

**Subaqueous Disposal of Reactive
Mine Tailings Louvicourt Mine Test
Cells Geochemical Sampling and
Analysis**

MEND Project 2.12.1c

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Geochemical Sampling and Analysis

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Summary

The objective of this study was to assess the effectiveness of an engineered shallow water cover in reducing the oxidation of sulfidic mine tailings and thus preventing the development of acid rock drainage. Fresh tailings from the Louvicourt Mine (Louvicourt, Abitibi, QC) were submerged under a 0.3-m water cover in experimental field cells. From 1996 to 1998, we followed the chemistry of the interstitial water near the tailings-overlying water interface using *in situ* dialysis, and determined pH and dissolved oxygen (DO) profiles across the tailing-water interface using micro-electrodes. Penetration of DO into the tailings was limited to < 7 mm, even in the presence of DO produced by benthic periphyton. Anoxia in the tailings was further demonstrated by the appearance of dissolved $\Sigma\text{H}_2\text{S}$, Fe and Mn in pore water at depths ~ 1.5 cm below the interface. However, there was clear evidence of surface oxidation of the mine tailings at the mm scale (i.e., DO depletion, coupled with localized increases in $[\text{H}^+]$ and $[\text{SO}_4^{2-}]$). Mobilization of Cd and Zn from this surface layer was indicated by the presence of sub-surface peaks in the concentrations of these two metals in the tailings interstitial water and by a change in their solid phase partitioning from refractory to more labile fractions. In contrast, there was no evidence for mobilization of Cu from tailings.

Unlike previous reports, which suggested that submerged tailings were effectively inert, our results show some alteration of the superficial layer over time. The observed Cd and Zn releases from the submerged tailings are however very small. For a typical disposal operation (a 1 km x 1.5 km impoundment with an average depth of 1 m, an overlying water volume of 1.5×10^9 L, and an average water residence time in the impoundment of 1 year), calculations indicate that these releases would increase the overlying water Zn concentration by 47 nM (3 ppb) and the Cd concentration by 0.31 nM (0.04 ppb). The Cd and Zn fluxes from the tailings to the overlying water would thus have only minor impacts on the overlying water quality.

Résumé

Cette étude avait pour objectif d'évaluer l'efficacité de la disposition subaquatique de résidus miniers réactifs comme moyen à réduire l'oxydation des sulfures présents dans les résidus, et ainsi à prévenir le drainage minier acide. De telles études avaient été réalisées dans le passé dans des lacs relativement profonds ; la présente étude visait plutôt à simuler les conditions susceptibles de se rencontrer dans un réservoir artificiel de faible profondeur. Les résidus miniers de la mine Louvicourt (Louvicourt, Abitibi, Québec) ont été submergés directement sous 0.3 m d'eau dans des cellules expérimentales construites à même le site. La chimie de l'eau interstitielle près de l'interface résidus-eau surnageante a été étudiée de 1996 à 1998 au moyen de la dialyse *in situ*. Des profils de pH et d'oxygène dissous (OD), à travers l'interface résidus-eau surnageant, ont également été obtenus à l'aide de micro-électrodes. La pénétration de l'OD était limitée aux premiers 7 mm de profondeur, et ce même en présence d'algues periphytiques produisant de l'OD à la surface des résidus. L'absence d'OD à des profondeurs > 7 mm a de plus été confirmée par la présence de sulfures, de Fe(II) et de Mn(II) dissous dans l'eau interstitielle prélevée à 1.5 cm sous l'interface. Néanmoins, malgré cette pénétration limitée de l'oxygène, plusieurs observations indiquent que les sulfures près de l'interface résidus-eau surnageante subissaient une oxydation à l'échelle du mm (i.e., diminution localisée de OD, avec augmentation concomitante de $[H^+]$ et $[SO_4^{2-}]$). La mobilisation du Cd et du Zn près de l'interface résidus-eau surnageante s'est révélée par la présence de maximums, juste en dessous de l'interface, pour les concentrations de ces deux métaux dans l'eau interstitielle des résidus, et par un déplacement progressif de ces métaux des phases solides les plus réfractaires vers des phases solides plus labiles au cours de l'étude. Par ailleurs, aucun des paramètres étudiés ne suggère une mobilisation semblable du Cu.

Contrairement aux études précédentes, qui ont suggéré que les résidus miniers submergés soient totalement inertes, nos résultats montrent une altération graduelle de la couche superficielle des résidus avec le temps. Cependant, la diffusion du Cd et Zn des résidus vers l'eau surnageante est demeurée très faible. Par exemple, pour un parc à résidus de 1 km x 1.5 km ayant

une profondeur moyenne de 1 m, soit un volume d'eau approximatif de 1.5×10^9 L, et en supposant un temps de résidence de la colonne d'eau d'un an, nous estimons que les flux diffusifs de Zn et de Cd provenant des résidus submergés augmenteraient la concentration de Zn dans l'eau surnageante de 47 nM (3 ppb) et la concentration en Cd de 0.31 nM (0.04 ppb). Les flux diffusifs de Cd et de Zn auraient donc un impact mineur sur la qualité de l'eau surnageante.

1. INTRODUCTION

Acid mine drainage is a major environmental concern of the mining industry world-wide. Many of the ores exploited contain a large proportion of sulfides, present mainly as pyrite (FeS_2). The pyrite-containing tailings produced can be oxidized when exposed to the atmosphere and rainfall, generating large amounts of sulfuric acid. The major oxidants of pyrite are dissolved oxygen (DO) and, once the oxidation process has been initiated, Fe^{3+} . In this latter process, the rate-limiting step of the oxidation process is the oxidation of $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$, catalyzed by microorganisms (Evangelou and Zhang, 1995). The resulting acidic solution can leach metals from the tailings, constituting a threat for the quality of the receiving environment (Geller et al., 1998).

Several techniques have been developed for the treatment of acid mine drainage, such as chemical neutralization and treatment in wetland systems (Evangelou and Zhang, 1995). However, the treatment of drainage water is unappealing as a long term solution, given the high cost and open-ended nature of the operation, which could potentially last for hundreds of years after the mining operation has stopped (Filion et al., 1990). Accordingly, considerable effort has been expended to develop techniques for the prevention of acid mine drainage (e.g., the Mine Environment Neutral Drainage (MEND) program, run by Natural Resources Canada). These prevention techniques are based on processes such as the inhibition of the activity of iron-oxidizing bacteria by the addition of anionic surfactants, the precipitation of Fe^{3+} by the addition of phosphate, or the limitation of DO diffusion into the tailings by physical barriers (Evangelou and Zhang, 1995). Because of its economic and environmental relevance, the utilization of water covers for the prevention of acid mine drainage has been considered in recent years.

Underwater disposal of reactive tailings attenuates the input of DO to the tailings, ambient DO concentrations in overlying water and sedimentary interstitial water being much lower than in air. In addition, the resulting suboxic to anoxic conditions should inhibit the microbial catalysis associated with the oxidation process (Kleinmann and Crerar, 1979). The underwater disposal of tailings to prevent oxidation is different from inundation of already-altered tailings, in which case the oxidation products already present strongly influence the fate of the tailings after flooding. Pedersen and co-workers studied the diagenesis of tailings submerged in Buttle Lake, British Columbia, Canada (Pedersen, 1983; Pedersen and Losher, 1988; Pedersen et al., 1991) and concluded that no significant oxidation occurred after underwater disposal of the tailings. No release of Cd, Cu or Zn from the submerged tailings could be detected. However, Buttle Lake is affected by acid mine drainage and the overlying water metal concentrations are already elevated. In 1991, Pedersen et al. sampled additional cores from Buttle Lake; based on comparisons of the porewater and overlying water metal concentrations, they concluded that there was no metal efflux from the submerged tailings. Pedersen et al. (1993) also studied submerged tailings in the shallower Anderson Lake, Manitoba, Canada. This lake is also affected by acid mine drainage and because of the resulting high metal concentrations in the water column, the submerged tailings were acting as a sink for metals.

