processing started with the creation of two small holes in the Gelman filter through which samples were withdrawn using an acid-washed polyethylene pipette.

All peeper samples were apportioned for measurements of trace metals (Sb, As, Cd, Cu, Fe, Pb, Mn and Zn) preserved by acidification to pH 2 with Seastar™ nitric acid, nutrients (NO_3^-, $PO_4^{3-}$and SO_4^{2-}), preserved frozen, CN preserved with NaOH, and Σ H_2S preserved with Zn-acetate where the volume permitted.

2.2.3 Sediment Sampling

One core was collected for solid phase sampling at each of the two stations. A standard reconnaissance coring technique was employed, whereby a retrieved core was assessed for an undisturbed interface. When a core failed to meet this requirement, additional cores were collected until a satisfactory core was retrieved. Core locations remained proximal to the predetermined stations.

Cores were collected using the light-weight Pedersen Gravity Corer (Pedersen *et al*. 1984) with an eight cm, *i.e.*, catcher-free, butyrate core barrel. Typically, the corer was lowered to the lake floor and allowed to penetrate the sediments slowly (< 10 cm/s). After returning to the surface, the bottom of the core barrel was quickly capped by insertion of an o-ring-fitted piston. The barrel was removed from the corer, sealed completely with plastic core-caps and electrician’s tape. The core was logged, extruded and sampled in 3 cm sections in the field.

2.3 Analytical Protocols

All analyses was performed by Analytical Service Laboratories Ltd. (ASL) and at the University of British Columbia, both in Vancouver, B.C.

2.3.1 Water Column Sample Analysis

Analyses of water column samples included temperature, conductivity, DO, pH (measured on-site), CN, NO_3^-, PO_4^{3-}, SO_4^{2-}, Cl, dissolved (<0.45 µm-filtered) and total Sb, As, Cd, Cu, Fe, Pb, Mn, and Zn.

All ASL analytical methodologies for water quality measurements are presented in Appendix B. The method detection limit (MDL) is considered the most realistic approach to calculating a detection limit because it is based on a complete analytical procedure; it includes matrix effects and is derived from the analysis of samples, or standards rather than blanks. The process involves an actual determination of detection limit by analyzing a number of low-level spikes in reagent grade water. The MDL has been adopted by US Environmental Protection Agency and the Canadian Association of Environmental Analytical Laboratories, and is used to define all detection limits for the present program. MDLs for the water column analyses are presented in Appendix B.

2.3.2 Sediment and Pore Water Sample Analysis

Concentrations of major and minor elements including Al, Sb, As, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Zn, TOC, N, and S were determined on the solid-phase portion of the core sections. Interstitial water analyses included Sb, As, Cd, Cu, Fe, Pb, Mn, Zn, Ca, CN, nitrate, sulphate and sulphide.

Oxygen and pH mini-electrodes were used for the measurement of these two parameters in peeper sample wells. Mini-electrodes require very small sample volumes (one drop), and therefore may be used for high resolution profiling of DO and pH across the sediment-water interface (Archer *et al*. 1989). The membrane on selected peeper wells were punctured, the mini-electrodes inserted into the sample, and the results recorded in field log books. The oxygen and pH mini-electrodes were calibrated immediately prior to the field survey.

The standard method for the analysis of cyanide requires 500 mL of sample. The low sample volumes derived from peepers (3-5 mL) therefore precludes the use of this method. A new method has recently been developed by ASL which is capable of analysing 3-5 mL sample volumes for total cyanide. The method involves an on-line acid/ultraviolet digestion of the sample, which converts metal-bound cyanides to HCN. The HCN gas is then separated and trapped in a weak NaOH solution. The resulting cyanide ions are then analyzed amperometrically.

All ASL analytical methodologies for sediment and interstitial water samples and all MDLs for sediment and interstitial water analyses are presented in Appendix B.

2.4 Quality Assurance, Quality Control Specifications

Specific quality assurance/quality control (QA/QC) procedures were rigorously followed and are documented throughout the program. All QA/QC data obtained are provided as standard documentation in conjunction with all analytical results. A brief explanatory report which accompanies these data provides a summary of compliance/non-compliance with the rigorous criteria applied throughout all phases of the program.

General QA/QC protocols such as maintenance of field records and chain of custody forms were strictly adhered to during the implementation of this program. The MEND QA/QC program has two principal components: field program QA/QC and analytical program QA/QC. The field QA/QC and the analytical QA/QC programs are briefly described below.

2.4.1 Field Program

All equipment and procedures in the field and laboratory were photographed, creating an extensive visual log of the fieldwork.

Water Column Sampling

Replication of water column samples was also included in the field program. One replicate water column sample was collected and submitted as a blind sample, with the five water column samples.

Dialysis Array

Four tandem peepers were deployed within ten metres of each other at each of the two stations. At each sampling station three peepers were sampled for metals and nutrients and one peeper was sampled for cyanide.

All peepers at each station were retrieved and sub-sampled within two days; identical sampling intervals were utilized on each bank of wells of each peeper. While peepers afford the opportunity to sample at very high resolution throughout the length of the sediment column, such detail is not germane to geochemical interpretation except near the sediment-water interface. Sub-sampling for metals and nutrient analyses consisted of twenty depths in total; three above the sediment-water interface (0.5, 5.0 and 20.0 cm above the sediment-water interface) and seventeen below within the sediments (0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 9.0, 11.0, 13.0, 15.0, 20.0, 30.0 and 40.0 cm below the sediment-water interface). Sub-sampling for cyanide consisted of ten depths in total; three above the sediment-water interface (0.5, 5.0 and 20 cm above the sediment-water interface), and seven below the sediment-water interface (0, 0.5, 1.0, 1.5, 2.0, 3.0 and 4.0 cm below the sediment-water interface).

2.4.2 Analytical Program

Precision was determined wherever possible (and practicable) by making replicate analyses of discrete samples, both in the water column work, and in the interstitial water and solid-phase sediment component. Combined sampling and analytical precision was also monitored by invoking the principle of "oceanographic consistency," which states that variations in the concentration profiles of dissolved constituents in closely-spaced aqueous samples should be smooth. Sharp discontinuities are considered to be real only if they are reproducible, and if they can be reasonably explained by acceptable physico-chemical phenomena.

The QC data was evaluated by the laboratory on a batch by batch basis. Pre-determined criteria have been developed for data acceptability, and are as follows:

- *Method Blanks:* below method detection limit;
- *Replicate Data:* agree to within ±10% of a calculated mean (when concentrations are more than 10x detection limit); and

- *Reference Materials:* meet manufacturers/suppliers 95% acceptance criteria.

If the data did not meet the above criteria but meets the following warning criteria, an explanation is provided:

- *Method Blanks:* reported blank result is less than 5x the detection limit and less than lowest reported result;
- *Replicate Data:* agree to within ±15% of a calculated mean; and
- *Reference Material:* data reported meet a calculated 99% acceptance criteria.

If the data did not meet the above criteria, the analytical batch was repeated.

3.0 Results

3.0 RESULTS

While both the water column and sediments were sampled, emphasis is placed on the latter as the focus of the project is on the post-depositional reactivity of the material within the tailings pond. The useful data base is limited relative to many of the previous MEND studies as many of the components (*i.e.*, dissolved Pb and Cd) are below the analytical detection limit.

All parameters within the water column are invariant both with depth and between locations (with the exception of cyanide species) and are presented to complement the pore water data. While free cyanide is below the detection limit (<0.005 mg/L), total and WAD cyanide both increase with depth in the water column. Total CN increases from 0.03 to 0.07 mg/L from the surface to bottom samples while WAD CN increases from ~0.02 to 0.05 over the same interval (Figure 3-1).

3.1 Stratigraphy and Diagenetic State of the Tailings Deposits

The stratigraphies of the two sites differ significantly. The shallow site (Station S) hosts a discontinuity between 36 and 42 cm depth according to solid trace metals and major element distributions (Figure 3-2). The compositional change corresponds to field observation of a sharp demarkation from typical gray tailings to a distinctly orange facies in the lower portion of the core. Communications with Equity Silver (Aziz 1995) suggest that this material likely represents deposition of neutralization sludge in the south-west corner of the pond (continuing until as late as August, 1992 followed by additional tailings deposition until closure in January 1994). Diminished major elements (Al, K and Na) and elevated trace elements (Cd, Co, Cu, Ni and Zn; discussed below) support this notion. The stratigraphy at the deep site, is uniform by comparison, suggesting that the deposits in the central deep hole accumulated in an uninterrupted fashion (Figure 3-2).

Organic carbon in both deposits is near or below the detection limit of 0.05 wt.% (Figure 3-3). The concentrations in the shallow site ranged from <0.05 to 0.25 wt.% while the maximum value at the deep site was only 0.15 wt.% and was lower in general. Both sites supported marginally elevated organic carbon in surface horizon. Observations of periphyton in the near-shore, rocky substrate

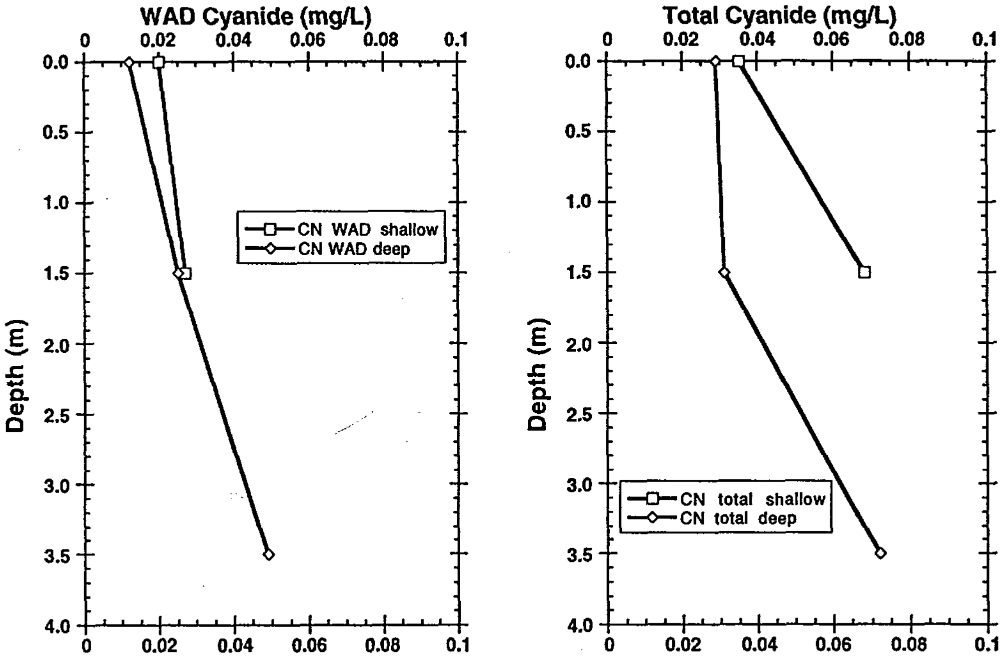

Figure 3-1 WAD and total cyanide in the water column of the Equity Silver Tailings Pond.

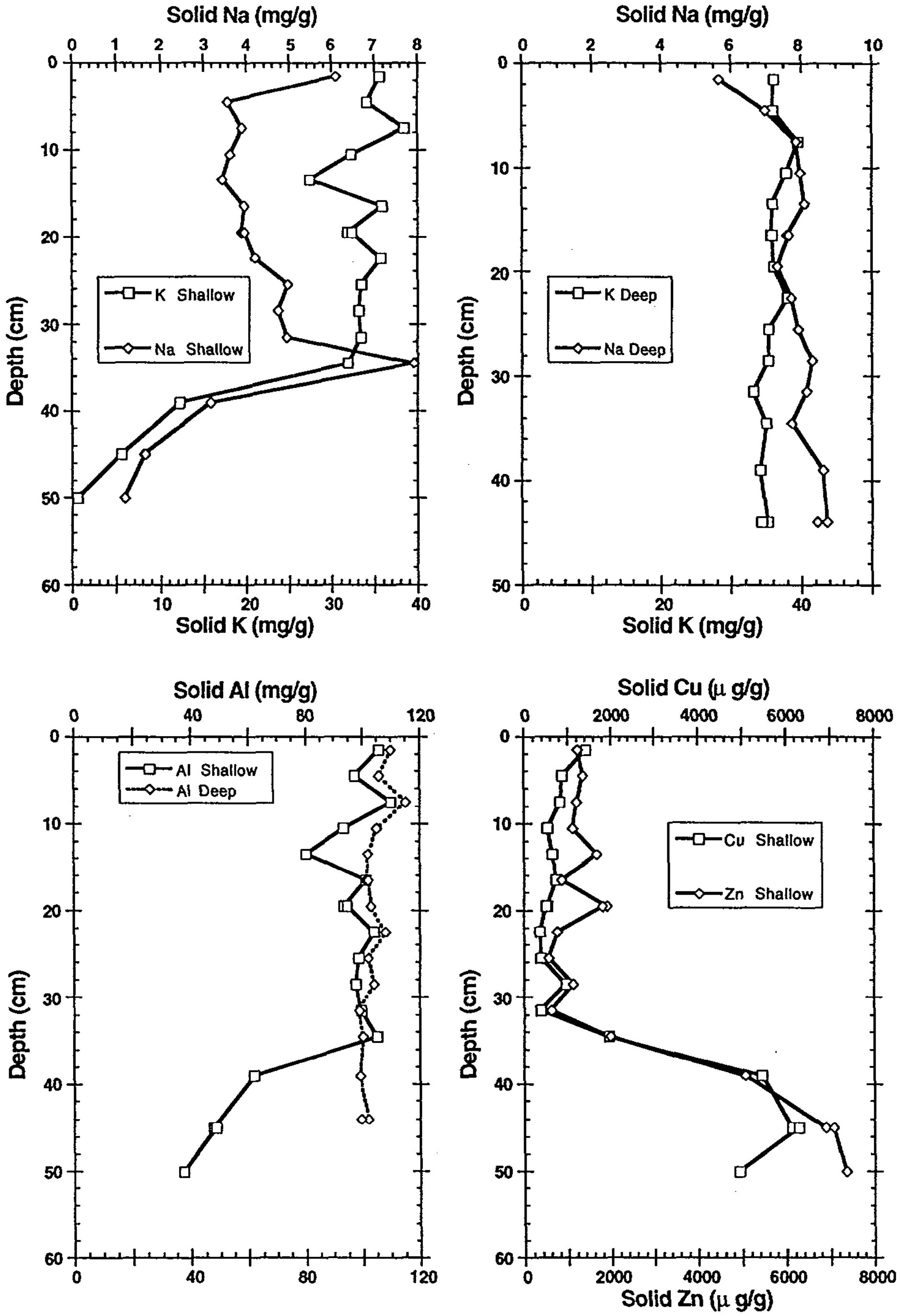

Figure 3-2 Solid-phase Na, K, Al, Cu and Zn in the shallow and deep deposits of the Equity Silver Tailings Pond.

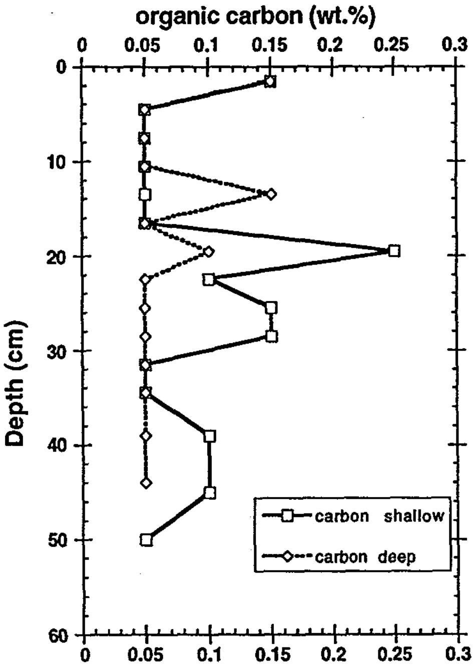

Figure 3-3 Organic carbon in the deposits of the Equity Silver Tailings Pond.

in concert with substantial accumulation of algae on the exposed surfaces of the peepers suggest that elevated organic carbon in surface sediments is likely aquatic in origin and as a result, very labile. However, it is unlikely that sufficient quantities have accumulated to profoundly alter the diagenetic state of the near-surface deposits.

Dissolved oxygen concentrations in bottom water are ~5 mg/L at both sites, decreasing across the sediment-water interface to near-zero values within the upper few centimetres of each deposit (Figure 3-4; described in greater detail below). The onset of sub-oxic and eventually anoxic conditions within the near-surface horizons is supported by dissolved Fe profiles which indicate Fe reduction within the upper 2 cm followed by rapid precipitation immediately below in pore waters of the shallow site (Figure 3-5). While Fe remobilization also occurs in the near-surface sediments of the deep site, its consumption is not as rapid. Free sulphide is below detection limit in all of the pore waters sampled.

Dissolved Mn at each of the sites decreases from uniform bottom-water concentrations of ~1.2 mg/L, across the sediment-water interface into the surficial sediments (Figure 3-5). In the shallow site, the decrease is rapid, such that a uniform concentration of ~0.3 mg/L is attained within a few centimetres below the interface. However, while dissolved Mn in the pore waters of the deep site decrease with depth, they do so less rapidly, attaining the same concentration (~0.3 mg/L) but not until depths of greater than 30 cm (Figure 3-5).

pH values are very consistent among replicate peepers. In all cases, pH increases gradually from bottom water values of 7.6 to deeper values of ~8.2. The pore waters at depth in the shallow deposit hosts higher pH values than the overlying material, increasing to values as high as 9.5 (Figure 3-6). This likely reflects the nature of material deposited at this location.

Dissolved Ca exists in bottom waters at a concentration of 400 mg/L (Figure 3-6). While the concentration generally increases with depth in the interstitial waters, Ca in the shallow and deep sites displays contrasting behaviour across the sediment-water interface. Where dissolved Ca at the deep station increases to 450 mg/L across the interface, it decreases to values as low as 300 mg/L within the upper few centimetres at the shallow site before increasing to the base of the peeper.

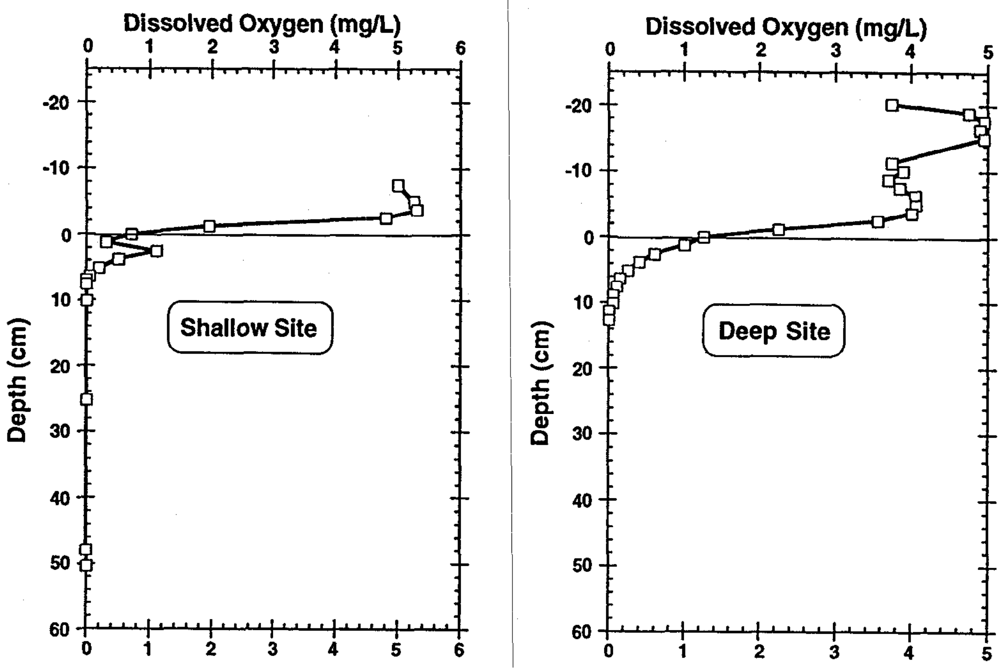

Figure 3-4 Dissolved oxygen in the bottom waters and pore waters of the Equity Silver Tailings Pond.