Although underwater disposal seems beneficial in the context of stabilizing reactive sulfides, the use of natural lakes to provide the water cover (as was the case in the examples studied by Pedersen and co-workers) raises environmental conservation issues. The utilization of man-made reservoirs is inherently appealing, but there are legitimate concerns regarding the long-term stability of such structures and the need for dike maintenance. For engineering, geotechnical and economic reasons, a minimum water cover depth will be preferable. However, tailings under

shallow water covers (e.g., < 1 m) will potentially be affected by climatic conditions such as sediment resuspension resulting from wind-induced turbulence and the complete freezing of the water column in northern areas. Because of the shallower depth of water, the DO concentration will be maintained at higher levels and the higher amount of light reaching the tailings surface could allow the establishment of a periphyton layer, the photosynthetic activity of which will constitute a localized source of DO. These potential perturbations of the tailings raise legitimate questions regarding the effectiveness of a shallow water cover.

The present investigation was thus designed to assess the efficiency of shallow water covers in man-made reservoirs for the prevention of the oxidation of sulfidic mine tailings. We have monitored reactive mine tailings submerged in field test cells, with a water cover of about 0.3 m.¹ From 1996 to 1998, we followed the chemistry of the interstitial water near the tailings-overlying water interface using *in situ* dialysis (porewater peepers), and determined pH and DO profiles across the tailing-water interface using microelectrodes. These latter techniques have revealed diagenetic processes occurring near the interface at the mm scale. Because of their lower vertical resolution, the conventional geochemical techniques such as *in situ* dialysis and coring did not detect these processes. We have also monitored changes in the lability of the metals in the tailings solid phase over the same period, using sequential extractions to probe metal partitioning in the superficial layer of tailings, sampled by coring. Previous reports suggested that submerged tailings were effectively inert in water bodies with an active depositional regime and a settling flux of organic matter. For settled tailings with no significant accumulation of organic matter, our

¹ Complementary column studies were performed by CANMET researchers on these same tailings, under controlled laboratory conditions; their results are presented in a separate report.

results show slight but measurable alteration of the superficial layer over time.

To evaluate physical and chemical interactions within the deposited tailings, our measurements focused primarily on the interstitial water, as it is well recognized that the composition of the aqueous phase is far more sensitive to diagenetic reactions than is that of the solid phase. The experimental program emphasized measurements of:

- diffusion of O₂ from the water cover into the sediments;
- diffusion of dissolved metals and anions across the tailings-water interface;
- interactions between the aqueous and solid phases (sorption; oxidation; dissolution).

In addition, changes in metal partitioning were monitored in the exposed tailings at the tailings-water interface (i.e., the solid phase). The solid-phase, porewater and water-column geochemical data were used to interpret controls on the chemical behavior of the submerged tailings.

2. MATERIALS AND METHODS

2.1. Site description / Sampling

Located about 20 km east of Val d'Or, Québec, Canada, the Louvicourt Mine is a Cu and Zn underground mine that has been in operation since 1994. About 18 % of the ore processed produces metal concentrates, 50 % is used as underground back fill, and the remaining 32 % is disposed of underwater in an artificial reservoir. Grain size measurements indicate that the tailings are mainly composed of particles in the silt and fine sand fractions (Li and St-Arnaud, 2000). The tailings consist of silicate, sulfide, carbonate and oxide minerals. The dominant sulfide is pyrite, with chalcopyrite, sphalerite and galena present in trace quantities. Silicate minerals include quartz, muscovite, ferroan clinocllore, plagioclase and K-feldspar. Magnesian

siderite and ankerite (or ferroan dolomite) were identified as the dominant carbonate minerals (Li and St-Arnaud, 2000).

In order to evaluate the effectiveness of the current water cover as well as the possible post-closure options, two field test cells (21 m x 21 m) were constructed adjacent to the reservoir. The cells were filled with about 3 m of mine tailings and covered by 0.3 m of water, pumped from an adjacent pond, at the end of August 1996. The two experimental cells, designed as replicate treatments, were filled in parallel over a period of about three weeks by bleeding tailings off the main tailings pipeline. However, Cell 1 took slightly longer to fill than did Cell 2. During the additional 48 h needed to fill Cell 1, the mine's flotation plant changed from a Cu and Zn recovery mode to a Cu-only recovery procedure. The final layer of tailings was thus enriched in metals (and less homogeneous) in Cell 1 compared to Cell 2. Nevertheless, the geochemical behavior of the tailings in the two cells proved similar.

A floating sampling deck was installed in the center of the cells to facilitate sampling. Water levels were maintained with V-notched weirs. In the event of insufficient inputs from precipitation and drainage waters, the cells were topped up periodically by pumping from the adjacent pond. From the third week of May to the first week of November (i.e., the ice-free season), outflow, water pH, temperature and conductivity were automatically recorded at 1-h intervals in 1997 and 2-h intervals in 1998; these data were collected by the Louvicourt Mine personnel. Unfortunately, sporadic failure of the pH electrode limited the usefulness of the pH data set, but the flow data were considered to be reliable. We sampled the cells on four occasions, 15-16 October 1996, 10-11 June 1997, 25-26 August 1998, and 15-16 June 1999. The tailings were allowed to settle/consolidate for six weeks after filling, before the first sampling campaign

in October 1996; this was the maximum possible period that would still allow for installation and retrieval of the porewater peepers before the fall freeze-up. The June 1997 campaign was a reduced effort² and the interstitial waters were sampled only to a depth of 2.5 cm. Similarly, the June 1999 campaign was limited to microelectrode measurements.

2.2. Electrochemical micro-profiles of pH and DO

A submersible micro-manipulator, consisting of a hand-operated micrometer attached to a tripod support inserted into the tailings, was used to displace the O₂ and pH electrodes incrementally across the interface, both downward and upward. The micro-manipulator was equipped with a flexible illuminated boroscope, with which the position of the microsensor's tip (a white dot was painted close to the sensor's tip) could be determined relative to the tailings-water interface with a precision of ± 0.5 mm. O₂ micro-profiles were measured *in situ* using Clark-type O₂ micro-electrodes with a guard cathode (Diamond General Corporation; type 737-GC; tip size 15-35 μm ; response time < 1 s). The pH micro-profiles were obtained with glass combination micro-electrodes from Orion Research Inc. (No. 9803BN), which were also fixed to the end of the micro-manipulator. The O₂ and pH micro-profiles were obtained in June 1997, August 1998 and June 1999. Micro-profiles were measured from about 9h00 to 15h00 under sunny or partly-covered sky, except for the profiles that were measured at night. The micro-manipulator was deployed at different points adjacent to the sampling deck, allowing us to obtain several profiles within each cell.