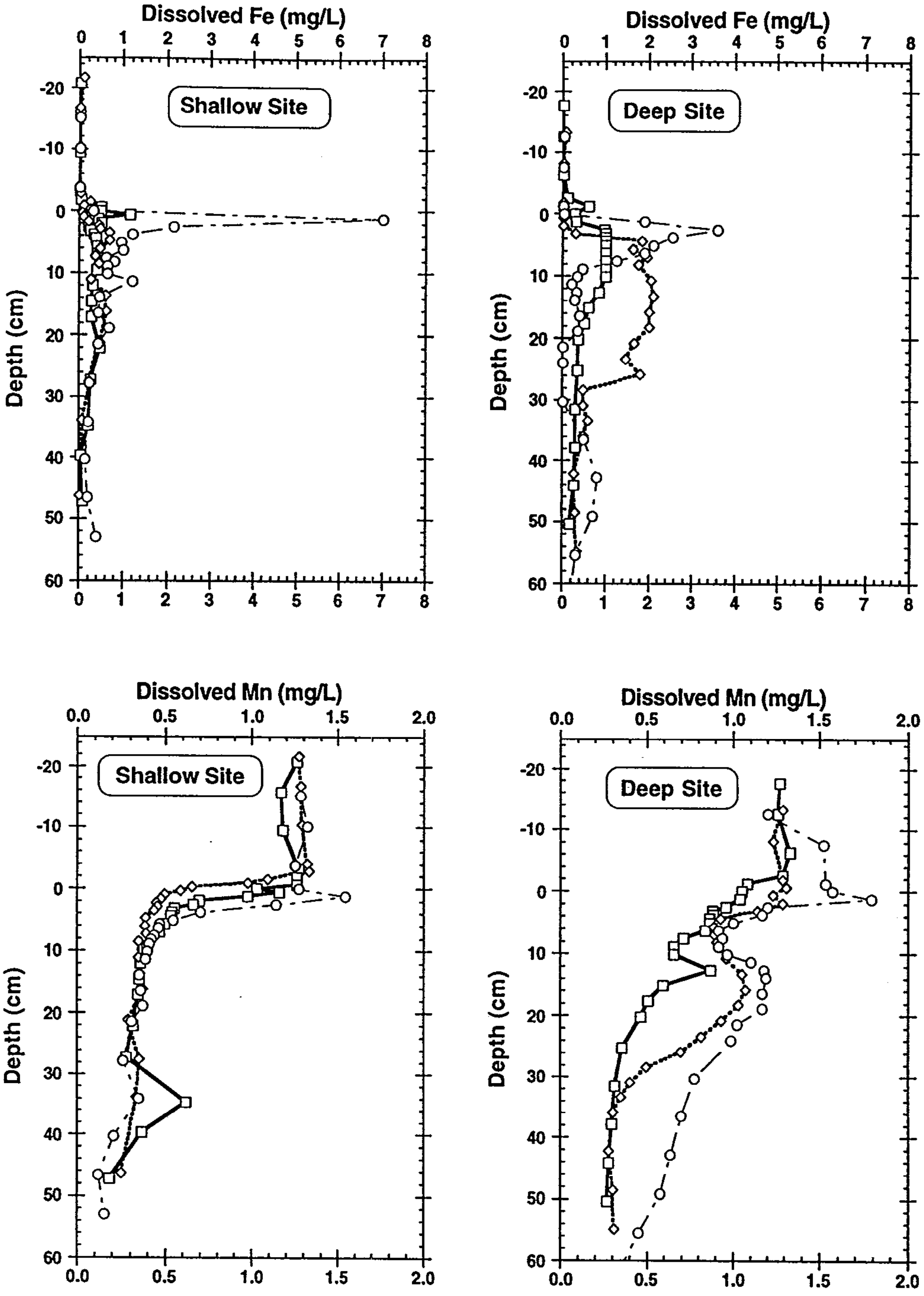

Figure 3-5 Dissolved Fe and Mn in the pore waters of the Equity Silver Tailings Pond. Square symbols represent peepers #13 (shallow) and #14 (deep); triangle symbols represent peepers #12 (shallow) and #3 (deep) while circles represent peepers #15 (shallow) and #11 (deep).

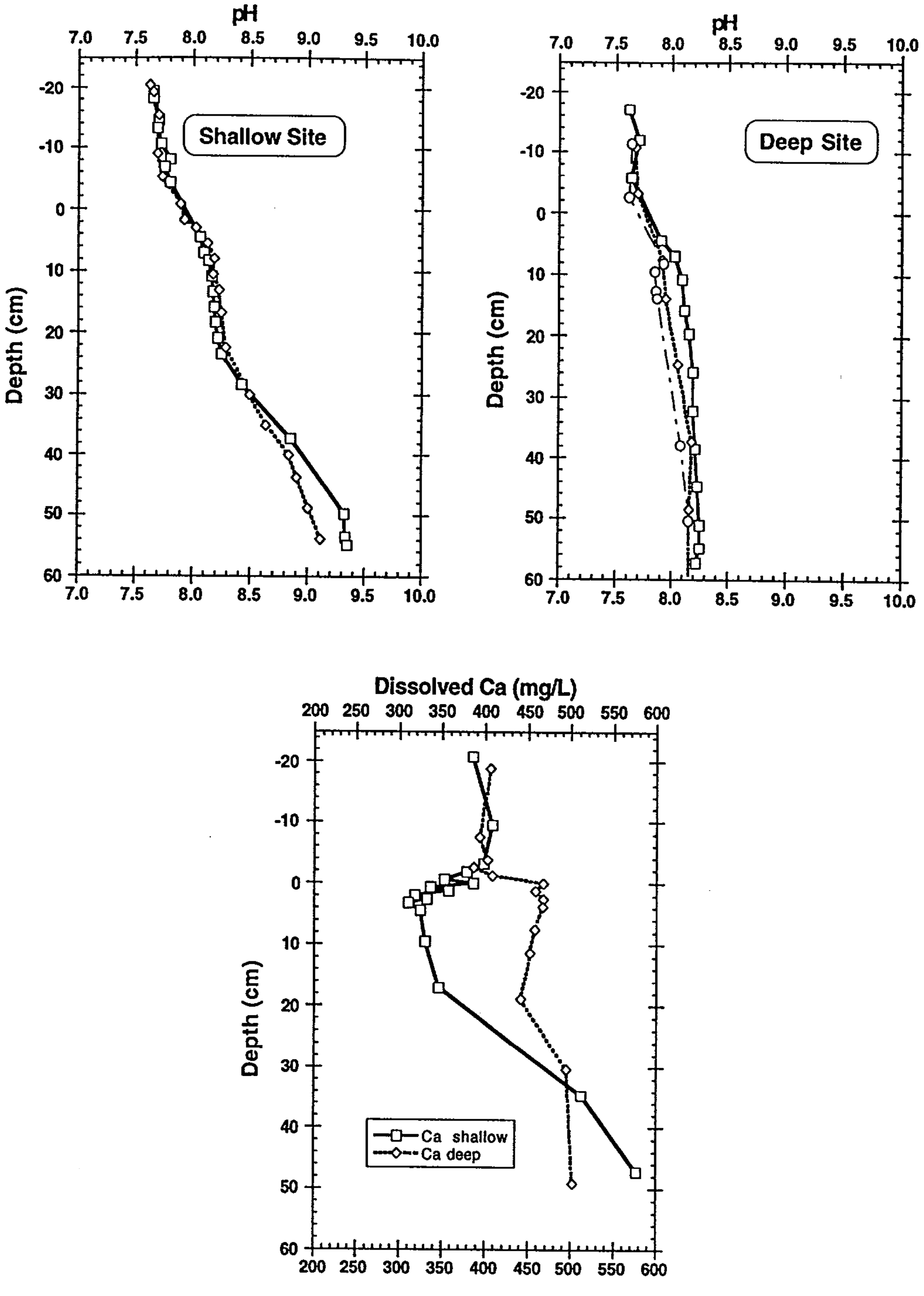

Figure 3-6 pH and dissolved Ca in the pore waters of the Equity Silver Tailings Pond.

Dissolved oxygen profiles across the sediment-water interface displayed “classic” consumption profiles (Figure 3-4). Bottom waters are of uniform concentration until a zone immediately above the sediment-water interface through which dissolved oxygen decreased linearly from ~5 mg/L at both sites to values of ~1 mg/L at the sediment-water interface. Below the interface, dissolved oxygen decreased in concentration exhibiting the concave-downward profile indicative of the balance between chemical consumption and diffusive replacement.

3.2 Trace Components

With the exception of the base of the shallow deposit, distribution of solid-phase Cu at both sites is relatively uniform with depth with concentrations averaging ~600 µg/g in each of the deposits (Figure 3-7). While solid-phase Zn is distributed in a similar fashion, it is elevated slightly at the shallow site relative to the deep site having respective averages of 1,100 and 600 µg/g. Below 34 cm depth at the shallow site, both Cu and Zn increase profoundly to values in excess of 6,200 and 7,300 µg/g, respectively. To some degree, the dissolved fraction of these metals reflect a similar distribution.

Dissolved Cu in the shallow deposit shows two zones of remobilization (Figure 3-8). In one of the three shallow sites (Peeper #13), Cu is released to near-surface pore waters, increasing from a bottom water value of 0.007 to 0.19 mg/L before decreasing to below detection limit (<0.005 mg/L). Below ~34 cm in all three shallow replicates, dissolved Cu concentrations increased from below detection to values ranging from 0.06 to 0.63 mg/L, suggesting release from an unstable phase at depth. Dissolved Cu at the deep site remains below the detection limit with the exception of a zone between 6 and 30 cm depth in peeper #15. Here, a broad, symmetric zone of release is defined by a maximum concentration of 0.11 mg/L; it does not appear in either of the other two replicates nor at the shallow site.

Dissolved Zn profiles at both sites in all replicates are relatively uniform in distribution with the exception of sporadic excursions (Figure 3-8). As these data points exist virtually in isolation (*i.e.*, they are not supported geochemically by adjacent or ancillary data), it is possible that they represent sample contamination.

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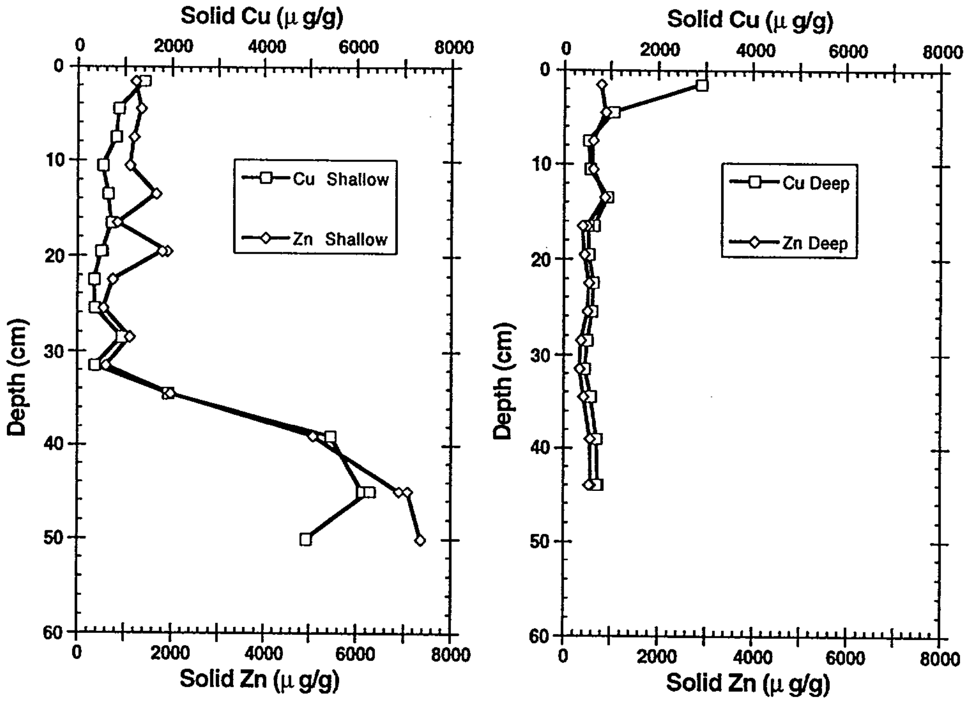

Figure 3-7 Solid-phase Cu and Zn in the shallow and deep deposits of the Equity Silver Tailings Pond.

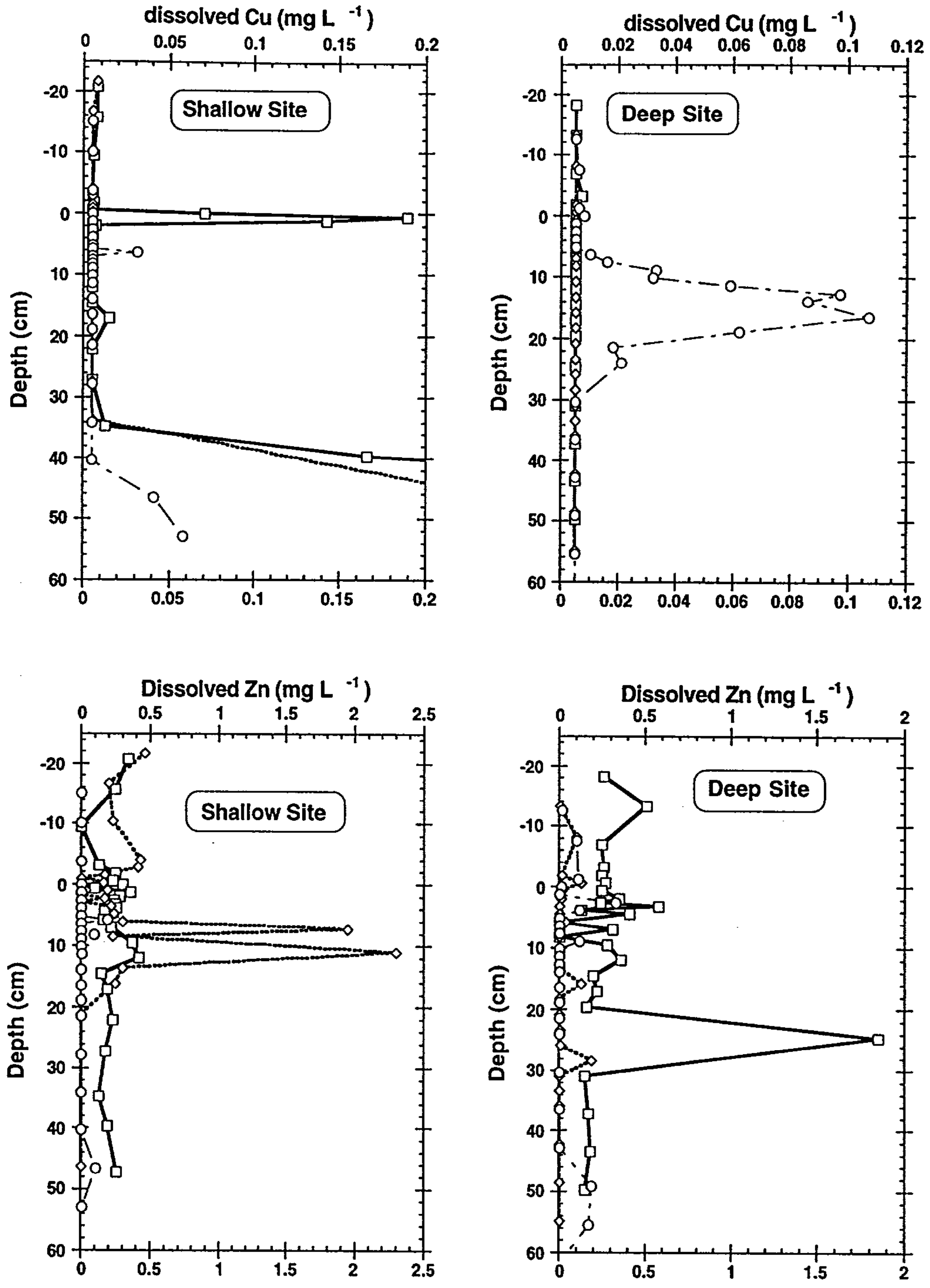

Figure 3-8 Dissolved Cu and Zn in the pore waters of the Equity Silver Tailings Pond. Square symbols represent peepers #13 (shallow) and #14 (deep); triangle symbols represent peepers #12 (shallow) and #3 (deep) while circles represent peepers #15 (shallow) and #11 (deep).

The distribution of solid-phase As differs between the two cores (Figure 3-9). Arsenic at the shallow site increases from a surface sediment value of 6.7 mg/g to 1.8% a maximum of 18 mg/g at 13 cm depth. Below this depth, As decreases steadily to a concentrations of 1.2 mg/g by the base of the core. In contrast, As in the deep site decreases from 6.2 mg/g at the sediment surface to a shallow minimum of 0.26 mg/g at 10 cm depth before increasing steadily to the base of the core where it reaches values as high as 2.0 mg/g.

The distribution of dissolved As among all replicates and between sites is consistent. Arsenic increases from uniform bottom water concentrations of ~0.027 mg/L across the sediment water interface to a shallow subsurface maximum ranging from 0.5 to 2.5 mg/L. Below the dissolved maximum, As decreases in concentration to ~0.1 mg/L at the base of each core. The primary difference between the two sites lies in the depth range over which the dissolved maximum occurs. At the shallow site, the dissolved maximum occurs between 0 and 40 cm depth while the same zone at the deep site spans the interval from 2 to 20 cm. This difference reflects either differing zones of As consumption at depth, or more likely, differing zones of release of a soluble solid.

The distribution of solid-phase Sb is variable at both sites; however, enrichments of up to 260 and 390 µg/g are discernable in the near-surface horizons of the shallow and deep deposits respectively (Figure 3-10). The average concentrations of the shallow and deep deposits are 140 and 200 µg/g, respectively.

Dissolved Sb, like As, displays consistent behaviour among all replicates at both sites. From uniform bottom water concentrations of 0.035 mg/L, dissolved Sb decreases to ~0.01 mg/L within several centimetres of the sediment-water interface. Within one of the shallow water peepers, Sb undergoes remobilization at 25 cm depth to levels of 0.03 mg/L. The overall distribution is similar in form to that of dissolved Mn (Figure 3-5).

Cyanide distributions in pore waters are by analytical necessity of lower resolution; adjacent cells spanning depth intervals of up to 8 cm were combined to furnish sufficient volume for analysis. Free cyanide concentrations were below the detection limit of 0.005 mg/L except at the base of each peeper where concentrations for the shallow and deep deposits were 0.008 and 0.015 mg/L, respectively (Figure 3-11). The vertical resolution for total cyanide was

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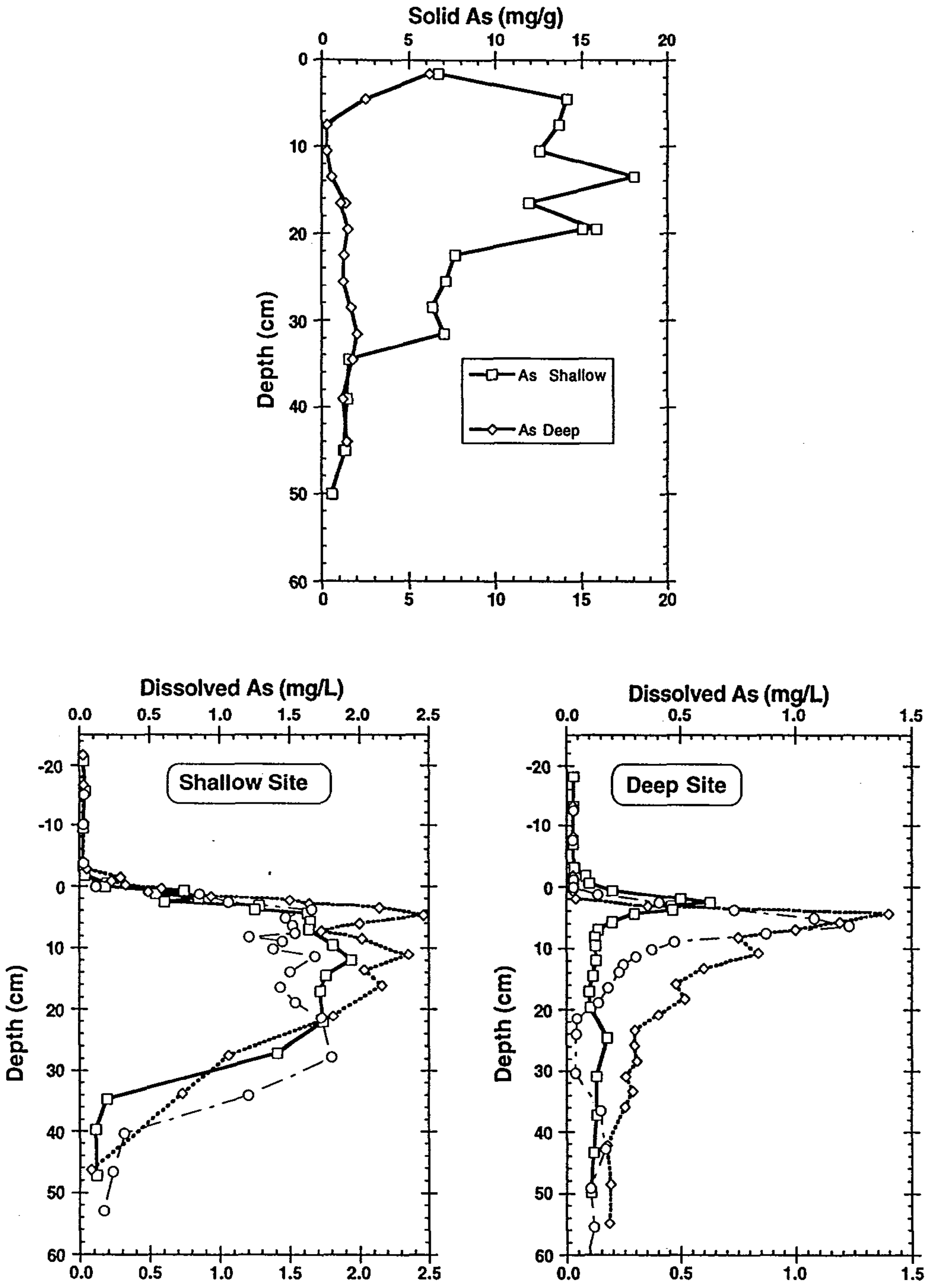

Figure 3-9 Solid and dissolved arsenic in the deposits of the Equity Silver Tailings Pond. For dissolved As, square symbols represent peepers #13 (shallow) and #14 (deep); triangle symbols represent peepers #12 (shallow) and #3 (deep) while circles represent peepers #15 (shallow) and #11 (deep).

insufficient to discern any clear trends with depth in either deposit. However, at both sites, the total CN concentration appears to increase across the sediment-water interface from ~0.04 in both bottom waters to subsurface maxima of 0.05 and 0.13 mg/L for the shallow and deep sites, respectively. Total CN decreases with depth to 0.04 mg/L before increasing marginally at the base of each peeper.

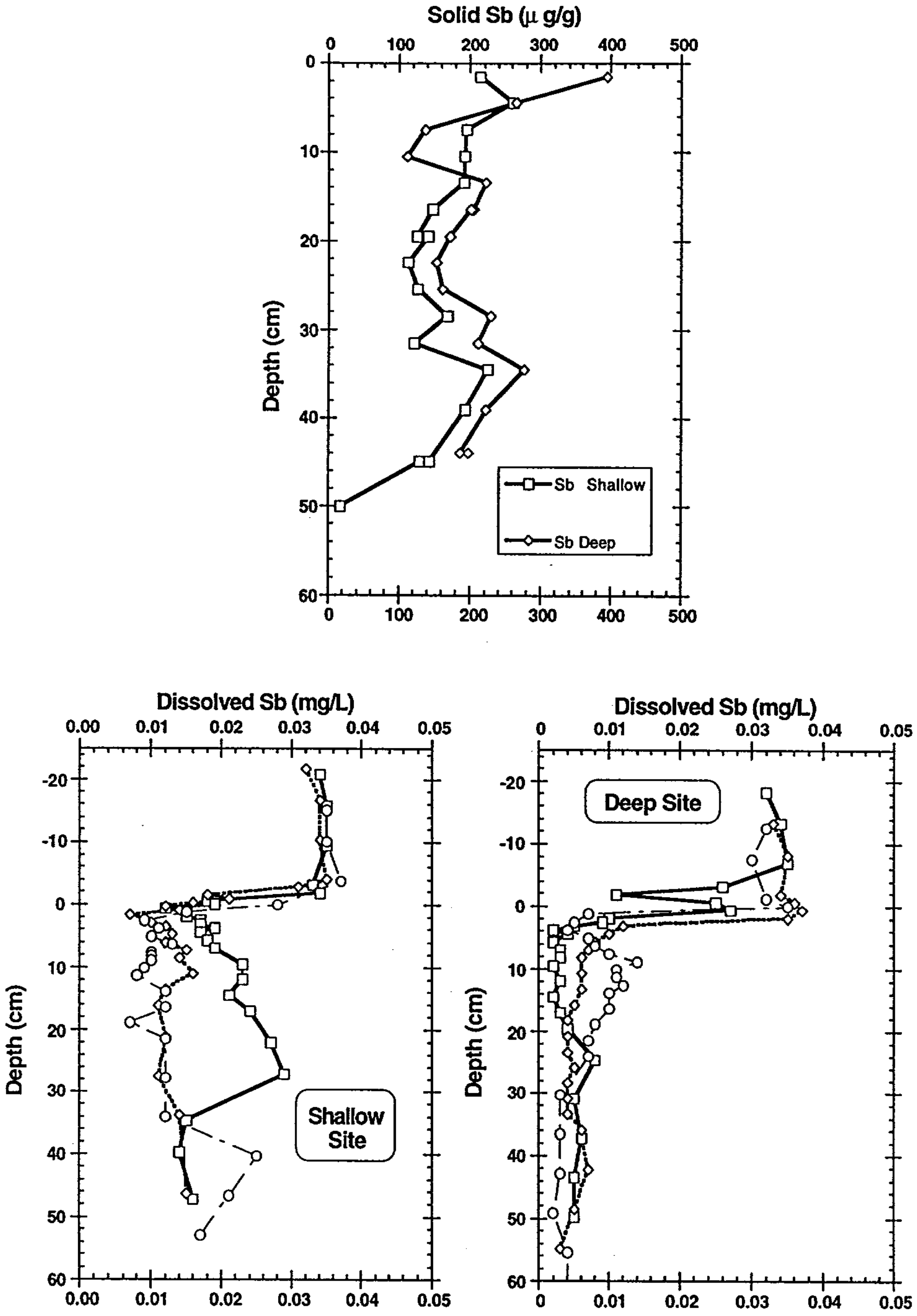

Figure 3-10 Solid and dissolved antimony in the deposits of the Equity Silver Tailings Pond. For dissolved antimony, square symbols represent peepers #13 (shallow) and #14 (deep); triangle symbols represent peepers #12 (shallow) and #3 (deep) while circles represent peepers #15 (shallow) and #11 (deep).

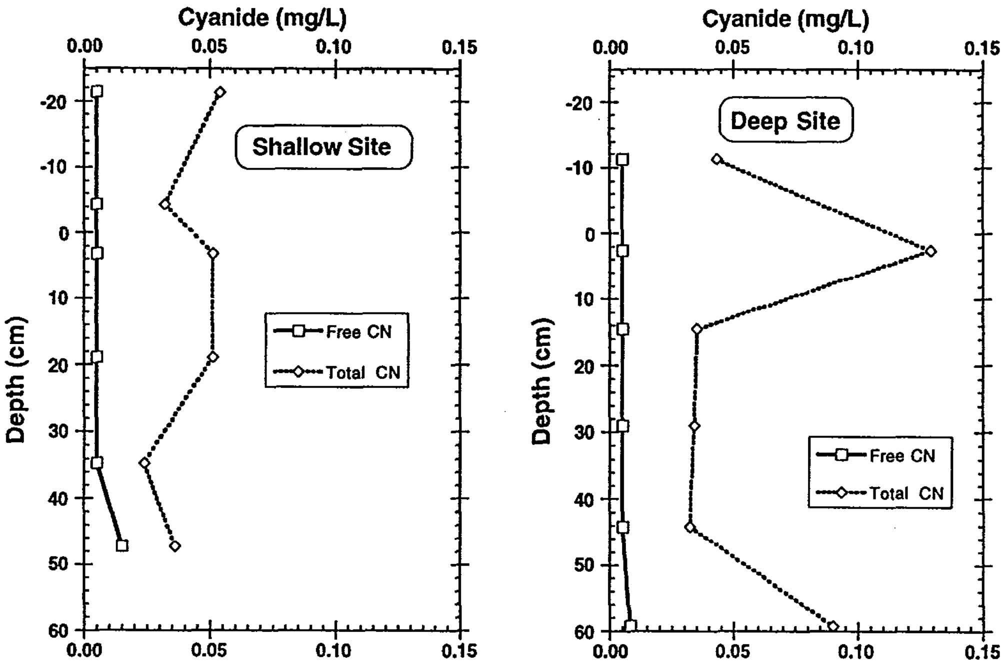

Figure 3-11 Total and free cyanide in the pore waters of the deposits of the shallow and deep stations in the Equity Silver Tailings Pond.

3.0 RESULTS 1

4.0 Discussions

4.0 DISCUSSIONS

While the geochemical framework of the Equity Silver Tailings Pond differs considerably from that of a natural lake, the principles upon which metal cycling are interpreted are the same. Following are discussions of each of the parameters of interest in addition to an independent assessment of tailings reactivity as predicted from dissolved oxygen profiles.

4.1 Copper

Of the trace metals studied, Cu was the only one to display any indications of active cycling. The sedimentary geochemistry of Cu is well documented both in previous MEND studies (Rescan 1989; Rescan 1991; Rescan 1993; Rescan 1995) and in the primary literature (Pedersen *et al*. 1985; Pedersen *et al*. 1986; Pedersen *et al*. 1993; Hamilton-Taylor and Davison 1995).

Metal Cycling

The high degree of variability seen in dissolved Cu between the two sites and indeed, among the replicate peepers suggests that there is both large and small scale lateral variability in the deposits of the tailings pond.

Only one of the Cu profiles (peeper 13) indicated interfacial remobilization. Defined by three data points, the maximum is likely real representing a localized zone of dissolution immediately below the sediment-water interface. In typical lacustrine (and marine) sediments, such a feature is often attributed to release of Cu associated with organic material remineralization. Indications of organic carbon are supported by field observation of abundant periphyton in the rocky shallows of the pond as well as substantial accumulation of unidentified green algae on the exposed surfaces of the peepers and landers during their 14 day deployment. However, it is unlikely that organic matter remineralization is responsible for the release of Cu at this one site as the magnitude of the maximum is in excess of that typically seen in other sediments (190 µg/L cf. 1 to 30 µg/L; Pedersen *et al*. 1986; Shaw *et al*. 1990). Furthermore, it is expected that such a release would be ubiquitious among all sites of the pond, particularly the deep, calm areas where organic matter should preferentially accumulate. That the near-surface release of Cu is restricted to one peeper and that none of the deposits are visibly enriched in organic carbon suggests that another mechanism is responsible.

It is possible that dissolution of Fe oxyhydroxide could account for some of the release of dissolved Cu as Fe dissolution is evident in the same peeper (peeper 13). However, release of Cu does not occur in the adjacent peeper 11 which hosts dissolved Fe concentrations elevated by almost a factor of five. Thus, it is suspected that this localized release is associated with the accumulation of an unknown, soluble Cu-containing phase.

Like the surface sediments at Station S, one peeper profile (Peeper #15) in the deposits of Station D displays a broad zone of dissolved Cu enrichment. Centred at approximately 15 cm depth (Figure 3-8), this zone of 4% Cu release corresponds to a similar release of dissolved Mn (Figure 3-5), suggesting that reductive dissolution of Mn-oxyhydroxides may be responsible. While Cu is known to associate with oxides of Mn and Fe (Balistrieri and Murray 1986), the zone of Mn release is displaced to deeper depths than would be expected in a deposit accumulating under conditions of steady-state. Furthermore, it is unusual that similar releases are not observed for the replicate peepers which both indicate similar regions of Mn dissolution. The data suggest a phase in disequilibrium with the ambient redox potential, and implies the presence of a local slump or other depositional event. The disparate behaviour among the replicate pore water profiles reinforces the implication that the deposits in the pond are laterally heterogeneous.

The consistency of the dissolved Cu distributions at the base of all three peepers from the shallow site suggests that the orange sediment underlying the tailings contains an unstable phase that is presently releasing Cu. As neutralized mine-water sludge is known to have been deposited at this site until August, 1992, it is likely that this material is dominated by oxides and hydroxides of Fe (hence the characteristic orange colour). It is possible that the release of dissolved Cu is associated with reduction of Cu-containing Fe oxyhydroxides; however, there is no commensurate release of dissolved Fe or Zn (which should also be released during oxide reduction). Furthermore, there is no free sulphide to explain the absence of dissolved Fe. Rather, the diminished dissolved Fe likely reflects the nature of these facies. If the orange deposits below 30 cm at the shallow station are comprised of neutralized sludge (supported by elevated pore water pH relative to both the other site and the horizons above), the absence of sulphides or organic matter will limit the demand for oxidant: presumably nitrate (or perhaps Mn-) reduction can meet the oxidant requirements and could account for the lack of iron oxyhydroxide reduction. Consequently, the presence of Fe oxide-enriched facies at depth in the shallow site are poised with an elevated redox potential relative to the deposits above and presumably below.

If Fe is not reduced in this zone, the source of dissolved Cu must arise from dissolution of another soluble solid phase. Irrespective of the source, the release of Cu is too far removed from the sediment-water interface for the diffusional flux to impact the tailings pond waters. Indeed, the abrupt change in slope of the copper profile at 34 cm depth implies that Cu is precipitating at this level.

4.2 Arsenic

Arsenic has a well known affinity for iron (and to some degree manganese) oxyhydroxides. Solid-phase oxyhydroxides efficiently coprecipitate or scavenge AsO_4^{3-} from water and release it upon dissolution (Aggett and O'Brien 1985; Aggett and Roberts 1986; Aggett and Kreigman 1988; Belzile 1988; Belzile and Tessier 1990; de Vitre *et al*. 1991; Kuhn and Sigg 1993). Arsenate is adsorbed strongly to the oxyhydroxide surface. Upon burial, when the oxide is reduced, arsenic is released as arsenite. It typically diffuses from a subsurface maximum both upward and downward. That fraction diffusing toward oxygenated bottom waters is reoxidized to arsenate and may be rescavenged in the zone of Fe precipitation, or it may be returned to the water column.

Arsenic Cycling

Arsenic is released from the sediments at both the shallow and deep sites suggesting that dissolution from a thermodynamically unstable phase or release from a soluble phase or alteration product is occurring. As discussed above, arsenic is known to cycle in association with diagenetic Fe; Fe is seen to undergo reductive dissolution in some of the near-surface deposits of both sites. However, the uniform release of As is not consistent with the variable degrees of release of Fe in the same zone of replicate peepers, suggesting that oxide dissolution may not be responsible for its behaviour. Rather, the profile of dissolved As at both sites corresponds very well with solid-phase As, suggesting that its release to pore waters may result from non-steady-state dissolution. Solid-phase arsenic concentrations as high as 18,000 and

6,100 µg/g are observed in the shallow and deep deposits respectively (Figure 3-9) suggesting that alteration products (perhaps formed in the milling process) may account for its behaviour. The distribution of solid As at the shallow site suggests that it is abundant within the tailings and much less abundant in the neutralization sludge. Thus, if the porewater distribution arises from dissolution, a possible candidate is the sulpho-salt tennantite; however, the aqueous solubility of tennantite is unknown.

4.3 Antimony

Few data are available on the natural cycling of Sb in the aquatic environment, either lacustrine or marine. Like arsenic, antimony is a group VA metalloid and is therefore expected to share some properties with arsenic. In reality, the geochemistry of Sb differs from that of arsenic as a result of its greater metallic character (Cotton and Wilkinson 1980; Byrd 1990). Like other metalloids, Sb is capable of forming organo-metallic compounds (Andreae and Froelich 1984).

In oxic water bodies, Sb exists as the oxyanion antimonate having a +5 oxidation state. Under anoxic conditions, Sb is reduced to the +3 state where it appears to associate more strongly with particulate matter, presumably coprecipitating with FeS (Cutter 1992). However, Sb(V) is known to exist at significant concentrations in anoxic waters (Cutter 1991) as a result of either slow reduction kinetics or possible stabilization through the formation of thio-complexes (Andreae and Froelich 1984). In many ways, Sb shares properties with both As and Mo.

Antimony Cycling

Dissolved antimony concentration in natural surface waters generally range from 0.1 to 0.5 µg/L (Rossmann and Barres 1988). The behavior of antimony in ESTP is characterized by rapid uptake in the near-surface sediments. Bottom water concentrations (0.035 mg/L) are elevated relative to typical background levels by as much as two orders of magnitude (Rossman and Barres 1988; Byrd 1990). The source of Sb to pond waters is presently unknown. However, the data show unequivocally that Sb is consumed within the surficial tailings and that a diffusive influx exists across the sediment-water interface (Figure 3-10). The similarity between the dissolved Sb and dissolved Mn distributions suggest that a common mechanism (perhaps pH driven) may account for their consumption. It is unlikely that Sb is coprecipitated with FeS or as a discrete sulphide as there is no evidence of sulphate reduction within the deposits nor is there sufficient organic matter to drive the redox potential to sulphate reduction. However, it is possible that consumption of Sb in the near-surface sediments is associated with adsorption to or coprecipitation with oxyhydroxides. Such behavior has been observed previously in the sub-oxic zone in the Baltic Sea (Andreae and Froelich 1984).

Antimony has been shown to adsorb rapidly to various forms of particulate material; its partition coefficient remains constant with time (Nyffeler *et al*. 1984). Indeed, the presence of Sb(V) in anoxic water columns has been attributed to rapid delivery via settling particles coupled with slow rates of reduction (Cutter 1992). Antimony has also been suggested to associate with pyrite (Cutter 1992). Thus, it may be that the distribution of Sb in ESTP deposits reflects partitioning between the available solids; the near constant distribution of dissolved Sb with depth in the interstitial waters in concert with a temporally stable partition coefficient supports this supposition.

4.4 Cyanide

Cyanide within the interstitial waters must have arisen from the process water trapped during deposition of the tailings. WAD cyanide is below detection limit in all but the deepest sample at each site while total cyanide is somewhat variable in its distribution. Total cyanide is elevated above bottom water concentrations only at the deep site, most notably immediately below the sediment-water interface. Given the high concentrations of dissolved Fe at this location, it is possible that much of the total cyanide is Fe-complexed. As the samples were collected by peeper, the cyanide can be considered mobile within the porewaters; however, the lower level of sampling resolution and the unknown degree of complexation precludes any estimates of efflux.

4.5 Tailings Reactivity from Dissolved Oxygen Profiles

Significant technical advances have been make in recent years in the development and application of oxygen micro and mini-electrodes in the fields of microbial ecology (Revsbech *et al*. 1980; Jorgensen and Des Marais 1990) and marine research (Reimers *et al*. 1984; Reimers and Smith 1986; Archer *et al*. 1989; Sahami *et al*. 1996). Oxygen mini-electrodes have been used to measure oxygen gradients across the sediment/water interface at high spatial and temporal resolution. Measured oxygen gradients have been used in conjunction with the published molecular diffusion coefficient (corrected for temperature and salinity) for oxygen, to calculate the flux of oxygen across the sediment/water interface (Jorgensen and Revsbech 1985; Revsbech *et al*. 1986; Gundersen and Jorgensen, 1990; Sahami *et al*. 1996). Accurate measurements of the oxygen flux into sub-aqueous tailings provides a new tool in assessing the geochemical stability of such deposits. The present study represents the first application of oxygen mini-electrode technology to mine tailings reactivity studies.