² The second sampling campaign was designed around the two components of the field program that had not been carried out in October 1996: (i) sampling of the groundwater and (ii) determination of pH and O₂ profiles across the tailings-water interface. However, in the light of the October 1996 results, specifically the indication of dissimilar geochemical behavior in the two cells, we decided to repeat some of the porewater measurements and determine whether the heterogeneity was still present after the first winter.

2.3. *Interstitial water analysis*

Water samples were collected with *in situ* samplers (porewater peepers; 1 cm vertical resolution; Gelman HT-200 polysulfone membrane, 0.2 μm nominal pore size) similar to those described by Carignan et al. (1985). The Plexiglas components of the peepers were kept under an N_2 atmosphere for a minimum of 15 d (Carignan et al., 1994), prior to filling the compartments with Milli-Q water ($> 18 \text{ M}\Omega$). The assembled peepers were then further deoxygenated under a N_2 atmosphere for at least 48 h, and were also maintained under N_2 during transport to the field site.

At the sampling site, peepers were inserted vertically into the tailings at four sites in each cell (10-15 m apart), using a small boat. Once in place, the peepers extended 7-9 cm above the tailings-overlying water interface; the remaining 21-23 cm were within the tailings. They were allowed to equilibrate for two weeks; no major outflow events occurred during these sampling periods.

After the equilibration period, the peepers were retrieved, rinsed with the overlying water from the cell and sampled immediately in the ambient air in the mobile laboratory. The whole process of sampling each peeper generally took < 15 min. Samples for $\Sigma\text{H}_2\text{S}$ determinations were processed first to minimize losses of this unstable analyte. Samples for $\Sigma\text{H}_2\text{S}$ analysis (1.5 mL) were obtained from the compartments of one of the vertical rows with N_2 -purged syringes. They were injected through a septum into pre-washed 3 mL amber glass bottles, which had been purged with N_2 and contained 60 μL of N,N'-dimethyl-p-phenylenediamine sulfate (2.7 mM in 6 M HCl) and 60 μL of FeCl_3 (5.55 mM in 6 M HCl). These samples were maintained at 4 $^\circ\text{C}$ in the dark during their transport to the laboratory. A second set of subsamples of approximately 0.5

mL was also retrieved from the same row of compartments with a micropipette and injected into 1.5 mL pre-washed polypropylene tubes for Cl^- and SO_4^{2-} analyses. For dissolved inorganic carbon (DIC) determinations, a third set of subsamples was collected using a syringe that had previously been purged with nitrogen; the aqueous sample (1.5 mL) was injected through a rubber septum into a bottle that had previously been acidified with HCl (1 N; 60 μL) and purged with helium. Samples (3 mL) for metals were then collected from the compartments of the second vertical row by piercing the peeper membrane with a micropipette fitted with an acid-cleaned tip: these samples were injected into pre-washed and pre-acidified (40 μL 10 % HNO_3 Anachemia ultrapur) vials. The remaining 1 mL was removed with a syringe for immediate pH measurement, using a combination glass micro-electrode and a portable pH meter.

$\Sigma\text{H}_2\text{S}$ was measured within 24 h by a spectrophotometric method (Cline, 1969), using a segmented-flow colorimetric analyzer (Autoanalyser II, Technicon Instruments Corporation, NY). Standard solutions for the calibration curve were prepared in the laboratory at the time of each sampling. The samples for DIC analysis were returned to the central laboratory and the CO_2 trapped in the headspace was analyzed on arrival by gas chromatography (Perkin Elmer Sigma 300 HWD chromatograph). Chloride and SO_4^{2-} concentrations were determined with an ion chromatography system equipped with a conductivity detector (DX-300 Gradient Chromatography Systems, Dionex, CA). An AS12A column with an AG12A pre-column and an injection loop of 100 μL were used.

Depending on their concentrations, metals were analyzed either by atomic absorption spectroscopy on a SpectrAA-20 spectrophotometer (Varian Instruments, CA), by electrothermal

atomic absorption spectroscopy (ETAAS) on a SIMAA 6000 graphite furnace equipped with an autosampler (model AS72) (Perkin-Elmer Corporation, Norwalk, CT), or by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an AtomScan 25 spectrophotometer (Thermo Jarrell Ash Corporation, Franklin, MA).

2.4. Diffusive fluxes across the tailings - overlying water interface

Diffusive fluxes of species "i" across the tailings-water interface, J_i , were calculated according to Fick's law, neglecting porewater advection:

$$J_i = - \Phi \tau D_i \frac{dC_i}{dx}$$

where Φ is the porosity of the tailings, τ the tortuosity, D_i the molecular diffusion coefficient and dC_i/dx is the concentration gradient. The porosity of settled tailings (0.4) and a tortuosity value of 0.2 were obtained from an earlier study by Li and St-Arnaud (2000) on the same tailings.

The O_2 concentration gradients were calculated from the slope of the micro-profiles in the tailings. O_2 diffusivity was obtained from Broecker and Peng (1974) and corrected for temperature according to Zhang and Davison (1995); the mean temperature over the O_2 measurement period was used, 23 ± 2 °C.

For Cl^- and SO_4^{2-} fluxes, tracer diffusion coefficients were obtained from Li and Gregory (1974) and corrected for temperature according to Zhang and Davison (1995). The mean temperature over the equilibration period was used, 19 ± 3 °C in June 1997 and 17 ± 3 °C in August 1998. For

1996, the first available 24-h temperature data set was used, as obtained 3 d after the sampling of the peepers, 8.1 ± 0.8 °C. Mean concentrations at +0.5 cm in the overlying water and at -0.5 cm in the tailings were used to calculate the concentration gradients.

2.5. Solid phase analysis

In October 1996 and August 1998, 3 and 4 cores per cell respectively were collected close to the peeper sampling sites, with Plexiglass coring tubes (9 cm inside diameter). The tubes were tightly closed and handled with care to minimize any perturbation of the tailings during their transport to shore. The cores were immediately extruded using a piston extruder. The uppermost 0.5 cm layer was sampled and placed in a 500 mL centrifugation bottle, half-filled with overlying water from the cells; the resulting suspension was kept frozen until analysis.

Before analysis, the superficial sediment samples were thawed, shaken gently for 30 min and then centrifuged at 12 000 g for 30 min to remove excess water. Metals in the sediment (Cd, Cu, Zn and Fe) were partitioned into operationally defined fractions by extracting the sediment sample sequentially according to the methods used by Tessier et al. (1989). These extractions have been developed for natural oxic lake sediments and their application to mine tailings is not straightforward, given the differences in composition between lake sediments and mine tailings. Nevertheless, this sequential fractionation procedure yields results that are roughly indicative of the lability of the metals in the superficial tailings.

The October 1996 results indicated considerable heterogeneity at the surface of Cell 1 (see **RESULTS**). To confirm these results, we undertook an additional sampling campaign in June 1997, during which four additional cores were taken from each experimental cell. These surface

sediments were not subjected to the sequential fractionation procedure, but were simply analyzed for total metal concentrations.

2.6. Quality assurance – Quality control (QA/QC)

To assess analytical accuracy, certified reference materials (CRMs) were run as blind samples during each analytical run. Sources of appropriate CRMs included the National Research Council of Canada (standard riverine water, NRCC SLRS-3; standard sediment NRCC MESS-2) and the U.S. National Institute of Standards and Technology (trace elements in water SRM 1643d). Measured concentrations were verified by standard additions and consistently compared well with the certified values. Analytical precision was monitored by performing replicate analyses, either in the field (pH; [O₂]) or in the central laboratory (major cations; major anions; trace metals). In addition, combined sampling and analytical performance was evaluated according to the principle of "geochemical consistency" (e.g., Pedersen et al., 1993), which requires that variations in concentration profiles of dissolved constituents in closely-spaced aqueous samples should be smooth.