Measurements of oxygen concentration in solutions by mini-electrodes is based on the well established polarographic technique. A potential applied between the oxygen mini-electrode and a silver/silver chloride reference electrode electrochemically reduces oxygen on the active electrode's gold surface, producing a current that is directly proportional to the activity of oxygen in the medium in contact with the electrode tip. The current is amplified, converted to a voltage and recorded. The measurements are then calibrated by measuring the electrode's response, in solutions with known dissolved oxygen concentrations (as determined by the Winkler titration method).

Oxygen gradients were measured across the tailings/water interface at Equity Silver's tailings pond using an oxygen minielectrode to measure the dissolved oxygen concentrations of appropriate peeper cells. The minielectrode used required less than one drop of sample, had a fast response time (<20 seconds), and due to the very low oxygen consumption (approximately 2.5×10^{-4} µl O_2/hour at 25°C) required no stirring.

The maximum measured oxygen gradients were used to estimate the oxygen flux into two sites in the tailings pond. The oxygen flux was calculated using an equation derived from Fick's first law of diffusion:

$$\text{Oxygen flux} = D\,(\delta O_2/\delta Z)$$

where D is the *in situ* molecular diffusion coefficient for oxygen and ($[\delta O_2]/\delta Z$) is the maximum oxygen gradient across the tailings/water interface.

Oxygen fluxes of 30.7 mg O_2/m^2/day and 14.0 mg O_2/m^2/day have been calculated for the deep site and the shallow site, respectively. An oxygen diffusion coefficient of 1.57 x 10^{-5} cm^2/s (Broecker and Peng 1974) was used for the oxygen flux calculations, with the assumption that this value would not be significantly decreased in the top centimeter of the tailings. This assumption is supported by field observations of the unconsolidated nature of the tailings surface.

Oxygen consumption rates by sub-aqueous tailings in Equity Silver tailing pond are generally an order of magnitude lower than oxygen uptake rates by natural organic-rich lake sediments. For example oxygen uptake rates of approximately 900 mg O_2/m^2/day are typical for meso-eutrophic lakes (Sweerts *et al*. 1991).

Previously measured oxidation rates in sub-aqueous tailings have ranged between 2.6 to 8.7 mg O_2/m^2/day (David and Nicholson 1995; Nicholson *et al*. 1995). These oxidation rates are somewhat lower than those measured in ESTP by this approach, as they have been measured in pure sulphide tailings containing no organic carbon. In ESTP oxygen is consumed at the tailings/water interface by the aerobic oxidation of organic matter, as well as by the oxidation of sulphide minerals.

Assuming Redfield stoichiometry for the organic matter in ESTP the aerobic oxidation of organic matter is expressed by the following equation:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ O_2 \Rightarrow 106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 122\ H_2O$$

Estimates of oxygen consumption by organic matter degradation processes are necessary to support the hypothesis that the main sink for dissolved oxygen in ESTP is the aerobic degradation of organic matter, rather than the oxidation of sub-aqueous tailings. Organic matter input rates to ESTP, together with high resolution determination of the oxygen gradients across the tailings/water interface are therefore required to quantify the actual oxygen uptake by the tailings as inferred by gradient through the sediment-water interface. Another way to accomplish this is to compare O_2 fluxes as determined above with those estimated from the form of the concave-downward profile within the tailings. Assuming organic matter is restricted to sediment-water interface and thus, only effects the flux through the diffusive sub layer allows for an estimation of the oxidation rate of the tailings by themselves.

A diffusion-consumption model (applied to the data of the shallow site) is derived by assuming that the observed oxygen profile is a result of the steady-state balance between diffusive resupply of oxygen from bottom water and the consumption of oxygen within the deposits through tailings oxidation. Thus, the integration of Fick's equation corrected for consumption provides the working equation:

$$D(\delta^2 C/\delta z^2) - kC = 0$$

where D is the diffusion coefficient for oxygen corrected for porosity and tortuosity, C is the oxygen concentration, z is depth and k is the reaction rate constant (determined from a regressed fit to field oxygen data). Using the same diffusion coefficient as above (1.57×10^{-5} cm^2/s) results in a conservative over-estimate for the calculation; if D is corrected (lowered) for tortuosity effects, the net effect will result in a lower calculated flux of oxygen into the tailings. In this way, the resulting estimate of 5 $mg/m^2/day$ (the value derived from the oxygen data of the shallow site) is viewed as the maximum oxygen flux into the sediments arising from tailings oxidation. This value is used to determine the maximum amount of acid generated assuming all oxygen goes to the oxidation of pyrrhotite.

Assuming the main sulphide mineral in the tailings to be pyrrhotite, a simplified equation describing its oxidation is:

$$FeS + 9/4\ O_2 + 5/2\ H_2O \Rightarrow SO_4^{-2} + Fe(OH)_3 + 2\ H^+$$

and that the entire calculated oxygen flux of 5 $mg/m^2/yr$ is consumed by oxidation of pyrrhotite as described by the above equation, an estimated impact on water quality can be calculated, knowing the pond volume and surface area. Note that for the sake of conservatism, the liberated products are assumed to be returned quantitatively to the water column through diffusion.

Sulphate is chosen as the best parameter as it is anticipated to display the most conservative behaviour of the oxidation by-products. Sulphate is a major ion, and therefore has lesser degrees of chemical reactivity than either trace metals or protons. While sulphate may undergo reduction to sulphide and thus be removed from solution through subsequent precipitation, this process is suspected not to occur in ESTP as there was no evidence of free sulphide in the pore waters, nor was there any evidence of a sufficiently reducing environment. Sulphate may, however, precipitate as gypsum and be removed from solution if sufficient dissolved Ca exists. Irrespective of any secondary reactions, it is assumed that all liberated sulphate is free for diffusive return to the water column to derive the most conservative potential impact prediction.

The flux and quantitative consumption of 5 mg/m^2/day of oxygen by sulphide oxidation creates a “counter-flux” of approximately 6.7 mg/m^2/day of sulphate and 2.8 µmol/m^2/day in the form of protons. While it is difficult to predict the effect of the generation of a flux of acid on proton activity (*i.e.*, pH), it is comparatively simple to infer the water column loading of sulphate. The 6.7 mg/m^2/day as an upward flux (in reality, a significant fraction would be downward, deeper into the sediments and would not enter the water column) translates to an annual loading of approximately 0.5 mg/L to the water column (based on a median pond depth of 4.3 m). This incremental annual loading represents <0.03% of the water column sulphate inventory (~1,900 mg/L); it is highly unlikely that the existing sulphate in the water column could arise from subaquous tailings oxidation.

5.0 Summary and Conclusions

5.0 SUMMARY AND CONCLUSIONS

A detailed geochemical survey was performed on the Equity Silver Tailings Pond focusing on the post-depositional reactivity of the tailings material as determined by porewater and solid-phase distributions of a suite of parameters. Special emphasis was placed on illuminating the post-depositional diagenesis of antimony and cyanide species neither of which have been the focus of previous porewater research. Dissolved oxygen microgradients across the sediment-water interface were measured and used to directly infer tailings oxidation rates; copper and arsenic also received attention.

The Equity Silver mine tailings are the byproduct of a copper concentrate which contained chalcopyrite $CuFeS_2$, tennantite $(Cu, Fe, Zn, Ag)_{12}As_4S_{13}$ and tetrahedrite $(Cu, Fe, Zn, Ag)_{12}Sb_4S_{13}$. As the recovery from the mill circuit was approximately 90% there were small residual quantities of these minerals in the tailings. A leach plant was installed at the mine commissioning in 1980 and operated to upgrade the concentrate for the smelter markets by removing arsenic and antimony from the concentrate. This plant ran for approximately 2½ years but was discontinued as the smelter eventually would accept the unleached concentrate products.

The distribution of Cu (and indeed, most other elements studied) was seen to reflect small-scale (on the order of decimetres to metres) inhomogeneity. At the deep site, Cu was neither released nor consumed by the tailings with the exception of one well defined zone possibly arising from dissolution of Mn-oxides. Solubilization of a secondary oxide or hydroxide likely accounts for the release of dissolved Cu in the orange, neutralization sludge at depth in the shallow site as redox potential is insufficiently low to reduce the oxides.

Arsenic and antimony display opposing behaviour. While arsenic is released universally within the tailings pond deposits via the dissolution of an unidentified solid, antimony is consumed rapidly within the surface sediments. Consumption of antimony is suspected to arise from an association with oxyhydroxides or possibly via adsorption to tailings particles (perhaps pyrite).

Dissolved oxygen microgradients across the diffusive sub-layer infer oxidation rates lower than natural lake sediments but marginally higher than other subaqueous tailings deposits. The disparity between oxidation of ESTP tailings and other sub-aqueous tailings likely reflects the recent addition of organic matter to the sediment-water interface. While organic matter is depleted throughout the deposits, observations suggest that a substantial carbon flux now exists. This material likely accounts for the marginally elevated oxygen consumption rate. This supposition is supported through the application of a diffusion-consumption model as described in Lerman (1977) to the dissolved oxygen data immediately below the sedment-water interface where organic matter presumably does not exist. The data suggest a maximum oxygen flux (consumption) of approximately 5 mg/m^2/day for the shallow site, a value roughly 30% of that determined from linear diffusion through the benthic boundary layer (14 mg/m^2/day).

Given the possibility of primary productivity within the pond in the future, it is possible that a seasonal cycle will develop as observed in other systems (*i.e.*, Anderson Lake). This may impact the cycling and long-term stability of metals such as As, Cu and conceivably Sb.

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Appendix A - Data

Peeper Rescan #13 (shallow)

Depth (cm)	Sb (mg/L)	As (mg/L)	Cd (mg/L)	Cu (mg/L)	Fe (mg/L)	Pb (mg/L)	Mn (mg/L)	Zn (mg/L)	Ca (mg/L)	nitrate (uM)	sulphate (uM)	Depth (cm)	pH
-20.79	0.034	0.028	0.0001	0.008	0.022	<0.0025	1.26	0.34	385	41.67	23184	-19.53	7.65
-15.75	0.035	0.037	0.0002	0.008	0.015	<0.0025	1.17	0.25		44.257	23085	-18.27	7.65
-9.45	0.035	0.026	0.0001	0.006	0.008	<0.0025	1.18	0.005	408	20.526	23609	-14.49	7.7
-3.15	0.033	0.027	0.0001	<0.005	0.011	<0.0025	1.27	0.13	398	29.901	24299	-13.23	7.69
-1.89	0.034	0.033	0.0001	0.006	0.042	<0.0025	1.26	0.25	378	17.178	23488	-10.71	7.72
-0.63	0.018	0.193	0.0001	<0.005	0.5	<0.0025	1.26	0.23	352	78.373	23146	-8.19	7.8
0	0.019	0.178	0.0001	0.07	0.49	<0.0025	1.03	0.3	386	6.869	240322	-6.93	7.75
0.63	0.012	0.746	<0.0001	0.189	1.15	<0.0025	1.16	0.1	336	8.222	21978	-4.41	7.8
1.26	0.015	0.542	0.0001	0.142	0.43	<0.0025	0.975	0.36	357			4.41	8.06
1.89	0.015	0.851	<0.0001	0.007	0.5	<0.0025	0.693	0.28	318	8.315	21087	6.93	8.09
2.52	0.017	0.605	0.0001	<0.005	0.21	<0.0025	0.658	0.24	332	3.814	213033	8.19	8.13
3.15	0.017	1.28	<0.0001	<0.005	0.25	<0.0025	0.549	0.25	310	6.627	20862	10.71	8.16
3.78	0.019	1.25	<0.0001	<0.005	0.33	<0.0025	0.538	0.26				13.23	8.17
4.41	0.017	1.63	<0.0001	<0.005	0.37	<0.0025	0.53	0.17	324	3.759	21400	15.75	8.18
5.67	0.018	1.65	<0.0001	<0.005	0.4	<0.0025	0.494	0.16		3.815	23559	18.27	8.19
6.93	0.019	1.64	<0.0001	<0.005	0.4	<0.0025	0.465	0.22		3.762	23398	20.79	8.21
9.45	0.023	1.81	<0.0001	<0.005	0.4	<0.0025	0.396	0.37	330	6.698	23173	23.31	8.24
11.97	0.023	1.94	<0.0001	<0.005	0.3	<0.0025	0.358	0.42		4.883	24700	28.35	8.42
14.49	0.021	1.76	<0.0001	<0.005	0.28	<0.0025	0.349	0.15		6.902	24309	37.17	8.85
17.01	0.024	1.72	<0.0001	0.015	0.27	<0.0025	0.345	0.19	346	7.484	23390	49.77	9.32
22.05	0.027	1.74	0.0001	<0.005	0.48	<0.0025	0.316	0.23		3.511	22616	53.55	9.33
27.09	0.029	1.41	<0.0001	<0.005	0.26	<0.0025	0.277	0.18		14.675	22187	54.81	9.35
34.65	0.015	0.194	0.0003	0.013	0.21	<0.0025	0.616	0.13	512	3.032	24312		
39.69	0.014	0.111	0.0003	0.166	0.033	<0.0025	0.365	0.19		14.805	244584		
47.25	0.016	0.118	0.0002	0.632	0.08	<0.0025	0.181	0.26	576	67.462	23498		

Peeper Rescan #14 (deep)

Depth (cm)	Sb (mg/L)	As (mg/L)	Cd (mg/L)	Cu (mg/L)	Fe (mg/L)	Pb (mg/L)	Mn (mg/L)	Zn (mg/L)	Ca (mg/L)	nitrate (uM)	sulphate (uM)	Depth (cm)	pH
-18.9	0.032	0.027	0.0001	0.005	0.01	<0.0025	1.27	0.26	406	24.001	24499	-17.01	7.61
-13.86	0.034	0.027	0.0001	<0.005	<0.005	<0.0025	1.26	0.51		21.081	24251	-11.97	7.7
-7.56	0.035	0.028	0.0001	0.005	0.007	<0.0025	1.33	0.25	393	20.467	24356	-5.67	7.63
-3.78	0.026	0.031	0.0003	0.007	0.11	<0.0025	1.29	0.26	402	18.265	24198	4.41	7.9
-2.52	0.011	0.081	<0.0001	<0.005	0.6	<0.0025	1.08	0.25	386	47.388	24448	6.93	8.02
-1.26	0.025	0.096	<0.0001	<0.005	0.28	<0.0025	1.05	0.27	408	11.64	24642	10.71	8.09
0	0.027	0.198	<0.0001	<0.005	0.3	<0.0025	1.04	0.25	467	7.753	24368	15.75	8.11
1.26	0.01	0.499	<0.0001	<0.005	0.96	<0.0025	0.957	0.35	458	19.348	28763	19.53	8.15
1.89	0.009	0.629	<0.0001	<0.005	1	<0.0025	0.881	0.24		6.602	29569	25.83	8.19
2.52	0.005	0.457	<0.0001	<0.005	1	<0.0025	0.885	0.58	467	12.044	31183	32.13	8.19
3.15	0.002	0.466	<0.0001	<0.005	1	<0.0025	0.864	0.13		30.769	29239	38.43	8.21
3.78	0.004	0.294	<0.0001	<0.005	1	<0.0025	0.864	0.41	466	13.428	30731	44.73	8.23
5.04	0.002	0.198	<0.0001	<0.005	1	<0.0025	0.837	<0.001		3.945	31994	51.03	8.25
6.3	0.003	0.135	<0.0001	<0.005	1	<0.0025	0.71	0.31		28.923	32143	54.81	8.25
7.56	0.003	0.124	<0.0001	<0.005	1	<0.0025	0.656	<0.001	457	46.244	31845	57.33	8.22
8.82	0.002	0.125	<0.0001	<0.005	1	<0.0025	0.656	0.28		6.9765	31843		
11.34	0.003	0.125	<0.0001	<0.005	0.84	<0.0025	0.87	0.36	451	14.79	30351		
13.86	0.002	0.113	<0.0001	<0.005	0.6	<0.0025	0.594	0.2		6.005	30379		
16.38	0.003	0.097	<0.0001	<0.005	0.5	<0.0025	0.504	0.22		28.304	29601		
18.9	0.004	0.101	<0.0001	<0.005	0.36	<0.0025	0.463	0.16	441	8.118	30050		
23.94	0.008	0.176	<0.0001	<0.005	0.35	<0.0025	0.354	1.85		4.773	25822		
30.24	0.005	0.129	<0.0001	<0.005	0.29	<0.0025	0.311	0.15	494	6.332	27015		
36.54	0.006	0.13	<0.0001	<0.005	0.29	<0.0025	0.294	0.17		11.252	25901		
42.84	0.005	0.114	0.0003	<0.005	0.26	<0.0025	0.277	0.18		6.722	26988		
49.14	0.005	0.106	<0.0001	<0.005	0.17	<0.0025	0.265	0.15	502	22.868	27625		

Rescan Peeper #12 Shallow

Depth (cm)	Sb (mg/L)	As (mg/L)	Cd (mg/L)	Cu (mg/L)	Fe (mg/L)	Pb (mg/L)	Mn (mg/L)	Zn (mg/L)	nitrate (uM)	sulphate (uM)	Depth (cm)	pH
-21.74	0.032	0.027	0.0001	0.008	0.1	<0.0025	1.27	0.46	27.974	16515	-20.48	7.62
-16.7	0.034	0.026	0.0002	<0.005	0.005	<0.0025	1.28	0.2	28.118	14776	-19.22	7.65
-10.4	0.034	0.028	0.0001	<0.005	<0.005	<0.0025	1.29	0.23	26.904	13746	-15.44	7.7
-4.095	0.035	0.026	0.0001	<0.005	<0.005	<0.0025	1.32	0.43	20.106	14170	-9.135	7.69
-2.835	0.031	0.045	0.0001	<0.005	0.024	<0.0025	1.33	0.41	37.766	15193	-5.355	7.73
-1.575	0.018	0.287	<0.0001	<0.005	0.25	<0.0025	1.09	0.17	10.984	16824	-0.945	7.89
-0.945	0.021	0.224	0.0001	<0.005	0.1	<0.0025	0.976	0.001			1.575	7.92
-0.315	0.016	0.325	<0.0001	<0.005	0.25	<0.0025	0.651	0.16	14.71	15597	2.835	8.02
0.315	0.012	0.583	0.0001	<0.005	0.07	<0.0025	0.584	<0.001			5.355	8.12
0.945	0.014	0.486	<0.0001	<0.005	0.1	<0.0025	0.496	0.19	297.22	14630	7.875	8.18
1.575	0.007	0.937	<0.0001	<0.005	0.21	<0.0025	0.475	<0.001			10.395	8.17
2.205	0.009	1.5	<0.0001	<0.005	0.44	<0.0025	0.449	0.17	11.817	15133	12.915	8.22
2.835	0.01	1.64	<0.0001	<0.005	0.48	<0.0025	0.452	<0.001			16.695	8.24
3.465	0.012	2.14	<0.0001	<0.005	0.68	<0.0025	0.434	0.22	6.725	15159	22.365	8.28
4.725	0.013	2.46	<0.0001	<0.005	0.68	<0.0025	0.384	0.24	14.905	14815	29.925	8.49
5.985	0.012	2	<0.0001	<0.005	0.48	<0.0025	0.381	0.3	37.463	15117	34.965	8.63
7.245	0.015	1.73	<0.0001	<0.005	0.36	<0.0025	0.388	1.95	30.197	24445	40.005	8.83
8.505	0.014	2.02	<0.0001	<0.005	0.45	<0.0025	0.348	0.23	58.582	15197	43.785	8.9
11.025	0.016	2.35	0.0001	<0.005	0.26	<0.0025	0.346	2.3	12.576	14870	48.825	9
13.545	0.012	2.03	<0.0001	<0.005	0.6	<0.0025	0.354	0.3	4.945	15781	53.865	9.11
16.065	0.011	2.16	<0.0001	<0.005	0.62	<0.0025	0.37	0.25	23.417	16652		
21.105	0.012	1.81	<0.0001	<0.005	0.47	<0.0025	0.287	<0.001	9.652	15145		
27.405	0.011	1.06	<0.0001	<0.005	0.23	<0.0025	0.35	<0.001	15.444	13575		
33.705	0.014	0.733	0.0002	0.006	0.07	<0.0025	0.332	<0.001	4.392	13134		
46.305	0.015	0.076	0.0003	0.241	0.009	<0.0025	0.249	<0.001	43.386	22458		