2.7. Statistical analysis

Inter-annual comparisons of the calculated fluxes across the interface in Cell 2 were performed using the t-test for Cl⁻ and SO₄²⁻, between 1997 and 1998, or one-way ANOVA for Cu, among 1996, 1997 and 1998 (Jandel Scientific, Sigmastat Version 2.0, San Rafael, CA). Differences were considered significant at $P < 0.05$. Parametric assumptions of normality and equal variance were first checked with the Kolmogorov-Smirnov test (with Lilliefors's correction) and the Levene median test respectively.

3. RESULTS

3.1. General observations

In the present report, for simplicity, we have emphasized results from the second cell, where the total metal concentrations in the tailings were somewhat lower and the surface layer was more homogenous. However, the results for both Cell 1 and Cell 2 are presented in the tables and figures.

3.2. Electrochemical micro-profiles of pH and DO

The electrochemical micro-profiles show the disappearance of DO within only a few mm of the tailings-water interface (Fig. 1a). The first measurements, carried out in June 1997, revealed a sharp decrease in the DO concentration in the tailings, with anoxic conditions appearing < 5 mm below the tailings-water interface. In contrast, the midday results for August 1998 and June 1999 showed an DO peak just below the interface. This peak disappeared at night, however, and thus we attribute its transitory appearance to the photosynthetic production of DO by a periphyton layer that had established on the surface of the tailings by year 2. This green layer was observable by visual inspection of the interface. Note that even in the presence of this daytime DO production layer, anoxic conditions appeared at very shallow depths within the tailings (<7 mm).

The pH micro-profiles indicate a weak pH decrease below the tailings-overlying water interface (Fig. 1b). In 1997 this decrease developed immediately beneath the interface, but the pH increased sharply below about 5 mm, reaching values close to 8.4 at depths > 10-12 mm. In 1998 and 1999, the pH increased immediately below the interface (0 to 3 mm), and only at greater

depths did the acidic peak become evident. The pH increase just below the interface, coincident with that of DO, is also attributed to the photosynthetic activity of the periphyton layer at the time of sampling, since it was absent at night. The DO and pH micro-profiles indicated that the zone of influence of the established periphyton layer in August 1998 was 3-4 mm. The absence of a subsurface maximum in O₂ and pH at the sampling date in early June 1997 (nine months after the cells were filled) suggests that the photosynthetic activity of the developing periphyton layer was not yet sufficient to affect the O₂ concentration and pH.

3.3. Interstitial water analysis (peepers) – pH, anions, Fe, Mn

One month after the filling of the experimental cells, pH profiles in the overlying and interstitial water showed a marked increase of the pH with increasing depth in the tailings (Fig. 2), reflecting the fact that the tailings had been limed before they were introduced into the cells. The pH decreases observed in 1997 and 1998 with the pH microelectrode also appear in the pH profile obtained by *in situ* dialysis, but with a lower resolution. For both 1997 and 1998, the pH values obtained by dialysis at -0.5 cm are identical and are close to the average pH measured with the microelectrode over the first cm, 7.74 compared to 7.84 respectively. The constant pH at depths > 6 cm is reduced from 9.5 in 1996 to 8.5 in 1998.

In both cells and in all peepers, dissolved inorganic carbon concentrations decreased with depth. In October 1996 concentrations in the overlying water ranged from 0.9 to 1.1 mM, but at depths as shallow as 3 cm concentrations had decreased to about 0.2 mM and remained at this level all the way down to 15 cm; in 1998 the concentrations in the overlying water were somewhat higher (2-2.7 mM, consistent with the slightly higher pH values in 1998), but again they decreased with depth in the tailings. Such profiles suggest that the original pore water present in the tailings was

carbonate-poor (and/or that there is a sink for carbonate at depth), and that the tailings are acting as a sink for carbonates in the overlying water. In contrast, the initial concentrations of both Cl^- and SO_4^{2-} were much higher in the tailings than in the overlying water (Fig. 3), resulting in a diffusion of both anions from the tailings to the overlying water. Comparison of the results for the two full dialysis campaigns reveals that the absolute concentrations of both anions and their concentration gradients were lower in 1998 than in 1996, especially for Cl^- , which has a specific tracer diffusion coefficient about two times higher than SO_4^{2-} (Li and Gregory, 1973). In 1998, the profiles for Cl^- showed no abrupt change of slope around the interface area, which is consistent with the absence of diagenetic reactions involving Cl^- . In contrast, an increase in SO_4^{2-} concentrations appeared in the 1998 profiles, just below the interface.

The *in situ* dialysis results also indicate the development of reducing conditions at depths of 1.5 cm and deeper. Anoxic conditions in the tailings were confirmed by the presence in the interstitial water of SH_2S at depths ≥ -1.5 cm in both 1996 and 1998 (Fig. 4). Peaks for reduced Fe(II) in 1997 and 1998 and Mn (II) in 1998 also appeared at this depth (Fig. 5), likely corresponding to the dissolution of Fe- and Mn-containing carbonates, such as Mg-ankerite, which are present in the tailings material. Reduction of traces of Fe, Mn-oxides or oxyhydroxides might also contribute to these peaks. In 1996, results for Fe and Mn indicate that clearly defined interstitial concentration profiles had not yet developed after the one-month period following the underwater disposal. The apparent peak of Fe and Mn in the overlying water is likely an artifact, reflecting the difficulty inherent in precisely locating the tailings-water interface. Alternatively, the peepers could have shifted upwards sometime during the equilibration period.

3.4. Interstitial water analysis (peepers) – trace metals

Early in the experiment (1996 and 1997 profiles), trace metal concentrations (Cd, Cu, Zn) in the interstitial water close to the interface tended to be lower than in the overlying water (Fig. 6). This trend persisted for Cu in the 1998 profiles, with the exception of some where there was a small Cu peak just above the interface. By 1998, however, most of the Cd and Zn peaks appeared just below the interface at -0.5 cm, indicating some mobilization of these metals and their diffusion toward the overlying water.

3.5. Solid phase analysis

The apparent increase in dissolved metal concentrations just below the tailings-water interface is also associated with modifications in their partitioning in the solid phase of the surficial tailings (Table 1). Results for Cell 1 and Cell 2 are very similar, but as evidenced by the higher standard deviation of the Cell 1 results, the surface layer of this cell is much more heterogeneous than the Cell 2, as previously mentioned. Comparison of the total metal levels in the surface sediments (Figure 7) also reveals this greater heterogeneity in Cell 1. Cell 2 is thus more useful for understanding the evolution of the tailings solid phase from 1996 to 1998, and only the results from Cell 2 tailings are presented below.