Welcome Screen
Search
Report List

UBC Peeper #3 Deep

Depth (cm)	Sb (mg/L)	As (mg/L)	Cd (mg/L)	Cu (mg/L)	Fe (mg/L)	Pb (mg/L)	Mn (mg/L)	Zn (mg/L)	nitrate (uM)	sulphate (uM)	Depth (cm)	pH
-13.23	0.033	0.026	0.0001	0.005	0.06	<0.0025	1.29	0.005	32.493	15910	-10.71	7.67
-8.19	0.035	0.027	0.0001	<0.005	0.011	<0.0025	1.23	0.1	27.137	15346	-3.15	7.69
-1.89	0.034	0.025	0.0001	<0.005	0.007	<0.0025	1.29	0.015	22.187	12989	7.56	7.91
-0.63	0.036	0.028	0.0001	<0.005	0.008	<0.0025	1.31	0.13	37.624	14629	13.86	7.94
0.63	0.037	0.026	0.0001	<0.005	0.006	<0.0025	1.23	0.015	11.048	16079	24.57	8.05
1.89	0.035	0.039	0.0002	0.005	0.017	<0.0025	1.29	0.012	169.64	16674	37.17	8.18
3.15	0.012	0.355	<0.0001	<0.005	0.29	<0.0025	1.14	0.001	26.778	22835	48.51	8.16
4.41	0.01	1.4	<0.0001	<0.005	1.83	<0.0025	0.925	<0.001	23.089	21386	61.11	8.16
5.67	0.008	1.19	<0.0001	<0.005	1.63	<0.0025	0.889	0.039	41.006	15646		
6.93	0.007	1	<0.0001	<0.005	1.95	<0.0025	0.893	<0.001	11.305	19528		
8.19	0.006	0.753	<0.0001	<0.005	1.75	<0.0025	0.904	<0.001	19.365	22720		
10.71	0.006	0.839	<0.0001	<0.005	2.05	<0.0025	0.958	<0.001	15.335	19160		
13.23	0.006	0.599	<0.0001	<0.005	2.1	<0.0025	1.05	<0.001	27.284	30379		
15.75	0.005	0.479	<0.0001	<0.005	2	<0.0025	1.07	0.13	23.893	20680		
18.27	0.004	0.517	<0.0001	<0.005	2	<0.0025	1.03	0.001	57.616	21637		
20.79	0.004	0.401	<0.0001	<0.005	1.65	<0.0025	0.93	0.004	26.591	22477		
23.31	0.004	0.297	<0.0001	<0.005	1.45	<0.0025	0.813	0.006	22.28	22106		
25.83	0.005	0.295	<0.0001	<0.005	1.8	<0.0025	0.695	0.008	21.288	22263		
28.35	0.004	0.305	<0.0001	<0.005	0.475	<0.0025	0.494	0.19				
30.87	0.004	0.254	<0.0001	<0.005	0.48	<0.0025	0.401	<0.001	23.032	20045		
33.39	0.004	0.286	<0.0001	<0.005	0.58	<0.0025	0.347	<0.001				
35.91	0.006	0.252	<0.0001	<0.005	0.48	<0.0025	0.301	<0.001	30.68	20741		
42.21	0.007	0.172	<0.0001	<0.005	0.26	<0.0025	0.275	<0.001				
48.51	0.005	0.19	<0.0001	<0.005	0.29	<0.0025	0.3	<0.001				
54.81	0.003	0.184	<0.0001	<0.005	0.34	<0.0025	0.308	<0.001	25.773	21109		

Rescan Peeper #15 Deep

Depth (cm)	Sb (mg/L)	As (mg/L)	Cd (mg/L)	Cu (mg/L)	Fe (mg/L)	Pb (mg/L)	Mn (mg/L)	Zn (mg/L)	nitrate (uM)	sulphate (uM)
-12.6	0.032	0.027	0.0001	0.005	0.021	<0.0025	1.2	0.018	31.678	17960
-7.56	0.03	0.025	0.0001	0.006	0.014	<0.0025	1.52	0.1	44.222	17857
-1.26	0.032	0.027	0.0002	0.006	0.011	<0.0025	1.53	0.11	34.274	18359
0	0.035	0.028	0.0003	0.008	0.03	<0.0025	1.57	0.013	23.244	18170
1.26	0.007	0.134	<0.0001	<0.005	1.9	<0.0025	1.79	<0.001	13.776	19075
2.52	0.005	0.404	<0.0001	<0.005	3.6	<0.0025	1.2	0.33	51.172	20168
3.78	0.004	0.735	<0.0001	<0.005	2.55	<0.0025	1.17	0.12	17.773	20032
5.04	0.007	1.08	<0.0001	<0.005	2.1	<0.0025	1	<0.001	10.823	20762
6.3	0.008	1.23	<0.0001	0.01	1.9	<0.0025	0.916	<0.001	25.486	27181
7.56	0.01	0.873	<0.0001	0.016	1.25	<0.0025	0.937	<0.001	36.881	22340
8.82	0.014	0.473	0.0001	0.033	0.46	<0.0025	0.916	0.12	25.544	22349
10.08	0.011	0.373	0.0001	0.032	0.34	<0.0025	0.963	<0.001	27.803	21977
11.34	0.011	0.301	0.0001	0.059	0.2	<0.0025	1.1	0.001	27.882	22479
12.6	0.012	0.244	0.0001	0.097	0.325	<0.0025	1.18	0.002	32.084	22462
13.86	0.01	0.226	0.0001	0.086	0.275	<0.0025	1.19	0.001		22070
16.38	0.01	0.178	0.0002	0.107	0.39	<0.0025	1.17	0.004	62.093	21588
18.9	0.008	0.135	0.0002	0.062	0.35	<0.0025	1.17	0.002	33.387	21242
21.42	0.007	0.044	0.0001	0.018	0.005	<0.0025	1.02	0.001		22416
23.94	0.007	0.04	0.0001	0.021	0.006	<0.0025	0.986	0.001	32.356	23014
30.24	0.003	0.035	0.0002	0.005	0.011	<0.0025	0.774	<0.001		
36.54	0.003	0.146	<0.0001	<0.005	0.49	<0.0025	0.696	<0.001		
42.84	0.003	0.164	<0.0001	<0.005	0.8	<0.0025	0.635	<0.001		
49.14	0.002	0.101	<0.0001	<0.005	0.7	<0.0025	0.574	0.19		
55.44	0.004	0.118	<0.0001	<0.005	0.31	<0.0025	0.447	0.17		
61.74	0.004	0.076	<0.0001	<0.005	0.19	<0.0025	0.334	<0.001		

Rescan Peeper #11 Shallow

Depth (cm)	Sb (mg/L)	As (mg/L)	Cd (mg/L)	Cu (mg/L)	Fe (mg/L)	Pb (mg/L)	Mn (mg/L)	Zn (mg/L)	nitrate (uM)	sulphate (uM)
-15.12	0.035	0.028	0.0001	<0.005	0.009	<0.0025	1.28	0.005	57.877	17267
-10.08	0.035	0.027	0.0001	<0.005	0.009	<0.0025	1.32	0.005	265.04	19158
-3.78	0.037	0.027	0.0001	<0.005	0.008	<0.0025	1.25	0.004	59.264	16294
0	0.028	0.113	0.0001	<0.005	0.32	<0.0025	1.27	0.004	21.687	16294
1.26	0.015	0.853	<0.0001	<0.005	7	<0.0025	1.54	0.003	134.61	16978
2.52	0.009	1.06	<0.0001	<0.005	2.15	<0.0025	1.14	<0.001	181.05	17151
3.78	0.011	1.66	<0.0001	<0.005	1.2	<0.0025	0.701	<0.001	33.87	17563
5.04	0.01	1.47	<0.0001	<0.005	0.95	<0.0025	0.544	0.002		
5.67			0.0003	0.005		<0.0025	0.465	0.19	1377	15889
6.3	0.013	1.52	<0.0001	0.031	1	<0.0025	0.458	0.002		
6.93				<0.005		<0.0025				
7.56	0.01	1.54	<0.0001	<0.005	0.62	<0.0025	0.433	<0.001	137.61	16318
8.19	0.01	1.21	0.0003	<0.005	0.8	<0.0025	0.416	0.096		
8.82	0.01	1.45	<0.0001	<0.005	0.64	<0.0025	0.406	0.001	241.66	22330
10.08	0.009	1.38	<0.0001	<0.005	0.64	<0.0025	0.395	<0.001	243.65	19969
11.34	0.008	1.68	<0.0001	<0.005	1.2	<0.0025	0.384	0.009	140.3	17235
13.86	0.012	1.5	<0.0001	<0.005	0.46	<0.0025	0.351	0.001	156.43	16420
16.38	0.012	1.43	<0.0001	<0.005	0.43	<0.0025	0.358	0.001	315.37	17010
18.9	0.007	1.54	<0.0001	<0.005	0.68	<0.0025	0.373	0.002		
21.42	0.012	1.73	<0.0001	<0.005	0.43	<0.0025	0.308	0.002	713.72	15432
27.72	0.012	1.8	<0.0001	<0.005	0.24	<0.0025	0.259	<0.001		
34.02	0.012	1.2	<0.0001	<0.005	0.21	<0.0025	0.348	<0.001	27.105	17336
40.32	0.025	0.316	0.0001	<0.005	0.14	<0.0025	0.207	0.001		
46.62	0.021	0.233	0.0001	0.041	0.19	<0.0025	0.118	0.11	94.499	15578
52.92	0.017	0.171	0.0001	0.058	0.39	<0.0025	0.155	0.009		

Sediments - Shallow Site

Depth (cm)	Total N (wt.%)	Al (µg/g)	Sb (µg/g)	As (µg/g)	Cd (µg/g)	Cr (µg/g)	Co (µg/g)	Cu (µg/g)	Fe (µg/g)	Pb (µg/g)	Mg (µg/g)	Mn (µg/g)	Mo (µg/g)	Ni (µg/g)	K (µg/g)	Na (µg/g)	Zn (µg/g)	Total S (wt.%)	TOC (wt.%)
1.5	0.08	1E+05	214	6700	6.8	59	24	1420	83500	324	4840	782	<8	38	35600	6090	1220	5.8	0.15
4.5	0.07	97300	261	14100	7	57	25	872	93900	352	2550	520	<4	30	34100	3570	1340	7.5	<0.05
7.5	0.05	1E+05	195	13600	6	72	24	810	101000	280	2870	646	<4	29	38500	3900	1190	6.9	0.05
10.5	0.04	93200	192	12500	4.8	51	22	536	103000	202	2250	635	<8	23	32200	3620	1110	8.1	0.05
13.5	0.04	80300	191	18000	7.2	43	32	650	113000	255	2430	601	<8	31	27400	3440	1670	9.3	0.05
16.5	0.05	1E+05	147	11900	4.8	69	28	706	80900	346	2880	472	<4	29	35900	3940	841	6.9	0.05
19.5	0.05	93600	125	15800	10.3	51	18	520	86300	463	2610	423	<8	32	31800	3870	1910	7.9	0.25
19.5	-	94500	141	15000	10.1	52	16	487	87500	466	2400	431	<8	32	32300	3940	1790	-	-
22.5	0.05	1E+05	113	7650	4.7	59	13	348	78400	395	3020	579	<4	20	35700	4190	737	6.3	0.1
25.5	0.05	98600	126	7110	3.5	54	17	368	78300	279	3830	615	<4	25	33400	4960	550	5.9	0.15
28.5	0.04	97700	168	6360	7.1	59	24	943	65600	316	4620	733	<4	47	33100	4730	1100	5.5	0.15
31.5	0.05	99500	121	7010	4.1	49	14	365	87900	223	3020	676	<4	21	33400	4940	603	5.7	0.05
34.5	0.04	1E+05	225	1520	15.1	55	39	1930	57700	406	10400	1630	<8	91	31900	7900	1970	5	<0.05
39	0.04	61900	193	1430	44.8	31	141	5450	63200	133	22600	5100	10	322	12300	3170	5070	9.5	0.1
45	0.03	47700	143	1210	61.1	22	191	6120	63800	33	31400	6310	<12	427	5580	1620	6890	12.4	0.1
45	-	48700	129	1310	64	22	196	6280	65600	38	31900	6460	<12	441	5600	1650	7080	-	-
50	0.03	37300	16.7	535	68.2	13	181	4920	51500	6	37200	8170	<12	388	612	1190	7360	12.8	<0.05

Sediments - Deep Site

Depth (cm)	Total N (wt.%)	Al (µg/g)	Sb (µg/g)	As (µg/g)	Cd (µg/g)	Cr (µg/g)	Co (µg/g)	Cu (µg/g)	Fe (µg/g)	Pb (µg/g)	Mg (µg/g)	Mn (µg/g)	Mo (µg/g)	Ni (µg/g)	K (µg/g)	Na (µg/g)	Zn (µg/g)	Total S (wt.%)	TOC (wt.%)
1.5	0.1	1E+05	395	6180	5.6	58	19	2910	65100	444	4990	720	12	49	36100	5650	779	4.2	0.15
4.5	0.03	1E+05	265	2500	7.5	68	13	1050	56500	550	6320	792	7	33	36000	6970	875	3.2	0.05
7.5	0.03	1E+05	137	263	5.3	57	10	513	47600	554	5190	633	5	23	39500	7840	619	1.8	0.05
10.5	0.03	1E+05	111	277	4.7	53	11	562	47400	571	5600	616	5	26	37800	7960	617	2.5	0.05
13.5	0.05	1E+05	222	534	6.6	59	13	929	52500	645	5750	639	6	35	35900	8090	864	3	0.15
16.5	0.03	1E+05	204	1370	3.7	66	14	645	57600	305	6340	755	4	34	35600	7580	483	3.2	<0.05
16.5	-	1E+05	201	1090	3.2	66	11	515	57700	289	4990	756	<4	27	35800	7640	394	-	<0.05
19.5	0.03	1E+05	172	1450	3.2	65	13	529	58900	266	5830	793	<4	30	36100	7310	434	3.3	0.1
22.5	0.03	1E+05	153	1260	3.9	67	15	634	59400	253	6440	815	4	34	38000	7700	527	3.2	<0.05
25.5	0.03	1E+05	161	1230	3.7	64	15	602	58000	254	6320	749	<4	32	35400	7910	507	3.2	0.05
28.5	0.03	1E+05	229	1630	2.6	66	14	505	59200	273	6930	806	<4	34	35300	8300	364	3.2	<0.05
31.5	0.03	98800	210	2000	2.4	63	14	443	58300	258	6900	815	<4	35	33200	8140	339	3.8	0.05
34.5	0.03	1E+05	276	1760	3	61	14	578	57900	256	6390	826	<4	30	35000	7720	418	3.4	<0.05
39	0.03	99200	222	1190	4	58	15	702	59100	324	6050	739	<4	33	34100	8620	556	4	<0.05
44	0.03	1E+05	186	1420	4.1	60	16	729	59700	334	6580	798	<4	36	35200	8720	570	3.9	<0.05
44	-	99300	197	1390	3.8	64	15	692	58800	324	6430	784	<4	33	34300	8450	534	-	-

Water Column

Shallow Site

Depth (m)	Cond umhos/cm	TDS (mg/L)	Hardness (mg/L)	pH	TSS (mg/L	Turb (NTU)	Acidity (mg/L)	Alk (mg/L)	Chloride (mg/L)	Fluoride (mg/L)	Sulphate (mg/L)	Ammonia (mg/L)	Nitrate (mg/L)	ortho-Phosphate P (mg/L)	TD Phosphate (mg/L)	Total P (mg/L)	Free Cyanid (mg/L)	Total CN (mg/L)
0	3360	2500	1100	7.3	2	1.5	13.9	47.4	15.3	0.71	1850	69	0.364	0.003	0.065	0.074	<0.005	0.035
1.5	3420	2560	938	7.7	7	1.6	13.1	47.4	15.7	0.75	1900	73	0.348	0.003	0.067	0.076	<0.005	0.068

Deep Site

Depth (m)	Cond umhos/cm	TDS (mg/L)	Hardness (mg/L)	pH	TSS (mg/L	Turb (NTU)	Acidity (mg/L)	Alk (mg/L)	Chloride (mg/L)	Fluoride (mg/L)	Sulphate (mg/L)	Ammonia (mg/L)	Nitrate (mg/L)	ortho-Phosphate P (mg/L)	TD Phosphate (mg/L)	Total P (mg/L)	Free Cyanid (mg/L)	Total CN (mg/L)
0	3300	2500	969	7.3	3	1.2	16.5	47.1	16	0.72	1880	70	0.339	0.001	0.065	0.072	<0.005	0.029
1.5	3320	2600	979	7.7	4	1.3	11.5	47.6	15.8	0.74	1890	71	0.361	0.002	0.067	0.076	<0.005	0.031
3.5	3370	2560	964	7.7	9	1.5	10.6	48.3	15.7	0.79	1900	71	0.353	0.002	0.067	0.076	0.01	0.072
3.5	3370	2590	940	7.7	10	1.4	10.6	47.3	15.7	0.76	1930	72	0.356	0.003	0.067	0.074	-	-

Shallow Site

Depth (m)	T-Al	T-Sb	T-As	T-Cd	T-Ca	T-Cr	T-Co	T-Cu	T-Fe	T-Pb	T-Mg	T-Mn	T-Ni	T-K	T-Na	T-Zn
0	<0.20	0.036	0.0201	0.000	322	<0.015	0.031	0.003	<0.030	<0.001	31.4	1.18	<0.020	71.8	309	0.007
1.5	<0.20	0.034	0.0164	0.000	325	<0.015	0.034	0.006	0.041	<0.001	31.8	1.23	0.023	73.2	315	0.012

Note: All concentrations are expressed in mg/L unless otherwise stated.

Welcome Screen Search Report List

Water Column

Deep Site

Depth (m)	T-Al	T-Sb	T-As	T-Cd	T-Ca	T-Cr	T-Co	T-Cu	T-Fe	T-Pb	T-Mg	T-Mn	T-Ni	T-K	T-Na	T-Zn
0	<0.20	0.036	0.0178	0	314	<0.015	0.036	0.006	0.043	<0.001	30.5	1.18	0.02	70	298	0.012
1.5	<0.20	0.035	0.0193	0.000	363	<0.015	0.041	0.007	0.043	<0.001	35.2	1.37	0.03	81.9	349	0.013
3.5	<0.20	0.037	0.0177	0.000	344	<0.015	0.035	0.006	0.039	<0.001	33.9	1.32	<0.020	74.9	369	0.014
3.5	<0.20	0.036	0.0164	0.000	339	<0.015	0.036	0.006	0.04	<0.001	32.9	1.29	<0.020	73.9	360	0.014

Shallow Site

Depth (m)	D-Al	D-Sb	D-As	D-C	D-Ca	D-Cr	D-Co	D-Cu	D-Fe	D-Pb	D-Mg	D-Mn	D-Ni	D-K	D-Na	D-Zn	Sulphide
0	<0.20	0.034	0.0176	0.000	380	<0.015	0.043	0.003	<0.030	<0.001	36.7	1.42	0.036	85.6	365	0.013	<0.02
1.5	<0.20	0.034	0.0146	0.000	324	<0.015	0.041	0.003	<0.030	<0.001	31.4	1.21	0.035	72.2	307	0.012	<0.02

Deep Site

Depth (m)	D-Al	D-Sb	D-As	D-C	D-Ca	D-Cr	D-Co	D-Cu	D-Fe	D-Pb	D-Mg	D-Mn	D-Ni	D-K	D-Na	D-Zn	Sulphide
0	<0.20	0.035	0.0207	0.000	335	<0.015	0.037	0.003	<0.030	<0.001	32.3	1.25	0.023	74	317	0.012	<0.02
1.5	<0.20	0.033	0.018	0.000	338	<0.015	0.04	0.003	<0.030	<0.001	32.9	1.27	<0.020	76.4	326	0.013	<0.02
3.5	<0.20	0.034	0.0153	0.000	333	<0.015	0.031	0.004	<0.030	<0.001	32.2	1.26	<0.020	71.9	355	0.014	0.03
3.5	<0.20	0.036	0.0201	0.000	325	<0.015	0.035	0.004	<0.030	<0.001	31.2	1.21	<0.020	72	339	0.012	0.03

Note: All concentrations are expressed in mg/L unless otherwise stated.