The total concentrations of Cu and Cd remained unchanged from 1996 to 1998, but the total concentration of Zn in the surface layer declined slightly over the same period (t-test, $n = 3$ (1996) and $n = 4$ (1998), $P = 0.041$). Copper was extracted mainly with the H_2O_2 oxidation and HF, HNO_3 and $HClO_4$ digestion treatments, 89 % in 1996 and 93 % in 1998. These are the two least labile fractions and represent the metal associated with organic matter, unreactive sulfides and refractory minerals. Among the more labile fractions, Cu extracted at pH 5 by an acetate

buffer (fraction 2) decreased from 1996 to 1998. Over the two-year interval, the proportion of Cd in fractions 5 and 6 decreased, passing from 66 % in 1996 to 25 % in 1998, while Cd concentrations in the other more labile fractions increased - in 1998, 75 % of the Cd was either non-specifically adsorbed or associated with Fe- and Mn-oxyhydroxides (fractions 2, 3 and 4) and 10 % was found in the exchangeable fraction, this being the highest proportion observed for any metal in fraction 1. Zinc also shifted to more labile fractions over the two-year study period but to a lesser extent, passing from 52 % in fractions 5 and 6 in 1996 to 33 % in 1998.

4. DISCUSSION

4.1. DO consumption by the submerged tailings

The shallow water cover (0.3 m) in the experimental cells appears to act effectively to limit the oxidation process. The depth-integrated DO consumption of the tailings calculated from the micro-profiles obtained in June 1997 is $(0.324 \pm 0.005) \times 10^{-2} \text{ nmol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$. This DO consumption is about 2000 times lower than the observed DO consumption of Louvicourt tailings in humidity test cells, $6.5 \text{ nmol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ (Li and St-Arnaud, 2000).

Despite this markedly reduced DO consumption, the DO micro-profiles always showed the complete disappearance of DO in the tailings interstitial water within 5-7 mm of the tailings-water interface (see Figure 1b). In this respect, the tailings are behaving like normal fine-grained lake sediments, where the oxic surface layer is normally <1 cm in thickness (Rasmussen and Jorgensen, 1992; Berg et al. 1998). Clearly tailings lying more than 2 cm below the tailings-water interface are not exposed to DO.

4.2. Alteration of surficial tailings

Contrary to earlier indications in the literature (Pedersen et al., 1991), submerged sulfidic tailings do not appear to be completely inert and weathering does occur close to the overlying water-tailings interface. Oxidation of the tailings is demonstrated by the weak acidic peak observed in the pH micro-profiles just below the tailings surface, by the shoulder in the SO_4^{2-} porewater profiles observed at the same depth, as well as by the mobilization of Cd and Zn (see Section 4.3).

The increase in size of the acidic peak observed between 1996 and 1999, whether in the electrochemical micro-profiles or in the profiles obtained by *in situ* dialysis, is a strong indication of the oxidation process of pyritic material. As indicated by the pH micro-profile in 1999, fluxes of H^+ across the interface will depend on the photosynthetic activity of the periphyton layer: during daytime, tailings will act as a sink for H^+ , whereas at night they will act as a source of H^+ . The pH of the water measured at the outflow from the cells remained constant throughout the ice-free period at a value of about 8 from June 1997 through June 99 (data not shown). Globally tailings effects on the overlying water pH are negligible compared to the buffering capacity of the overlying water and the dilution from input water.

The SO_4^{2-} porewater profiles are also indicative of the oxidation process near the surface of the tailings. We attribute the weak SO_4^{2-} peak below the interface in 1998 to the production of SO_4^{2-} by oxidation of the tailings³. Diagenetic SO_4^{2-} production is also suggested by the calculated

³ Gypsum dissolution might also be contributing to the subsurface maximum in sulfate concentrations. If the rate of production of sulfate through this route were higher than the consumption of sulfate through SO_4^{2-} reduction, a subsurface sulfate maximum would result (T.F. Pedersen, University of British Columbia, personal communication, September 2000).

SO₄²⁻ flux across the interface (Table 2). While the Cl⁻ flux (mol·cm²·s⁻¹) decreased from (- 1.1 ± 0.2) × 10⁻¹³ in 1997 to (- 4.0 ± 0.5) × 10⁻¹⁴ in 1998 (t-test, *n* = 3, *P* = 0.003), the SO₄²⁻ flux (mol·cm²·s⁻¹) remained unchanged, (-7 ± 2) × 10⁻¹³ in 1997 and (-8 ± 3) × 10⁻¹³ (t-test, *n* = 3, *P* = 0.543).

4.3. Trace metal mobilization

Ion Activity Products (IAP) were compared with the solubility products of various Fe and Mn solid phases to identify possible processes that could explain the disappearance of these metals from interstitial waters at depths > 2.5 cm in the tailings. Ion activities were calculated with the computer code HYDRAQL (Papelis et al., 1988) from the 1998 measured concentrations. The concentrations of Ca and Mg were presumed to be depth-independent and the concentrations at -0.5 cm were used at subsequent depths for the purpose of these calculations. The original HYDRAQL thermodynamic database was updated as in Huerta-Diaz et al. (1998) and the program was modified to replace S⁻² by HS⁻. At -3.5 cm and -4.5 cm, the IAP calculations suggest that Fe was precipitating as the sulfide greigite, which is also the case for several natural lake sediments (Emerson et al., 1983; Huerta-Diaz et al., 1998). However, pore water appears strongly under-saturated with respect to Mn sulfide or carbonate. As suggested by Huerta-Diaz et al. (1998) for two Canadian Shield lakes, the adsorption of Mn to FeS(s) and the co-precipitation of Mn with FeS(s) could be responsible for the observed trapping of dissolved Mn below 2.5 cm in the tailings, rather than the precipitation of distinct Mn sulfide or carbonate solid phases.

Similar IAP calculations for Cu, Cd and Zn demonstrated that the interstitial waters at -1.5 cm were over-saturated with respect to the relevant sulfide solid phases (covellite for Cu, amorphous sulfides for Cd and Zn) - cf. Huerta-Diaz et al. (1998). This over-saturation suggests that the

interstitial waters were not in equilibrium with solid sulfide phases at this depth and/or that these metals were complexed in solution by ligands not considered in the thermodynamic calculation, such as polysulfides, organic thiols or other dissolved organic molecules.

In 1998, the Cd and Zn concentration profiles clearly indicate a mobilization of these metal from the tailings to the overlying water. However the interpretation of the dissolved metal profiles is difficult because of the 1 cm resolution of the peepers and their possible vertical displacement during deployment. The electrochemical micro-profiles demonstrate clearly that diagenetic reactions at the tailings-water interface are occurring at the mm scale, i.e. well below the scale sampled by the porewater peepers. Therefore the values obtained with the peepers are means over 1 cm intervals; sharp dissolved metal peaks and steep metal concentration gradients would be undetectable because of this dilution effect. However, despite these resolution limitations, the Cd and Zn fluxes in 1998 were undoubtedly from the tailings to the overlying water. Concomitant with this mobilization of Cd and Zn to the overlying water, there was a change in solid phase distribution of both these metals, from refractory fractions to more labile fractions.

In contrast, Cu appears to diffuse from the overlying water into the tailings and the magnitude of the Cu flux was unchanged from 1996 to 1998 (one-way ANOVA, $n = 3$ (1996 and 1997) and $n = 4$ (1998), $P = 0.69$). We considered the possibility that oxidation kinetics for Cu sulfides might differ from those for Cd and Zn sulfides, but could not find convincing evidence in the literature to support this explanation for the apparent differences in porewater metal profiles. For example, Simpson et al. (1998) found no significant differences in the oxidation kinetics of Cd, Zn and Cu sulfides during short-term sediment resuspension events. Given the poor resolution of the *in situ* dialysis, we cannot completely rule out the possibility that Cu is mobilized from the tailings (e.g.,

from the uppermost tailings layer). However, it appears unlikely that the near-interface cells in the peepers would have consistently missed the subsurface maximum in Cu concentration in every peeper deployment, and thus we conclude that there is no evidence for copper mobilization.