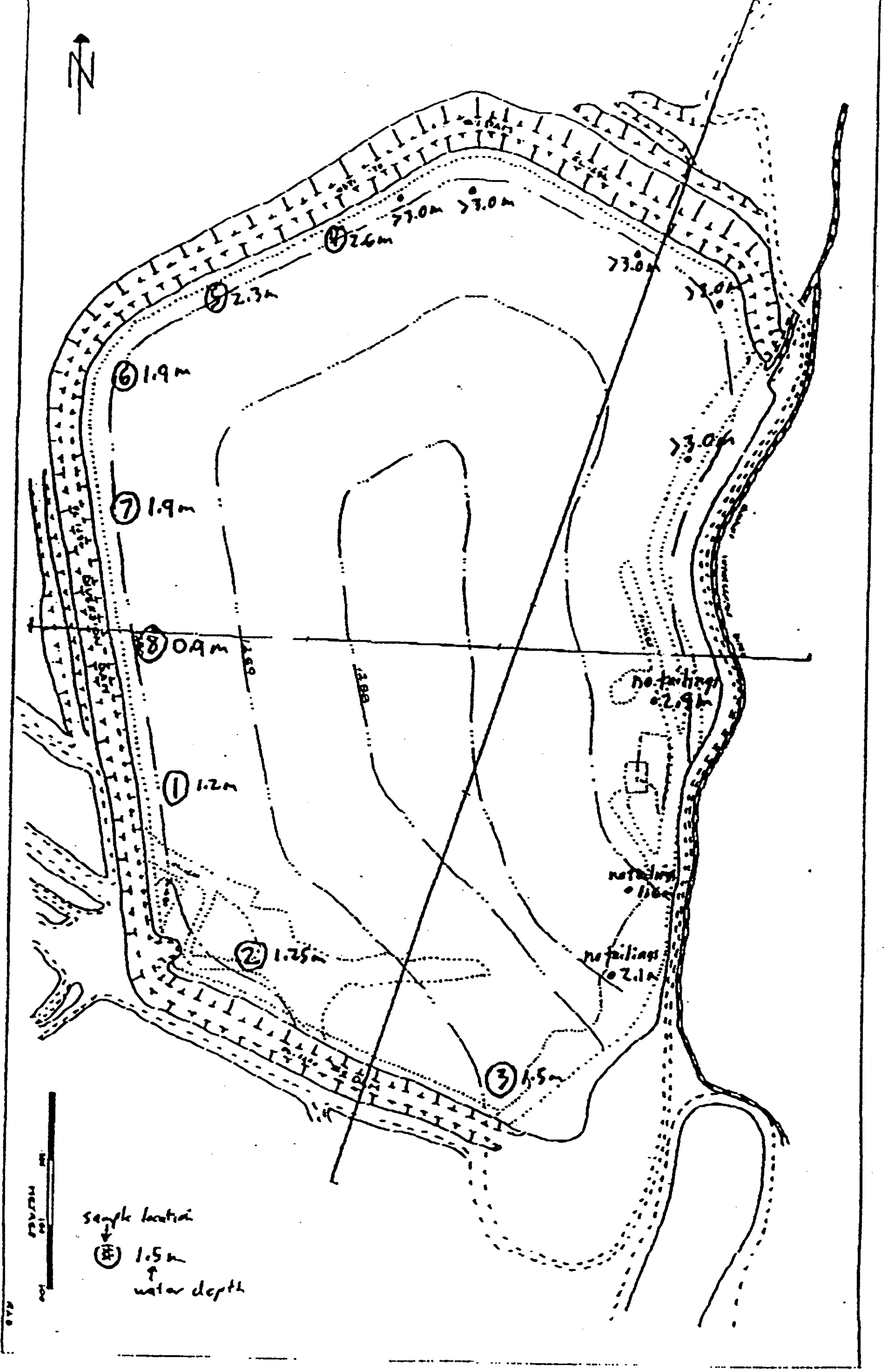
UBC Peeper #4 Deep

Cell #	Depth (cm)	D.O. (mg/L)
1	-7.56	5
8	-5.04	5.25
9	-3.78	5.3
10	-2.52	4.8
11	-1.26	1.95
12	0	0.7
13	1.26	0.3
14	2.52	1.1
15	3.78	0.5
16	5.04	0.2
17	6.3	0.05
17.5	6.93	0
18	7.56	0
20	10.08	0
32	25.2	0
50	47.88	0
52	50.4	0

Rescan Peeper #10 Shallow

Cell #	Depth (cm)	D.O. (mg/L)
6	-20.16	3.75
7	-18.9	4.75
8	-17.64	4.95
9	-16.38	4.9
10	-15.12	4.95
13	-11.34	3.75
14	-10.08	3.9
15	-8.82	3.7
16	-7.56	3.85
17	-6.3	4.05
18	-5.04	4.05
19	-3.78	4
20	-2.52	3.55
21	-1.26	2.25
22	0	1.25
23	1.26	1
24	2.52	0.6
25	3.78	0.4
26	5.04	0.25
27	6.3	0.15
28	7.56	0.1
29	8.82	0.05
30	10.08	0.05
31	11.34	0
32	12.6	0

Tailings Pond Sampling - Feb 28/95



PLACER DEVELOPMENT DIVISION RESEARCH CENTRE
ASSAY LABORATORY
STATIC ACID BASE ACCOUNTING TEST RESULTS BY EPA 600 PROCEDURES
EQUITY SILVER MINE

Sample Description	ABA No.	% C (Leco)	S % (Leco)	*SO4 %	Tons CaCO3 Equivalent/Thousand Tons of Material			Paste pH	Fizz Rating	Precipitate Colour
					Maximum Potential Acidity	Neutralization Potential	**Net Neutralization			
92568	3276	0.39	6.40	0.19	200	21	-179	7.69	Slight	Grey
92569	3277	0.32	8.18	0.12	256	15	-241	7.83	Slight	Grey
92570	3278	0.20	8.25	0.14	258	6	-252	7.46	Slight	Grey
92571	3279	0.31	5.09	0.35	159	24	-135	7.85	Slight	Grey
92572	3280	0.30	5.23	0.44	163	23	-140	8.02	Slight	Grey
92573	3281	0.37	4.81	0.37	150	24	-126	7.99	Slight	Grey
92574	3282	0.42	5.64	0.37	176	26	-150	7.85	Slight	Grey
92575	3283	0.30	6.38	0.11	199	16	-183	7.85/7.84	Slight	Grey

Welcome Screen Search Report List

Welcome Screen | Search | Report List

Placer Dome Inc. Research Centre
323 Alexander Street
Vancouver, BC
V6A 1C4

REQUISITION FOR ENVIRONMENTAL ANALYSIS

SUBMITTED BY:

NAME: Mike Aziz
COMPANY: Equity Silver Mines
PROJECT: Tailings Pond
P.O. No: - contact Jim Robertson
DATE: March 1/95
DATE RESULTS REQUIRED:

RESULTS & INVOICES TO:

COMPANY: PDI
ATTENTION: Jim Robertson
HARD COPY: ☒ Yes ☐ No
DISKETTE: ☒ 3.5" ☐ 5.25"
FAX RESULTS: ☒ Yes ☐ No
TEL: (604) 661-1557 FAX: (604) 661-3792

ADDITIONAL COPY SENT TO:

COMPANY: Equity Silver
ATTENTION: Mike Aziz
HARD COPY: ☒ Yes ☐ No
DISKETTE: ☐ 3.5" ☐ 5.25"
FAX RESULTS: ☒ Yes ☐ No
TEL: (604) 845-7799 FAX: (604) 845-2137

SAMPLE PREPARATION REQUESTED:

☒ ABA Prep.
☐ No Prep.
☐ Other (Specify) ______

ANALYSIS REQUESTED:

☒ Static ABA
☐ Kinetic Test (20 wk)
☐ Kinetic Test (52 wk)
☐ Mineralogy
☐ ICP (27 element)
☐ Particle Size
☐ Cyclosizer
☐ Other (specify)

HANDLING OF PULPS / REJECTS:

PULPS
☐ Return
☐ Discard 30 Days
☐ Discard end of year
☒ Long Term Storage

REJECTS
☐ Return
☐ Discard
☐ Discard 30 Days
☒ Long Term Storage

SAMPLE NUMBERS (SERIES)	SAMPLE TYPE	No. OF SAMPLES	ELEMENTS FOR ANALYSIS / SPECIAL REQUIREMENTS
92568 - 1	tailings	1	Static ABA
92569 - 2	↓	↓	↓
92570 - 3	↓	↓	↓
92571 - 4	↓	↓	↓
92572 - 5	↓	↓	↓
92573 - 6	↓	↓	↓
92974 - 7	↓	↓	↓
92975 - 8	↓	↓	↓

OR RESEARCH CENTRE
SE ONLY:

DATE REC'D: ______
LAB FILE NO: ______

REJECTS: ☐ DISCARDED ☐ STORED ☐ RETURNED
PULPS: ☐ DISCARDED ☐ STORED ☐ RETURNED

Page ____ of ____

(Jan. 1993)

PLACER DOME RESEARCH CENTRE

Geochemical Analysis

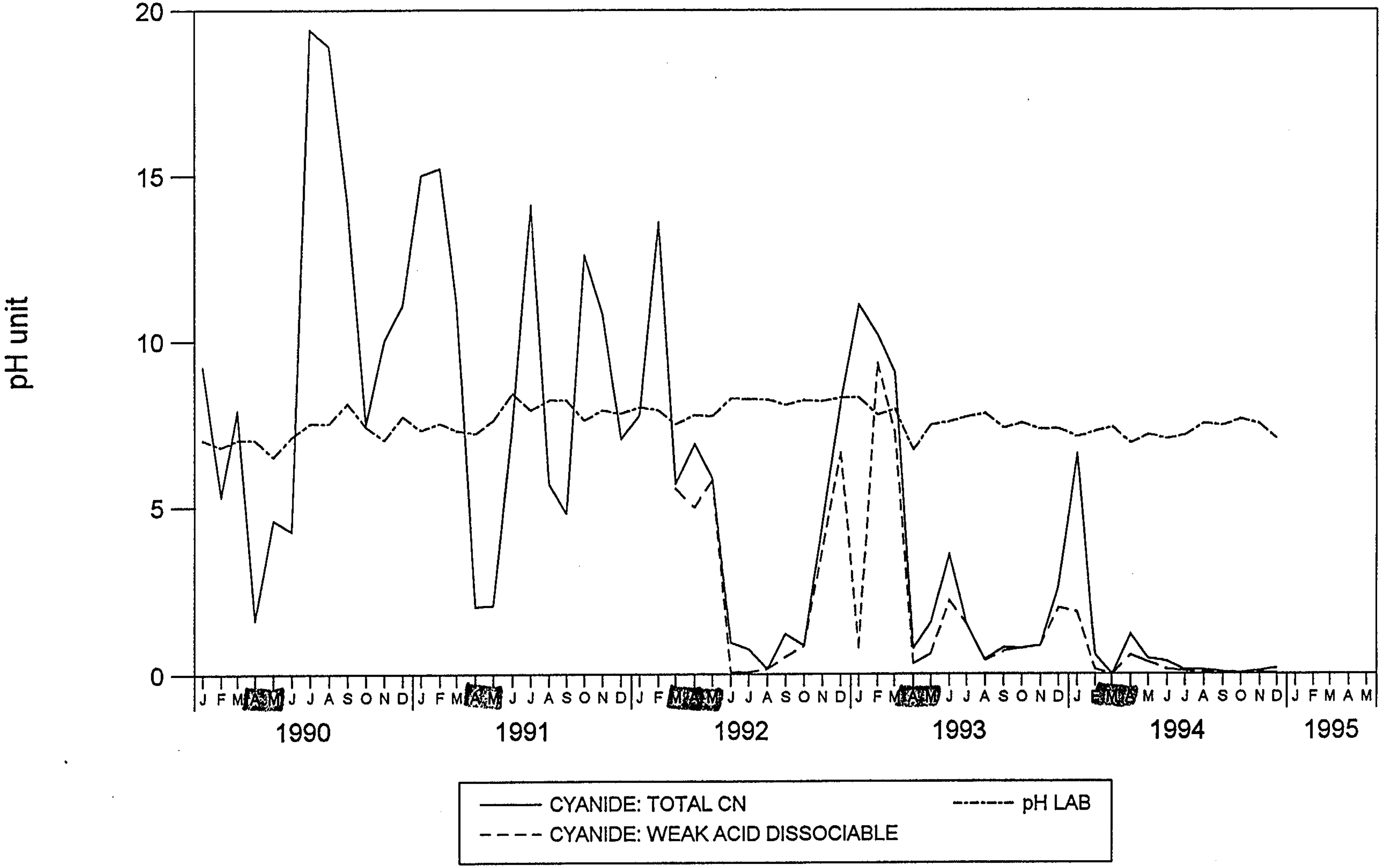
Project/Venture:	E95-13	Submitted by:	J ROBERTSON	Sample Type:		Date Received:	MAR 6, 1995	Page	1 of 1
Area:	EQUITY MINE	Lab Project No.:		NTS:		Date Completed:	MAR 22, 1995	Attn:	J ROBERTSON M AZIZ G RODGER
Remarks:									

ICP – 0.5 g sample digested with 4 ml Aqua Regia at 100 Deg. C for 2 hours.
N.B. The major oxide elements, Ba, Be, Cr, La and W are rarely dissolved completely with this acid dissolution method.

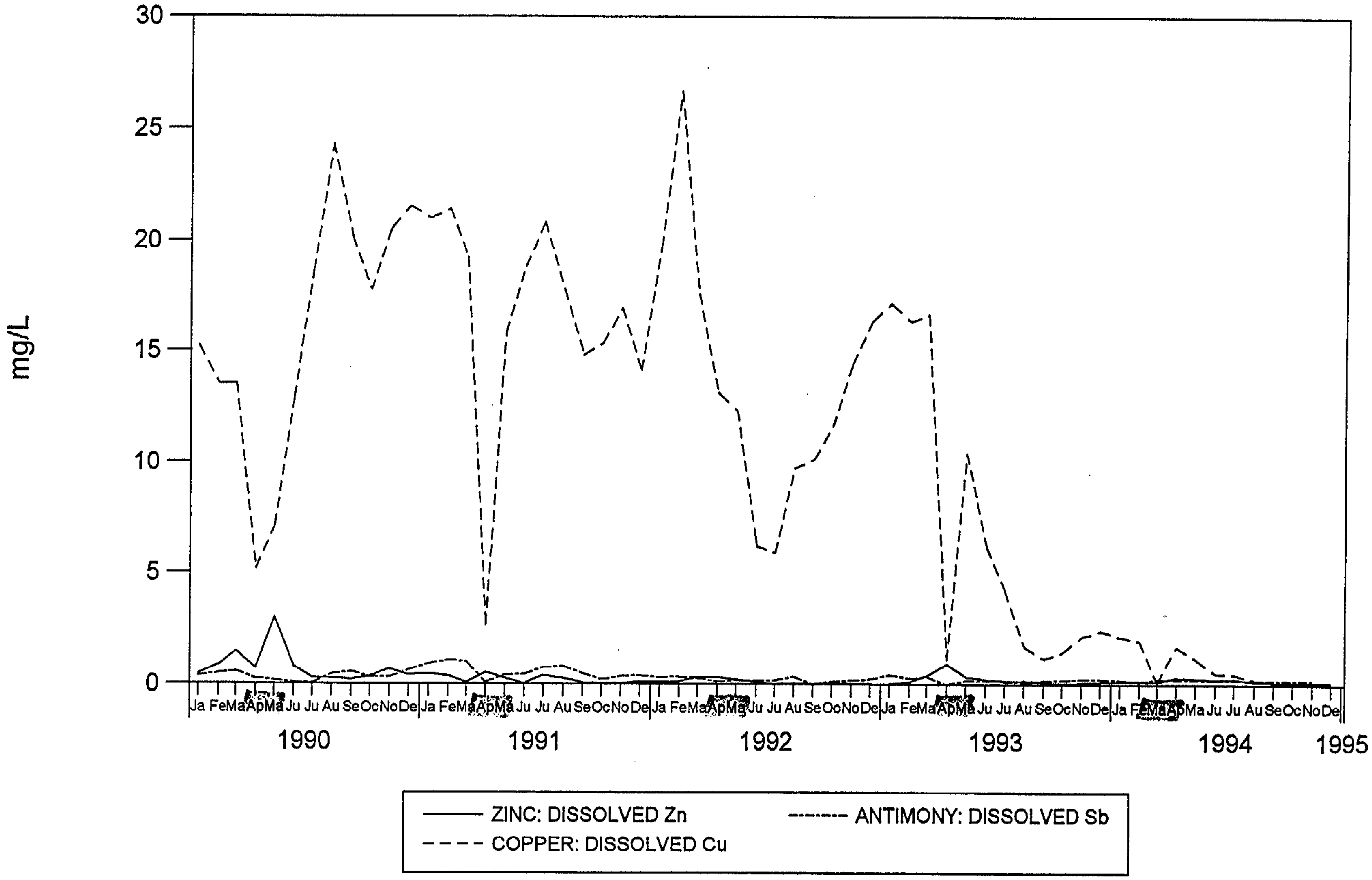
SAMPLE No.	Ag ppm	Mo ppm	Cu ppm	Pb ppm	Zn ppm	As ppm	Sb ppm	Cd ppm	Ni ppm	Co ppm	Mn ppm	Bi ppm	Cr ppm	V ppm	Ba ppm	W ppm	Be ppm	La ppm	Sr ppm	Ti %	Al %	Ca %	Fe %	Mg %	K %	Na %	P %
92568	34	4	842	454	2287	5706	131	11.7	42	37	646	11	15	24	24	58	0.9	11	97	<0.01	0.93	0.85	8.26	0.49	0.10	0.03	0.12
92569	51	2	1595	377	1881	11347	266	8.3	31	29	555	20	5	13	10	68	0.6	6	66	<0.01	0.60	0.56	9.08	0.27	0.07	0.02	0.08
92570	53	2	1689	416	4360	11857	267	18.3	38	27	490	11	6	15	9	61	0.6	6	46	<0.01	0.93	0.27	10.82	0.14	0.08	0.02	0.08
92571	38	3	942	333	811	1441	162	4.5	40	23	754	18	10	24	21	20	0.7	10	115	<0.01	1.01	1.05	7.01	0.55	0.14	0.03	0.13
92572	47	4	1094	450	888	1195	239	5.5	43	23	687	17	12	25	22	34	0.7	11	112	<0.01	0.99	1.00	6.81	0.55	0.16	0.03	0.13
92573	56	3	1027	592	837	1036	203	5.3	41	25	652	19	11	28	23	33	0.6	11	93	<0.01	0.86	0.97	6.67	0.57	0.13	0.02	0.13
92574	54	4	1240	401	1215	2452	224	6.6	40	23	786	14	9	22	24	69	0.9	9	124	<0.01	1.00	1.06	7.18	0.52	0.15	0.03	0.13
92575	43	3	1044	324	1567	7082	170	8.8	36	27	542	12	5	13	16	34	0.7	6	95	<0.01	0.62	0.67	7.69	0.28	0.11	0.02	0.10
92575 DUP	41	3	1054	312	1510	7255	177	8.3	35	27	539	14	4	13	17	35	0.7	6	94	<0.01	0.62	0.67	7.78	0.28	0.12	0.02	0.10
STD P1	0.3	64	26	62	144	217	<5	0.3	32	8	560	<2	111	34	167	<5	0.5	9	93	0.11	1.08	0.95	2.52	0.83	0.37	0.06	0.09

Welcome Screen Search Report List

EQUITY SILVER MINE
TAILINGS SUPERNATANT (RECLAIM)



EQUITY SILVER MINE
TAILINGS SUPERNATANT (RECLAIM)



EQUITY SILVER MINE
TAILING POND WATER QUALITY
RECENT DATA

STATION: TAILINGS SUPERNATANT (RECLAIM)

Date	TOTAL CYANIDE mg/L	WAD CYANIDE mg/L	LAB pH pH unit	DISSOLVED ZINC mg/L
Jan 15/90	9.20		7.0	0.47
Feb 19/90	5.30		6.8	0.84
Mar 26/90	7.88		7.0	1.49
Apr 23/90	1.62		7.0	0.71
May 22/90	4.60		6.5	3.03
Jun 25/90	4.26		7.1	0.79
Jul 23/90	19.40		7.5	0.28
Aug 20/90	18.90		7.5	0.27
Sep 24/90	14.1		8.1	0.20
Oct 29/90	7.46		7.4	0.35
Nov 26/90	10.00		7.0	0.69
Dec 31/90	11.10		7.7	0.41
Jan 28/91	15.0		7.3	0.460
Feb 25/91	15.2		7.5	0.371
Mar 25/91	11.1		7.3	0.078
Apr 29/91	2.02		7.2	0.529
May 27/91	2.07		7.6	0.280
Jun 24/91	7.52		8.4	0.030
Jul 29/91	14.1		7.9	0.396
Aug 26/91	5.69		8.2	0.285
Sep 30/91	4.80		8.2	0.093
Oct 28/91	12.6		7.6	0.034
Nov 25/91	10.8		7.9	0.030
Dec 30/91	7.04		7.8	0.125
Jan 27/92	7.75		8.0	0.098
Feb 24/92	13.6		7.9	0.122
Mar 30/92	5.69	5.55	7.49	0.32
Apr 28/92	6.90	4.98	7.76	0.323
May 25/92	5.87	5.80	7.72	0.221
Jun 29/92	0.956	0.088	8.25	0.097
Jul 27/92	0.774	0.067	8.23	0.023
Aug 31/92	0.169	0.162	8.21	0.051
Sep 28/92	1.22	0.534	8.06	0.020
Oct 26/92	0.860	0.854	8.20	0.067
Nov 30/92			8.17	0.042
Dec 28/92	8.15	6.62	8.27	0.035
Jan 25/93	11.1	0.800	8.27	0.017
Feb 22/93	10.2	9.32	7.75	0.119
Mar 29/93	9.02	7.22	7.93	0.384
Apr 26/93	0.783	0.332	6.70	0.914
May 31/93	1.54	0.624	7.45	0.353
Jun 27/93	3.59	2.22	7.55	0.231
Jul 26/93	1.52	1.52	7.69	0.160
Aug 30/93	0.446	0.426	7.80	0.168
Sep 27/93	0.811	0.708	7.36	0.106
Oct 25/93	0.787	0.787	7.52	0.095
Nov 29/93	0.860	0.860	7.32	0.114
Dec 27/93	2.62	1.99	7.34	0.133
Jan 31/94	6.60	1.87	7.11	0.152
Feb 28/94	0.594	0.148	7.26	0.145
Mar 28/94	0.005	<0.005	7.39	0.135
Apr 25/94	1.21	0.573	6.91	0.319
May 30/94	0.489	0.369	7.17	0.295
Jun 27/94	0.391	0.155	7.04	0.219

EQUITY SILVER MINE
TAILING POND WATER QUALITY
RECENT DATA

STATION: TAILINGS SUPERNATANT (RECLAIM)

Date	TOTAL CYANIDE mg/L	WAD CYANIDE mg/L	LAB pH pH unit	DISSOLVED ZINC mg/L
Jul 25/94	0.140	0.110	7.15	0.280
Aug 29/94	0.13	0.061	7.50	0.159
Sep 26/94	0.067	0.056	7.43	0.130
Oct 31/94	0.036	0.005	7.62	0.106
Nov 28/94	0.101	0.038	7.49	0.110
Dec 28/94	0.187	0.034	7.04	0.138
JAN 1985 - JUL 1995				
Std. Deviation	5.336	2.501	0.45	0.444
Num. Values	59	33	60	60

EQUITY SILVER MINE
TAILING POND WATER QUALITY
RECENT DATA

STATION: TAILINGS SUPERNATANT (RECLAIM)

Date	DISSOLVED ARSENIC mg/L	DISSOLVED COPPER mg/L	SPECIFIC CONDUCT(L)	DISSOLVED ANTIMONY S/cm	DISSOLVED ZINC mg/L	DISSOLV SILVE mg/L
Jan 15/90	0.0069	15.2		0.3700	0.47	
Feb 19/90	0.0062	13.5		0.4900	0.84	
Mar 26/90	0.0015	13.5		0.5900	1.49	
Apr 23/90	0.0021	5.18		0.2500	0.71	
May 22/90	0.0025	7.08		0.1900	3.03	
Jun 25/90	0.0150	12.9		0.0900	0.79	
Jul 23/90	0.0010	18.6		0.0310	0.28	
Aug 20/90	0.0021	24.3		0.4400	0.27	
Sep 24/90	0.0010	20.1		0.56	0.20	
Oct 29/90	0.0033	17.7		0.3100	0.35	
Nov 26/90	0.0008	20.5		0.3100	0.69	
Dec 31/90	0.0011	21.5		0.6200	0.41	
Jan 28/91	0.0021	21.0		0.92	0.460	
Feb 25/91	0.0067	21.4		1.08	0.371	
Mar 25/91	0.0091	19.2		1.02	0.078	
Apr 29/91	0.0019	2.69		0.0790	0.529	
May 27/91	0.0014	15.8		0.406	0.280	
Jun 24/91	0.0007	18.8		0.451	0.030	
Jul 29/91	0.0064	20.8		0.75	0.396	
Aug 26/91	0.0071	17.7		0.79	0.285	
Sep 30/91	0.0050	14.8		0.50	0.093	
Oct 28/91	0.0023	15.3		0.229	0.034	
Nov 25/91	0.010	16.9		0.369	0.030	
Dec 30/91	0.010	14.1		0.401	0.125	
Jan 27/92	0.0027	19.7		0.333	0.098	
Feb 24/92	0.0086	26.6		0.35	0.122	
Mar 30/92	0.0035	17.50	4070.00	0.27	0.32	
Apr 28/92	0.0013	13.10	3830.00	0.140	0.323	
May 25/92	0.0028	12.30	4000.00	0.180	0.221	
Jun 29/92	0.0034	6.18	4140	0.180	0.097	
Jul 27/92	0.0047	5.90	4290	0.173	0.023	
Aug 31/92	0.0031	9.71	4750	0.350	0.051	
Sep 28/92	0.0110	10.1	4500	0.0095	0.020	
Oct 26/92	0.0016	11.6	4490	0.137	0.067	
Nov 30/92	0.0256	14.4	4510	0.186	0.042	
Dec 28/92	0.0626	16.3	4760	0.228	0.035	
Jan 25/93	0.311	17.1	4910	0.415	0.017	
Feb 22/93	0.125	16.3	5010	0.278	0.119	
Mar 29/93	0.141	16.6	5200	0.356	0.384	
Apr 26/93	0.0046	1.14	882	0.0025	0.914	
May 31/93	0.0632	10.4	3740	0.175	0.353	
Jun 27/93	0.0832	6.16	3730	0.147	0.231	
Jul 26/93	0.106	4.22	3830	0.164	0.160	
Aug 30/93	0.115	1.70	2900	0.115	0.168	
Sep 27/93	0.0437	1.16	3740	0.185	0.106	
Oct 25/93	0.111	1.44	3800	0.205	0.095	
Nov 29/93	0.0430	2.16	4080	0.250	0.114	
Dec 27/93	0.0101	2.41	4070	0.240	0.133	
Jan 31/94	0.0310	2.16	4120	0.200	0.152	
Feb 28/94	0.0366	1.96	4080	0.137	0.145	
Mar 28/94	0.0330	0.093	4030	0.243	0.135	
Apr 25/94		1.71	3650		0.319	
May 30/94		1.17	3380		0.295	
Jun 27/94	0.20	0.506	3450	0.20	0.219	0.015

EQUITY SILVER MINE
TAILING POND WATER QUALITY
RECENT DATA

STATION: TAILINGS SUPERNATANT (RECLAIM)

Date	DISSOLVED ARSENIC mg/L	DISSOLVED COPPER mg/L	SPECIFIC CONDUCT(L)	DISSOLVED ANTIMONY S/cm	DISSOLVED ZINC mg/L	DISSOLV SILVE mg/L
Jul 25/94		0.456	3440		0.280	
Aug 29/94		0.217	3520.00		0.159	
Sep 26/94		0.106	3550.00		0.130	
Oct 31/94		0.061	3540		0.106	
Nov 28/94	0.20	0.060	3670	0.20	0.110	0.015
Dec 28/94		0.065	4060		0.138	
JAN 1985 - JUL 1995						
Mean	0.0357	10.688	3933.00	0.3263	0.311	0.015
Minimum Value	0.0007	0.060	882.00	0.0025	0.017	0.015
Maximum Value	0.3110	26.600	5200.00	1.0800	3.030	0.015
Num. Values	53	60	34	53	60	2

Appendix B - QA/QC

TABLE OF CONTENTS

APPENDICES

1.0 INTRODUCTION

ASL Analytical Service Laboratories Ltd. was contracted by Rescan Environmental Services Ltd. to carry out the analysis of water column, sediment and peeper water samples for trace metals and various other parameters for the Equity Silver Mine Closure Project.

This report covers the procedures used for preparing the samples, the analytical methodologies used in analyzing the samples, the analysis data, and the corresponding quality assurance information.

2.0 ANALYTICAL METHODOLOGY

All methods employed by ASL use state-of-the-art equipment and instrumentation for the preparation and analysis of samples. We incorporate a high degree of quality assurance in all testing procedures to ensure that only credible data is produced.

2.1 Water Column Methodologies

Conventional Parameters in Water Column Samples

These analyses were carried out in accordance with procedures described in "Standard Methods for the Examination of Water and Wastewater" 18th Edition published by the American Public Health Association (APHA), 1992. Specific details are as follows:

pH was analyzed electrometrically using a combination reference-potential glass electrode (APHA Method 4500-H^+).

Conductivity was analysed by the direct measurement of resistance using a HACH Conductivity/TDS Meter Model 44600 (APHA Method 2510).

Turbidity was analysed nephelometrically using a HACH turbidimeter (APHA Method 2130).

Hardness was determined by calculation using calcium and magnesium concentrations (APHA Method 2340).

Alkalinity was analyzed using a Roche Model COBAS FARA II spectrophotometer by potentiometric titration with sulphuric acid using methyl orange at a pH of 4.5 as an end point indicator (APHA Method 2320).

Acidity was analysed by potentiometric titration with sodium hydroxide using phenolphthalein at a pH of 8.3 as an end point indicator (APHA Method 2310).

Chloride was determined colorimetrically using mercuric thiocyanate and ferric nitrate reagents (APHA Method 4500-Cl^-).

Sulphate was analysed turbidimetrically using barium chloride reagent (APHA Method 4500-$S0_4^{2-}$).

Sulphide was analysed colourimetrically using a Perkin-Elmer Model Lambda 2 UV/Visible spectrophotometer (APHA 4500-S^{2-}).

Total Suspended Solids was determined gravimetrically by filtration of the sample onto a glass fibre filter and drying of the sample to a constant weight (APH 2540).

Total Dissolved Solids was determined gravimetrically by filtration of the sample and subsequent evaporation and drying of the filtrate to a constant weight (APHA 2540).

Total Phosphorus was analyzed colourimetrically with a Perkin-Elmer Model Lambda 2 UV/Visible spectrophotometer using an acid hydrolysis with sulphuric acid and ammonium persulphate (APHA Method 4500-P).

Total Dissolved Phosphate was analysed colorimetrically on a filtered (0.45 um) portion of the sample with a Perkin-Elmer Model Lambda 2 UV/Visible spectrophotometer using an acid hydrolysis with sulphuric acid and ammonium persulphate (APHA 4500-P).

Dissolved ortho-Phosphate was analysed colorimetrically on a filtered (0.45 um) portion of the sample with a Perkin-Elmer Model Lambda 2 UV/Visible spectrophotometer (APHA 4500-P).

Nitrate Nitrogen was determined by the difference between the colourimetric nitrate/nitrite analysis by a Roche Model COBAS FARA II spectrophotometer using hydrazine red and the colourimetric nitrite analysis using diazotization with N-1-naphthylethylenediamine dihydrochloride (APHA Method 4500-NO_3).

Ammonia Nitrogen was determined colourimetrically using a phenol and hypochlorite reagent in the presence of a manganous salt (APHA Method 4500-NH_3).

Total and Weak Acid Dissociable (WAD) Cyanide in Water Column Samples

These analyses were carried out in accordance with ASTM Method D2036-84, Annual Book of ASTM, Section 11 - Water and Environmental Technology, Vol. 11.02 Water (II), 1984. The procedure involves a distillation/reflux under vacuum, impingement of the released hydrogen cyanide followed by a colourimetric determination. For the Total Cyanide analysis, a Hydrochloric

Acid/Hydroxylamine Hydrochloride reagent was used. For the WAD Cyanide analysis, a Zinc Acetate/Acetic Acid reagent was used.

Free Cyanide in Water Column Samples

This procedure involves an on-line acid/ultraviolet digestion of the sample, which converts the metal bound cyanides to hydrogen cyanide (HCN). The HCN gas is then separated and trapped in a weak sodium hydroxide solution via a gas diffusion membrane. The resulting cyanide ion is then analysed amperometrically.

Total and Dissolved Metals in Water Column Samples

These analyses were carried out using procedures that are consistent with the requirements of the appropriate regulatory agencies and adapted from U.S. Environmental Protection Agency Method 3050 (Publ. # SW-836, 3rd ed., Washington, DC 20460). The procedures involve analysis by hydride-vapour atomic absorption spectrophotometry (HVAAS), graphite-furnace atomic absorption spectrophotometry (GFAAS), inductively coupled plasma (ICP) and cold-vapour atomic absorption spectrophotometry (CVAAS) to obtain the required detection limits. Specific details are as follows:

> **Arsenic and Antimony** were analyzed using a Perkin-Elmer Model 5000 dual-beam atomic absorption spectrophotometer coupled to a Perkin-Elmer Model MHS-20 automated hydride generation system (U.S. EPA Method 7000).

Aluminum, Calcium, Chromium, Cobalt, Iron, Magnesium, Manganese, Nickel, Potassium, Sodium and Zinc were analyzed using a Thermo Jarrel Ash Model ICAP61 simultaneous inductively coupled argon plasma spectrophotometer coupled with a cross-flow nebulizer (U.S. EPA Method 6010).

Cadmium, Copper, and Lead were analyzed using a Varian Model Spectra AA-300 single-beam atomic absorption spectrophotometer equipped with an automatic Zeeman background-corrected electrothermal atomizer (U.S. EPA Method 7000).

2.2 Sediment Methodologies

Total Organic Carbon (TOC) in Sediment

This analysis was carried out in accordance with U.S. EPA Method 9060A (Publ. #SW-846 3rd ed., Washington, DC 20460). The procedure involves a carbonate analysis (Leco gasometer) and a total carbon analysis (Leco induction furnace). The difference in carbon values is reported as Total Organic Carbon. This analysis was sublet to Chemex Labs Ltd. in North Vancouver, B.C.

Total Nitrogen in Sediment

This analysis was determined colorimetrically using a Technicon Auto-Analyser on a semi-micro Kjeldahl digest. This analysis was sublet to Pacific Soils Analysis Inc. in Richmond, B.C.

Total Sulphur in Sediment

This analysis was determined in the sediment using a Leco Induction Furnace. This analysis was sublet to Chemex Labs Ltd. in North Vancouver, B.C

Moderately Bound and Weakly Bound Metals in Sediment - Aqua-Regia Digestion

These analyses were carried out using procedures that are consistent with the requirements of the appropriate regulatory agencies and adapted from U.S. Environmental Protection Agency Method 3050 (Publ. # SW-836, 3rd ed., Washington, DC 20460). The procedure involves a digestion using a combination of nitric and hydrochloric acid (aqua-regia). The resulting extract is bulked to volume with deionized/distilled water. The digested portion is then analysed by a variety of instrumental techniques to obtain the required detection limits. Specific details are as follows:

Arsenic was analyzed using a Perkin Elmer Model 5000 dual-beam atomic absorption spectrophotometer coupled to a Perkin-Elmer Model MHS-20 automated hydride generation system (U.S. EPA Method 7000).

Cadmium and Lead were analysed using a Perkin Elmer Model 3100 dual beam atomic absorption spectrophotometer (flame model) equipped with automatic deuterium background correction (U.S. EPA Method 7000).

Cobalt, Copper, Magnesium, Manganese, Nickel and Zinc were analysed using a Thermo Jarrel Ash Model ICAP61 simultaneous inductively coupled argon plasma spectrophotometer interfaced with an IBM PS/2 486 data acquisition system (U.S. EPA Method 6010).

Silica Bound and Strongly Bound Metals in Sediment - Four-Acid Digestion

This procedure involves a digestion using a combination of nitric, hydrofluoric, hydrochloric, and perchloric acids. The resulting extract is bulked to volume with deionized/distilled water. The digested portion is then analysed by atomic emission spectrophotometry (ICP) to obtain the required detection limit for each element. Specific details are as follows:

Aluminum, Chromium, Iron, Potassium and Sodium were analysed using a Thermo Jarrel Ash model ICAP61 simultaneous inductively coupled argon plasma spectrophotometer interfaced with an IBM PS/2 286 data acquisition system (U.S. EPA Method 6010).

2.3 Peeper Water Methodologies

Total Metals in Peeper Waters

These analyses were carried out using procedures that are consistent with the requirements of the appropriate regulatory agencies and adapted from U.S. Environmental Protection Agency Method 3050 (Publ. # SW-836, 3rd ed., Washington, DC 20460). The procedure involve analysis by graphite-furnace atomic absorption spectrophotometry (GFAAS) and cold-vapour atomic absorption spectrophotometry (CVAAS) to obtain the required detection limits. Specific details are as follows:

Arsenic and Antimony were analyzed using a Perkin-Elmer Model 5000 dual-beam atomic absorption spectrophotometer coupled to a Perkin-Elmer Model MHS-20 automated hydride generation system (U.S. EPA Method 7000).

Cadmium, Copper, and Lead were analyzed using a Varian Model Spectra AA-300 single been atomic absorption spectrophotometer equipped with an automatic Zeeman background-corrected electrothermal atomizer (U.S. EPA Method 7000).

Iron, Manganese, and Zinc were analysed using a Perkin-Elmer Model 2380 dual-beam atomic absorption spectrophotometer equipped with an automatic deuterium background correction (U.S. EPA Metod 7000).

Total and Free Cyanide in Peeper Waters

This procedure involves an on-line acid/ultraviolet digestion of the sample, which converts the metal bound cyanides to hydrogen cyanide (HCN). The HCN gas is then separated and trapped in a weak sodium hydroxide solution via a gas diffusion membrane. The resulting cyanide ion is then analysed amperometrically.

2.4 Method Detection Limits (MDL)

The MDL is considered the most realistic approach to calculating a detection limit because it is based on a complete analytical procedure; it includes matrix effects and is derived from the analysis of samples, or standards rather than blanks. The process involves an actual determination of detection limit by analysing a number of low-level spikes in reagent grade water. The MDL method has been adopted by the U.S. Environmental Protection Agency (EPA) and the Canadian Association of Environmental Analytical Laboratories (CAEAL) and is used to define detection limits for the present program. All detection limits quoted for this project are MDLs.

2.5 Quality Assurance/Quality Control (QA/QC) Program

The U.S. EPA defines Quality Assurance (QA) as "the total program for assuring the reliability of monitoring data". Quality Control (QC) is defined as "the routine application of procedures for controlling the measurement process". QC is primarily concerned with the tools of the measurement system. Reagents used are of the highest quality and are checked for purity, strength, deterioration with time, and contamination. Class A volumetric glassware is thoroughly cleaned and calibrated when necessary. Balances are frequently checked with certified weights and records kept. All instruments are calibrated on a routine basis, with the maintenance of appropriate standards and operation logs on performance.

The QA/QC program for this study included the analysis of quality assurance samples to define the precision and accuracy of the method. For this project, the following quality control samples were employed:

- Method Blank - a blank which underwent processing identical to that carried out for samples. The results of this sample were used to assess contamination, and if specified in the method, to provide background correction.

- Laboratory Replicate - two or more indepentently subsampled portions of the same sample, separately prepared and analysed by the same methods. The replicate was presented to the analyst as an additional sample to check for the precision of a method.

- Certified Reference Material (CRM) - a reference material, one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body.