Pedersen et al. (1993) concluded that Cu and Zn in Anderson Lake and Cd, Cu and Zn in Buttle Lake (Pedersen, 1983 ; Pedersen et al., 1991) were not diffusing out of the submerged tailings. Their conclusions contrast with our 1998 results, which indicate fluxes of Cd and Zn from the tailings. The discrepancy might reflect problems with their flux calculations, since their concentrations in the overlying water were not determined at the same time as their porewater measurements. Note too, that metal concentrations in the lake water columns were higher than in the experimental cells. Both their lakes were affected by acid mine drainage so that the overlying water metal concentrations were higher than in the present study; for Buttle Lake, Pedersen (1983) reported bottom water concentrations of 2.6 μM for Zn, 9.9 nM for Cd and 173 nM for Cu, and up to 6.6 μM for Zn and 690 nM for Cu in the case of Anderson Lake (Pedersen et al. 1993).

It should be pointed out that the observed Cd and Zn releases from the submerged tailings are very small and that the shallow water cover effectively reduced metal releases from the reactive tailings. To calculate the impact of the Cd and Zn releases on a hypothetical disposal operation, we assume that the impoundment has a dimension of 1 km x 1.5 km with an average depth of 1 m, giving an overlying water volume of 1.5×10^9 L. We also assume that the average water residence time in the main impoundment will be 1 year and that the fluxes of Zn and Cd to the overlying water are the highest observed, 1.5×10^{-7} $\text{nmol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ for Zn and 1×10^{-9} $\text{nmol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ for Cd (Table 2). For the surface of this impoundment these fluxes give a release of

71 moles of Zn per year and 0.47 mole of Cd per year. Using the average residence time of 1 year and the impoundment water volume, these releases would increase the overlying water Zn concentration by 47 nM (3 ppb) and the Cd concentration by 0.31 nM (0.04 ppb). Therefore, Cd and Zn fluxes from the tailings to the overlying water will have only minor impacts on the overlying water quality.

5. CONCLUSIONS

- A shallow water cover (0.3 m) proved effective in reducing the rate of mine tailings oxidation. DO penetration into the tailings was very shallow (< 7 mm) and DO consumption was about 2000 times lower than in tailings samples exposed to air in humidity test cells.
- Progressive oxidation of tailings does occur, however, beneath the interface with the overlying water. Evidence for this oxidation comes from the increase in interstitial water acidity and from indications of SO_4^{2-} production just below the interface.
- Tailings are a source of Cl^- and SO_4^{2-} to the overlying water, and concentrations of these anions decreased at depth in the tailings over the two-year study.
- The electrochemical micro-profiles have shown that the oxidation occurs at the mm scale beneath the tailings-overlying water interface. Two years after tailings disposal under water, there was clear evidence for Cd and Zn mobilization from the tailings to the overlying water with concomitant changes in the solid-phase partitioning of these two metals (refractory \rightarrow more labile fractions). There was no evidence of Cu mobilization from tailings to the overlying water.
- Finally, the 1996-1998 geochemical evolution of Cells 1 and 2 is similar, except that the surface tailings layer of Cell 1 has a higher metal content (particularly Zn) and is more heterogeneous.

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7. REFERENCES

- Berg P., Risgaard-Petersen N. and Rysgaard S. (1998) Interpretation of measured concentration profiles in sediment pore water. *Limnol. Oceanogr.* **43**, 1500-1510.
- Broecker W.S. and Peng T.H. (1974) Gas exchange rates between air and sea. *Tellus* **26**, 21-34.
- Carignan R., Rapin F. and Tessier A. (1985) Sediment porewater sampling for metal analysis. *Geochim. Cosmochim. Acta* **49**, 2493-2497.
- Carignan R., St-Pierre S. and Gachter R. (1994) Use of diffusion samplers in oligotrophic lake sediments: Effects of free oxygen in sampler material. *Limnol. Oceanogr.* **39**, 468-474.
- Cline, J.D. (1969) Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnol. Oceanogr.* **14**, 454-458.
- Emerson S., Jacobs L. and Tebo B. (1983) The behavior of trace metals in marine anoxic waters: Solubilities at the oxygen-hydrogen sulfide interface. In *Trace Metals in Sea Water*,

- Wong C.S., Boyle E., Bruland K.W., Burton J.D. and Goldberg E.D. (Eds), Plenum Press, New York, NY, pp. 579-608.
- Evangelou V.P. and Zhang Y.L. (1995) A review: Pyrite oxidation mechanisms and acid mine drainage prevention. *Crit. Rev. Environ. Sci. Technol.* **25**, 141-199.
- Filion M.P., Sirois L.L. and Ferguson K. (1990) Acid mine drainage research in Canada. *CIM Bull.* **83** (944), 33-40.
- Geller W., Kapper H. and Salomons W. (1998) Acidic Mine Lakes: Acid Mine Drainage, Limnology and Reclamation, 418 pp., Springer-Verlag. New York, NY.
- Huerta-Diaz M.A., Tessier A. and Carignan R. (1998) Geochemistry of trace metals associated with reduced sulfur in freshwater sediments. *Appl. Geochem.* **13**, 213-233.
- Kleinmann R.L.P., and Crerar D.A. (1979) *Thiobacillus ferroxidans* and the formation of acidity in simulated coal mine environments. *Geomicrobiol. J.* **1**, 373-388.
- Li M., and St-Arnaud L. (2000) Reactivity assessment and subaqueous oxidation rate modelling for Louvicourt tailings - Final Report. MEND Report No. 2.12.1.d, Natural Resources Canada. CANMET. Mine Environment Neutral Drainage Program. Ottawa, ON, Canada.
- Li Y.-H. and Gregory S. (1974) Diffusion of ions in sea water and in deep-sea sediments. *Geochim. Cosmochim. Acta* **38**, 703-714.
- Papelis C., Hayes K.F. and Leckie J.O. (1988) HYDRAQL : A program for the computation of chemical equilibrium composition of aqueous batch systems including surface complexation modeling of ion adsorption at oxide/solution interface. Tech. Rep., Dept. Civil Eng., Stanford University, Stanford, CA.
- Pedersen T.F. (1983) Dissolved heavy metals in a lacustrine mine tailings deposit - Buttle Lake, British Columbia. *Mar. Pollut. Bull.* **14**, 249-254.