- Standard Reference Material (SRM) - a reference material distributed and certified by the U.S. National Institute of Standards and Technology (NIST). SRM's are certified for specific chemical or physical properties and are issued with certificates that report the results of the characterization and indicate the use of the material.

- Method Analyte Spike - a sample, clean matrix, or reagents which was fortified with a known quantity of the analyte(s) of interest prior to undergoing sample processing identical to that carried out for the samples. The results of this sample provided information on matrix effects and losses incurred during sample preparation.

3.0 RESULTS OF ANALYSIS

Five water column samples, twenty-nine sediment samples and one hundred and fifty peeper water samples were analysed for trace metals and various other parameters. The water column data is presented in Appendix A. The sediment data is presented in Appendix B. The peeper water data is presented in Appendix C.

The Quality Assurance/Quality Control Data are located in Appendices A to C.

Please note that from our laboratory analysis of the submitted water column samples, it was determined that the concentration of some dissolved metals exceed the concentration of the total metals found within a given sample. As defined by Standard Methods for the Examination of Water and Wastewater published by the American Public Health Association, dissolved metals are "those constituents (metals) of an unacidified sample that pass through a 0.45 micron membrane filter." Total metals are defined as "the concentration of metals determined on an unfiltered sample after a vigorous digestion, or the sum of the concentrations of metals in both dissolved and suspended fractions."

Theoretically, the concentration of dissolved metals cannot exceed the concentrations of the total metals within a given sample. When the results for a dissolved metals analysis are reported as being greater than the total metals, the following situations may have occured: 1) filter contamination in the field during sample collection, 2) contamination during transport, or 3) analytical variability (typically less than 10% at concentrations greater than 10 times the detection limit, or twice the detection limit at less than 10 times the detection limit).

The peeper water samples labelled "148-ES" and "149-ES" had insufficient volume available to complete all of the requested analyses. The missing parameters are labelled as "NS" in Appendix C.

4.0 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) RESULTS AND DISCUSSION

An extensive quality assurance/quality control program was incorporated with the sample analyses. This program included the analysis of quality control samples to define precision and accuracy, and to demonstrate contamination control for the type of samples and parameters under investigation.

For the water column samples for this project, the following quality control analyses were carried out:

- Method Blanks (n=1);
- Laboratory Replicates (n=1);
- Reference Materials (n=5):

ERA Lot 9964/9965 (Environmental Resource Associates), reference water certified for various water quality parameters.

SPEX Lot 1/2 (SPEX Industries Ltd.), reference water certified for various water quality parameters.

APG Lots 13959/13960, 14890/14892 and 14884/14885 (Analytical Products Group of Belpre, Ohio), reference waters certified for trace metals.

Method Blank, Laboratory Replicate and Reference Material results for all parameters analysed demonstrated that precision, accuracy, and contamination control met acceptance criteria.

For the sediment samples for this project, the following quality control analyses were carried out:

- Method Blanks (n=2);
- Laboratory Replicates (n=5);
- Reference Materials (n=5):

NRC BCSS-1 and NRC MESS-2 (National Research Council of Canada), Marine Sediment Reference Materials certified for trace metals.

CaCO3-STD, Chemex In-house reference material for total organic carbon.

Method Blank, Laboratory Replicate and Reference Material results for all parameters analysed demonstrated that precision, accuracy, and contamination control met acceptance criteria with the following exceptions:

Magnesium and Chromium results for one of the two, and Arsenic results for both of the NRC BCSS-1 samples fall outside of the manufacturer's 95% confidence limits but within the calculated 99.74% control limits.

Aluminum and Lead results for the NRC MESS-2 sample fall outside of the manufacturer's 95% confidence limits but within the calculated 99.74% control limits.

Potassium results for both of the NRC BCSS-1 samples fall outside of both the manufacturer's 95% confidence limits and the calculated 99.74% control limits.

It should be noted that these deviations reflect typical analytical variabilities for these parameters and should not in any way impact the interpretation of the results.

For the peeper water samples for this project, the following quality control analyses were carried out:

- Method Blanks (n=9);
- Reference Materials (n=9):
- Method Analyte Spikes (n=30).

APG Lot 14890/14892 (Analytical Products Group of Belpre, Ohio), reference water certified for trace metals.

Due to the limited volumes of sample available for these analyses, Laboratory Replicates were not performed.

Method Blank, Method Analyte Spike and Reference Material results for all parameters analysed demonstrated that precision, accuracy, and contamination control met acceptance criteria.

Welcome Screen Search Report List

5.0 REFERENCES

APHA. 1992. Standard Methods for the Examination of Water and Wastewater, 18th ed. American Public Health Association. Washington, DC.

ASTM. 1984. Annual Book of ASTM, Section 11 - Water and Environmental Technology, Vol 11.02 Water (II), American Society for Testing and Meterials, Washington, DC.

U.S. EPA, 1986. Test Methods for Evaluating Solid Wastes - Physical/Chemical Methods, SW-846, 3rd Ed., and Revisions (1990),

Welcome Screen Search Report List

APPENDIX A

Water Column Data

RESULTS OF ANALYSIS - Water Column Samples - Quality Control[1,2,3]

File No. F3839

		Method Blank	ERA Lot 9964/ 9965	ERA Lot 9964/ 9965 Target Values
Physical Tests				
Total Dissolved Solids		<1.0	-	-
Total Suspended Solids		<1	94	89
Turbidity (NTU)		<0.10	-	-
Dissolved Anions				
Acidity	CaCO3	1.7	-	-
Alkalinity - Total	CaCO3	<1.0	-	-
Chloride	Cl	<0.5	-	-
Fluoride	F	<0.02	-	-
Sulphate	SO4	<1.0	99.8	99.4
Nutrients				
Ammonia Nitrogen	N	<0.02		
Nitrate Nitrogen	N	<0.005		
Dissolved ortho-Phosphate	P	<0.001		
Total Dissolved Phosphate	P	<0.001		
Total Phosphorus	P	<0.001		
Cyanides				
Free Cyanide	CN	<0.005		
Total Cyanide	CN	<0.005		
WAD Cyanide	CN	<0.005		
Total Metals				
Aluminum	T-Al	<0.20		
Antimony	T-Sb	<0.0001		
Arsenic	T-As	<0.0001		
Cadmium	T-Cd	<0.0002		
Calcium	T-Ca	<0.050		
Chromium	T-Cr	<0.015		
Cobalt	T-Co	<0.015		
Copper	T-Cu	<0.001		
Iron	T-Fe	<0.030		
Lead	T-Pb	<0.001		
Magnesium	T-Mg	<0.050		
Manganese	T-Mn	<0.005		
Nickel	T-Ni	<0.020		
Potassium	T-K	<2.0		
Sodium	T-Na	<2.0		
Zinc	T-Zn	<0.005		
Inorganic Parameters				
Sulphide	S	<0.02		

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[1] Results are expressed as milligrams per litre except for Turbidity (NTU).

[2] < = Less than the detection limit indicated.

[3] ERA Lot Lot 9964/9965 is a reference water from the Environmental Resource Associates for water quality parameters.

Welcome Screen | Search | Report List

RESULTS OF ANALYSIS - Water Column Samples - Quality Control[1,2,3]

File No. F3839

		APG Lot 13959/ 13961	APG Lot 13959/ 13961 Target Values	APG Lot 14890/ 14892	APG Lot 14890 14892 Target Values
Total Metals					
Aluminum	T-Al	-	-	<0.20	0.147
Antimoney	T-Sb	-	-	0.0860	0.0821
Arsenic	T-As	-	-	0.0160	0.0152
Cadmium	T-Cd	0.0400	0.0365	-	-
Chromium	T-Cr	-	-	0.052	0.0557
Cobalt	T-Co	-	-	0.168	0.170
Copper	T-Cu	-	-	0.058	0.0600
Iron	T-Fe	-	-	0.151	0.150
Lead	T-Pb	-	-	0.530	0.482
Manganese	T-Mn	-	-	0.061	0.0624
Nickel	T-Ni	-	-	0.101	0.0953
Zinc	T-Zn	-	-	0.196	0.203

		APG Lot 14884/ 14885	APG Lot 14884/ 14885 Target Values
Total Metals			
Calcium	T-Ca	125	135 ± 18.2
Magnesium	T-Mg	12.6	13.2 ± 3.17
Potassium	T-K	109	106 ± 14.6
Sodium	T-Na	133	132 ± 19.0

---

[1] Results are expressed as milligrams per litre.

[2] < = Less than the detection limit indicated.

[3] APG Lots 13959/13961, 14890/14892 and 14884/14885 are reference waters from the Analytical Products Group for trace metals

Welcome Screen Search Report List

RESULTS OF ANALYSIS - Water column Samples Quality Control[1,2,3]

File No. F3839

		SPEX Lot #1 & #2	SPEX Lot #1 & #2 Target Values
Physical Tests			
Conductivity (umhos/cm)		274	277
pH		6.03	5.99
Dissolved Anions			
Alkalinity - Total	CaCO3	27.0	24.9
Chloride	Cl	49.0	51.3
Fluoride	F	1.01	0.99
Nutrients			
Ammonia Nitrogen	N	2.18	1.99
Nitrate Nitrogen	N	1.98	1.99
Dissolved ortho-Phosphate	P	0.500	0.50
Total Dissolved Phosphate	P	1.56	1.48
Total Phosphorus	P	1.61	1.48
Cyanides			
Total Cyanide	CN	0.560	0.48

---

[1] Results are expressed as milligrams per litre except for pH and Conductivity (umhos/cm).

[2] < = Less than the detection limit indicated.

[3] SPEX Lot #1 and #2 are reference waters from SPEX Industries Ltd. for water quality parameters.

RESULTS OF ANALYSIS - Quality Control[1,2,3]

File No. F3840

		Method Blank #1	Method Blank #2
Total Metals			
Aluminum	T-Al	<200	<200
Antimony	T-Sb	<0.1	<0.1
Arsenic	T-As	<0.01	<0.01
Cadmium	T-Cd	<0.1	<0.1
Chromium	T-Cr	<8	<8
Cobalt	T-Co	<2	<2
Copper	T-Cu	<1	<1
Iron	T-Fe	<200	<200
Lead	T-Pb	<2	<2
Magnesium	T-Mg	<50	<50
Manganese	T-Mn	<4	<4
Molybdenum	T-Mo	<4	<4
Nickel	T-Ni	<2	<2
Potassium	T-K	<10	<10
Sodium	T-Na	<10	<10
Zinc	T-Zn	<1	<1
Sublet Parameters			
Total Organic Carbon	% C	<0.05	<0.05
Total Nitrogen	% N	<0.01	<0.01
Total Sulphur	% S	<0.1	<0.1

---

[1] Total Metals results are expressed as milligrams per dry kilogram.

[2] Total Organic Carbon, Total Nitrogen and Total Sulphur results are expressed as percent.

[3] < = Less than the detection limit indicated.

Welcome Screen Search Report List

RESULTS OF ANALYSIS - Quality Control[1,2,3]

File No. F3840

		NRC BCSS-1 #1	NRC BCSS-1 #2	NRC BCSS-1 Target Values	NRC MESS-2 #1	NRC MESS-2 Target Values
Total Metals						
Aluminum	T-Al	64000	62500	62600	89900	85700
Antimony	T-Sb	0.6	0.5	0.59	1.0	1.09
Arsenic	T-As	9.44	9.39	11.1	20.1	20.7
Cadmium	T-Cd	0.2	0.2	0.25	0.2	0.24
Chromium	T-Cr	109	103	123	110	106
Cobalt	T-Co	10	10	11.4	12	13.8
Copper	T-Cu	16	17	18.5	40	39.3
Iron	T-Fe	32600	32400	32900	43400	43500
Lead	T-Pb	20	20	22.7	20	21.9
Magnesium	T-Mg	13300	12600	14700	-	-
Manganese	T-Mn	241	241	229	372	365
Molybdenum	T-Mo	-	-	1.9	<4	2.85
Nickel	T-Ni	53	53	55.3	47	49.3
Potassium	T-K	18800	19200	18000	-	-
Sodium	T-Na	19800	20300	20200	-	-
Zinc	T-Zn	113	116	119	157	172

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[1] Total Metals results are expressed as milligrams per dry kilogram.

[2] < = Less than the detection limit indicated.

[3] NRC MESS-2 and BCSS-1 are Certified Reference Materials from the National Research Council of Canada.

Welcome Screen | Search | Report List

RESULTS OF ANALYSIS - Quality Control

File No. F3840

		CaCO3-STD #1	CaCO3-STD #2	CaCO3-STD Target Value
Sublet Parameters				
Total Organic Carbon	% C	12.1	12.0	12.0

---

[1] Total Organic Carbon results are expressed as percent.

APPENDIX C

Peeper Water Data

RESULTS OF ANALYSIS - Peeper Waters[1,2] File No. F3841/F3482/F3484

		Method Blank #1	Method Blank #2	Method Blank 3
Total Metals				
Antimony	T-Sb	<0.001	<0.001	<0.001
Arsenic	T-As	<0.001	<0.001	<0.001
Cadmium	T-Cd	<0.0001	<0.0001	<0.0001
Copper	T-Cu	<0.001	<0.001	<0.001
Iron	T-Fe	<0.005	<0.005	<0.005
Lead	T-Pb	<0.0005	<0.0005	<0.0005
Manganese	T-Mn	<0.001	<0.001	<0.001
Zinc	T-Zn	<0.001	<0.001	<0.001

		Method Blank #4	Method Blank #5	Method Blank #6
Total Metals				
Antimony	T-Sb	<0.001	<0.001	<0.001
Arsenic	T-As	<0.001	<0.001	<0.001
Cadmium	T-Cd	<0.0001	<0.0001	<0.0001
Copper	T-Cu	<0.001	<0.001	<0.001
Iron	T-Fe	<0.005	<0.005	<0.005
Lead	T-Pb	<0.0005	<0.0005	<0.0005
Manganese	T-Mn	<0.001	<0.001	<0.001
Zinc	T-Zn	<0.001	<0.001	<0.001

		Method Blank #7	Method Blank #8	Method Blank #9
Total Metals				
Antimony	T-Sb	<0.001	<0.001	<0.001
Arsenic	T-As	<0.001	<0.001	<0.001
Cadmium	T-Cd	<0.0001	<0.0001	<0.0001
Copper	T-Cu	<0.001	<0.001	<0.001
Iron	T-Fe			
Lead	T-Pb	<0.0005	<0.0005	<0.0005
Manganese	T-Mn	<0.001	<0.001	<0.001
Zinc	T-Zn	<0.001	<0.001	<0.001

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[1] Results are expressed as milligrams per litre except where noted.
[2] < = Less than the detection limit indicated.

RESULTS OF ANALYSIS -Peeper Waters[1,2] File No. F3841/F3842/F3844

		APG Lot 14890/ 14892#1	APG Lot 14890/ 14892 #2	APG Lot 14890/ 14892 #3	APG Lot 14890/ 14892 Target Values
Total Metals					
Antimony	T-Sb	0.092	0.091	0.092	0.0821 ± 0.0251
Arsenic	T-As	0.014	0.014	0.014	0.0152 ± 0.00392
Cadmium	T-Cd	0.0780	0.0780	0.0780	0.0764 ± 0.00962
Copper	T-Cu	0.059	0.058	0.053	0.0600 ± 0.0082
Iron	T-Fe	0.150	0.150	0.163	0.150 ± 0.0214
Lead	T-Pb	0.480	0.480	0.480	0.482 ± 0.0698
Manganese	T-Mn	0.061	0.061	0.061	0.0624 ± 0.0067
Zinc	T-Zn	0.190	0.200	0.200	0.203 ± 0.0323

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[1] Results are expressed as milligrams per litre except where noted.

[2] APG Lot 14890/14892 is a Reference Water certified for trace metals by the Analytical Products Group of Belpre, Ohio.

Welcome Screen | Search | Report List

RESULTS OF ANALYSIS -Peeper Waters[1,2]

File No. F3841/F3842/F3844

		APG Lot 14890/ 14892#4	APG Lot 14890/ 14892 #5	APG Lot 14890/ 14892 #6	APG Lot 14890/ 14892 Target Values
Total Metals					
Antimony	T-Sb	0.092	0.091	0.092	0.0821 ± 0.0251
Arsenic	T-As	0.014	0.014	0.014	0.0152 ± 0.00392
Cadmium	T-Cd	0.0780	0.0780	0.0780	0.0764 ± 0.00962
Copper	T-Cu	0.059	0.058	0.053	0.0600 ± 0.0082
Iron	T-Fe	0.150	0.150	0.163	0.150 ± 0.0214
Lead	T-Pb	0.480	0.480	0.480	0.482 ± 0.0698
Manganese	T-Mn	0.061	0.061	0.061	0.0624 ± 0.0067
Zinc	T-Zn	0.190	0.200	0.200	0.203 ± 0.0323

		APG Lot 14890/ 14892 #7	APG Lot 14890/ 14892 #8	APG Lot 14890/ 14892 #9	APG Lot 14890/ 14892 Target Values
Total Metals					
Antimony	T-Sb	0.092	0.091	0.092	0.0821 ± 0.0251
Arsenic	T-As	0.015	0.015	0.015	0.0152 ± 0.00392
Cadmium	T-Cd	0.0780	0.0780	0.0780	0.0764 ± 0.00962
Copper	T-Cu	0.059	0.058	0.053	0.0600 ± 0.0082
Iron	T-Fe	0.150	0.150	0.163	0.150 ± 0.0214
Lead	T-Pb	0.480	0.480	0.480	0.482 ± 0.0698
Manganese	T-Mn	0.061	0.061	0.061	0.0624 ± 0.0067
Zinc	T-Zn	0.190	0.200	0.200	0.203 ± 0.0323

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[1] Results are expressed as milligrams per litre except where noted.

[2] APG Lot 14890/14892 is a Reference Water certified for trace metals by the Analytical Products Group of Belpre, Ohio.

Welcome Screen Search Report List

RESULTS OF ANALYSIS -Peeper Waters File No. F3841/F3842/F3844

Sample Identification	Parameter	Analyte Spike Conc. (mg/L)	Analyte Sample Conc. (mg/L)	Percent Recovery %
26-ES	Cadmium	0.001	0.0001	96
32-ES	Cadmium	0.001	<0.0001	100
76-ES	Cadmium	0.001	0.0001	91
98-ES	Cadmium	0.001	<0.0001	95
105-ES	Cadmium	0.001	<0.0001	95
106-ES	Cadmium	0.001	<0.0001	95
1-ES	Iron	0.010	0.022	75
2-ES	Iron	0.010	0.015	115
53-ES	Iron	0.010	<0.005	115
54-ES	Iron	0.010	<0.005	100
119-ES	Iron	0.010	0.006	85
120-ES	Iron	0.010	0.011	85
41-ES	Lead	0.005	<0.0025	75
42-ES	Lead	0.005	<0.0025	80
96-ES	Lead	0.005	<0.0025	75
99-ES	Lead	0.005	<0.0025	75
142-ES	Lead	0.005	<0.0025	85
146-ES	Lead	0.005	<0.0025	75
14-ES	Manganese	0.001	0.358	68
48-ES	Manganese	0.001	0.265	66
95-ES	Manganese	0.001	0.401	85
97-ES	Manganese	0.001	0.301	81
143-ES	Manganese	0.001	0.259	74
144-ES	Manganese	0.001	0.348	81
1-ES	Zinc	0.002	0.340	100
42-ES	Zinc	0.002	0.220	95
59-ES	Zinc	0.002	0.170	115
99-ES	Zinc	0.002	<0.001	85
102-ES	Zinc	0.002	0.100	115
146-ES	Zinc	0.002	0.110	90

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RESULTS OF ANALYSIS - Quality Control[1,2,3,4]

File No. F3853

	Free Cyanide CN	Total Cyanide CN
Method Blank	<0.005	<0.005

		Spex Lot #3-6 Found	Spex Lot #3-6 Target Value
Total Cyanide	CN	0.460	0.48

		Matrix Spike %
Total Cyanide	CN	96
Free Cyanide	CN	96

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[1] Results are expressed as milligrams per litre except where noted.

[2] Matrix Spike results are expressed as percent.

[3] < = Less than the detection limit indicated.

[4] SPEX Lot #3-6 is a Reference Water from SPEX Industries Ltd. certified for Total Cyanide.