- Pedersen T.F. and Losher A.J. (1988) Diagenetic Processes in Aquatic Mine tailings deposits in British Columbia. *In: Salomons W. and Forstner U., Eds. Chemistry and Biology of Solid Waste - Dredged Material and Mine Tailings.* New-York: Springer-Verlag. pp. 238-258.
- Pedersen T.F., Mueller B., McNee J.J. and Pelletier C.A. (1993) The early diagenesis of submerged sulfide-rich mine tailings in Anderson lake, Manitoba. *Can. J. Earth Sci.* **30**, 1099-1109.
- Pedersen T.F., Mueller B., Pelletier C.A. (1991) On the reactivity of submerged mine tailings in fjord and lake in British Columbia. *In: Gadsby J.W. and Malick J.A., Eds. Acid Mine Drainage: Designing for Closure.* Vancouver: Bi Tech Publishers. pp. 281-293.
- Rasmussen, H. and Jorgensen, B.B. (1992) Microelectrode studies of seasonal oxygen uptake in a coastal sediment: role of molecular diffusion. *Mar. Ecol. Prog. Ser.* **81**, 289-303.
- Simpson S.L., Apte, S.C. and Batley, G.E. (1998) Effect of short-term resuspension events on trace metal speciation in polluted anoxic sediments. *Environ. Sci. Technol.* **32**, 620-625.
- Tessier A., Carignan R., Dubreuil B. and Rapin F. (1989) Partitioning of zinc between the water column and the oxic sediments in lakes. *Geochim. Cosmochim. Acta* **53**, 1511-1522.
- Zhang H. and Davison W. (1995) Performance characteristics of diffusion gradients in thin films for the *in situ* measurement of trace metals in solution. *Anal. Chem.* **67**, 3391-3400.

Table 1. Sequential extraction of metals from surface tailings with (1) MgCl₂, (2) acetate buffer at pH 5, (3) NH₂OH·HCl at room temperature, (4) NH₂OH·HCl at 96 °C, (5) H₂O₂ and (6) HF, HNO₃ and HClO₄. Value are mean ± SD, n = 3 (1996) and n = 4 (1998). The 1998 Cd analyses in fractions 5 and 6 were made by ETAAS (in fraction 5 of Cell 1, only 1 out of 4 replicates).

Fraction	Cell 1: Solid-phase concentrations of metal (mg · kg ⁻¹)					
	Cu		Cd		Zn	
	1996	1998	1996	1998	1996	1998
1	0.8 ± 0.1	5 ± 1	0.6 ± 0.3	3 ± 2	8 ± 4	88 ± 55
(%)	(0.05)	(0.3)	(2)	(12)	(0.1)	(1)
2	175 ± 34	21 ± 4	2 ± 1	6 ± 3	670 ± 317	1859 ± 857
(%)	(11)	(1)	(7)	(23)	(9)	(28)
3	0.6 ± 0.3	86 ± 75	0.16 ± 0.09	1.4 ± 0.3	1073 ± 460	374 ± 99
(%)	(0.04)	(5)	(0.5)	(5)	(14)	(6)
4	< 0.08	8 ± 5	2 ± 1	2.8 ± 0.9	585 ± 294	1037 ± 419
(%)		(0.5)	(5)	(11)	(8)	(16)
5	1055 ± 194	1353 ± 310	16 ± 14	11 ± 12	3794 ± 3456	2872 ± 2854
(%)	(66)	(85)	(45)	(45)	(50)	(43)
6	377 ± 277	50 ± 7	14 ± 16	0.9 ± 0.7	1432 ± 1078	411 ± 200
(%)	(23)	(10)	(41)	(3)	(19)	(6)
Total	1609 ± 482	1586 ± 274	34 ± 32	25 ± 17	7562 ± 5295	6640 ± 4360

Table 1. (cont.) Sequential extraction of metals from surface tailings with (1) MgCl₂, (2) acetate buffer at pH 5, (3) NH₂OH·HCl at room temperature, (4) NH₂OH·HCl at 96 °C, (5) H₂O₂ and (6) HF, HNO₃ and HClO₄. Value are mean ± SD, n = 3 (1996) and n = 4 (1998). The 1998 Cd analyses in fractions 5 and 6 were made by ETAAS (in fraction 5 of Cell 1, only 1 out of 4 replicates).

Fraction	Cell 2: Solid-phase concentrations of metal (mg · kg ⁻¹)					
	Cu		Cd		Zn	
	1996	1998	1996	1998	1996	1998
1	0.7 ± 0.1	4 ± 2	0.36 ± 0.08	0.7 ± 0.1	3.5 ± 0.7	11 ± 6
(%)	(0.06)	(0.4)	(4.6)	(10)	(0.1)	(0.5)
2	118 ± 15	12 ± 3	1.3 ± 0.2	2.4 ± 0.7	398 ± 58	658 ± 184
(%)	(11)	(1)	(17)	(33)	(14)	(30)
3	0.5 ± 0.2	54 ± 40	0.09 ± 0.01	0.7 ± 0.2	655 ± 85	174 ± 69
(%)	(0.05)	(5)	(1)	(10)	(22)	(8)
4	< 0.08	8 ± 2	0.9 ± 0.1	1.6 ± 0.4	370 ± 45	611 ± 173
(%)		(0.7)	(11)	(22)	(13)	(28)
5	798 ± 98	905 ± 17	4.5 ± 0.9	1.6 ± 0.3	1073 ± 199	372 ± 38
(%)	(71)	(83)	(57)	(22)	(37)	(17)
6	204 ± 33	111 ± 32	0.7 ± 0.2	0.25 ± 0.07	432 ± 66	359 ± 45
(%)	(18)	(10)	(9)	(3)	(15)	(16)
Total	1112 ± 81	1094 ± 42	8 ± 1	7 ± 1	2932 ± 384	2185 ± 339

Table 2. Calculated diffusive flux of ions across the tailings – overlying water interface in Cell 2. Positive fluxes indicate ions, which diffuse from the overlying water into the tailings, whereas negative fluxes correspond to diffusion out of the tailings into the overlying water. Value are mean \pm SD, n = 3 (1996 and 1997) and n = 4 (1998).

Ion	Diffusive Flux ($\text{mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$)		
	Oct. 1996	June 1997	Aug. 1998
Cl^-	**	$(-1.1 \pm 0.2) \times 10^{-13}$	$(-4.0 \pm 0.5) \times 10^{-14}$
SO_4^{2-}	$(-4 \pm 2) \times 10^{-13}$	$(-7 \pm 2) \times 10^{-13}$	$(-8 \pm 3) \times 10^{-13}$
Cu^{2+}	$(1.2 \pm 0.7) \times 10^{-16}$	$(1.2 \pm 0.7) \times 10^{-16}$	$(9 \pm 5) \times 10^{-17}$
Cd^{2+}	$(9 \pm 7) \times 10^{-18}$	$(5 \pm 1) \times 10^{-18}$	$(-4 \pm 2) \times 10^{-18} *$
Zn^{2+}	**	$(9 \pm 4) \times 10^{-16}$	$(-6 \pm 2) \times 10^{-16} *$

* One of 4 replicate omitted in the calculation, the maximum concentration being in the overlying water instead of in the tailings, suggesting displacement of the peepers during the equilibration period or an error in fixing the position of the tailings – water interface.

** Diffusive fluxes were not calculated when the concentration gradient was not clearly defined.

Figure 1. Typical porewater DO concentrations (a) and pH (b) profiles measured with microelectrodes inserted in the tailings (1 mm vertical resolution). The horizontal broken line indicates the tailings – overlying water interface. Each curve is from one insertion of the micro electrode in the tailings using a micromanipulator deployed from a sampling platform at the center of the experimental cell.

(a): DO

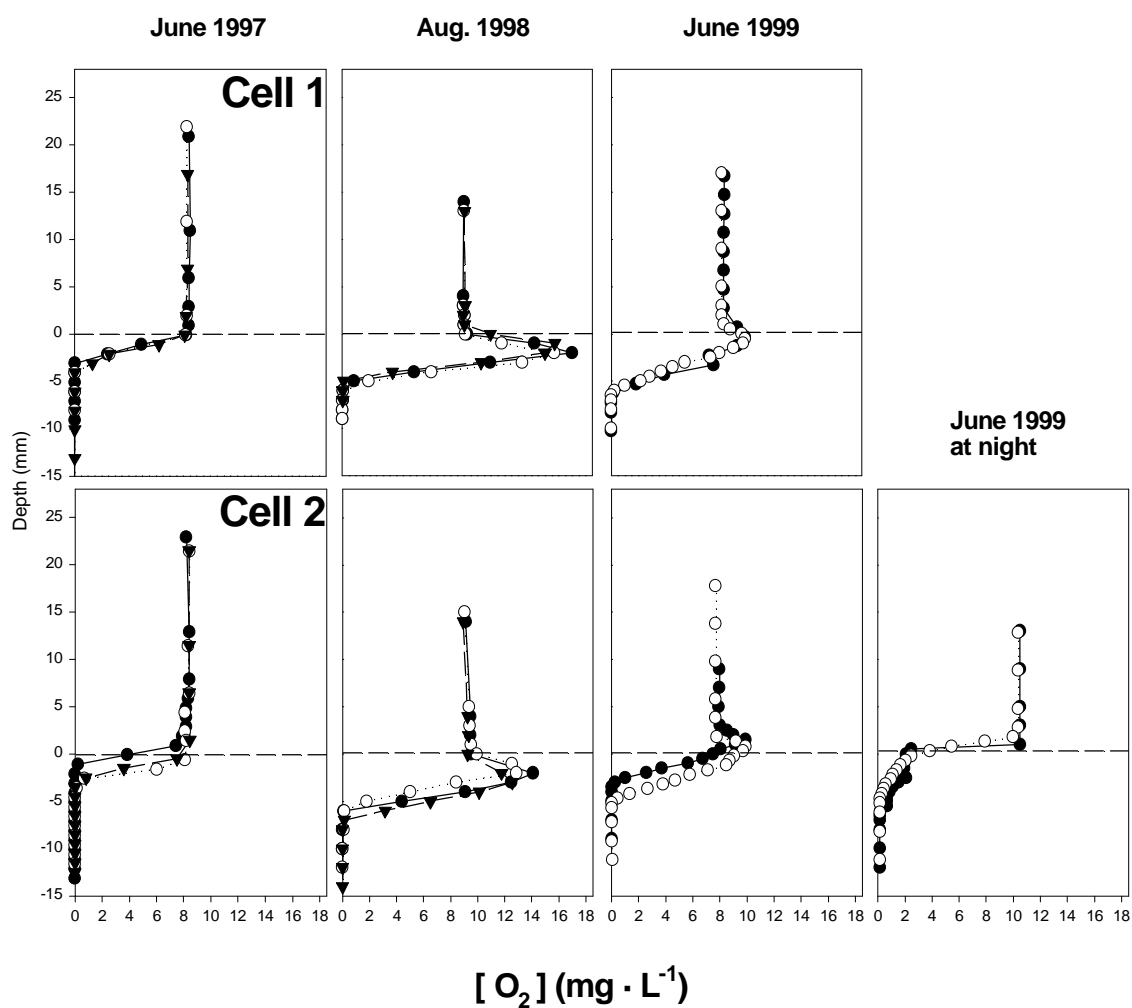


Figure 1 (continued)

(b): pH

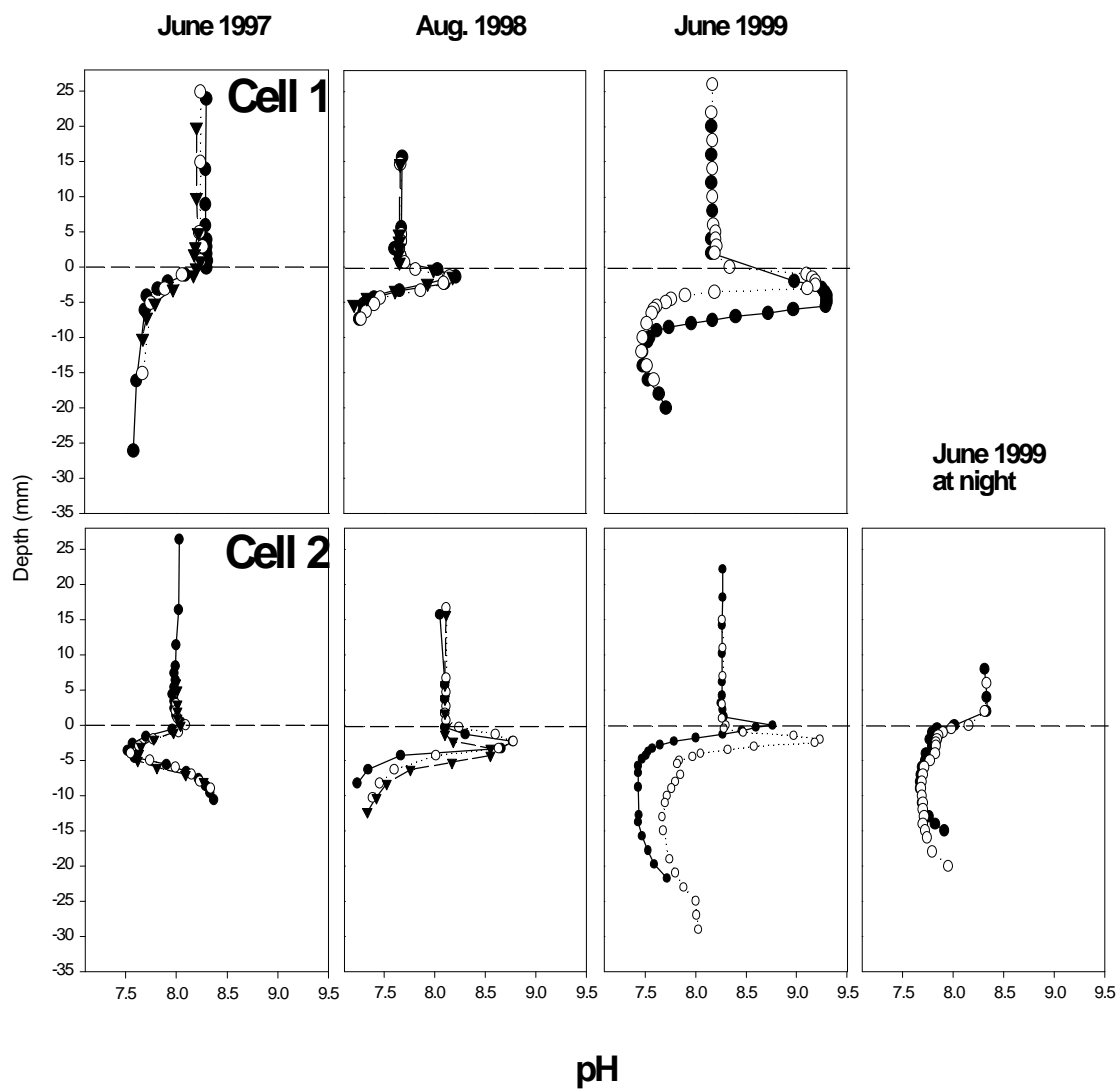


Figure 2. Porewater pH profiles sampled by *in situ* dialysis (1 cm vertical resolution). The horizontal broken line indicates the tailings – overlying water interface. Each curve is from an individual peeper inserted into the tailings in the experimental cell, $n = 3$ (1996 and 1997) and $n = 4$ (1998).

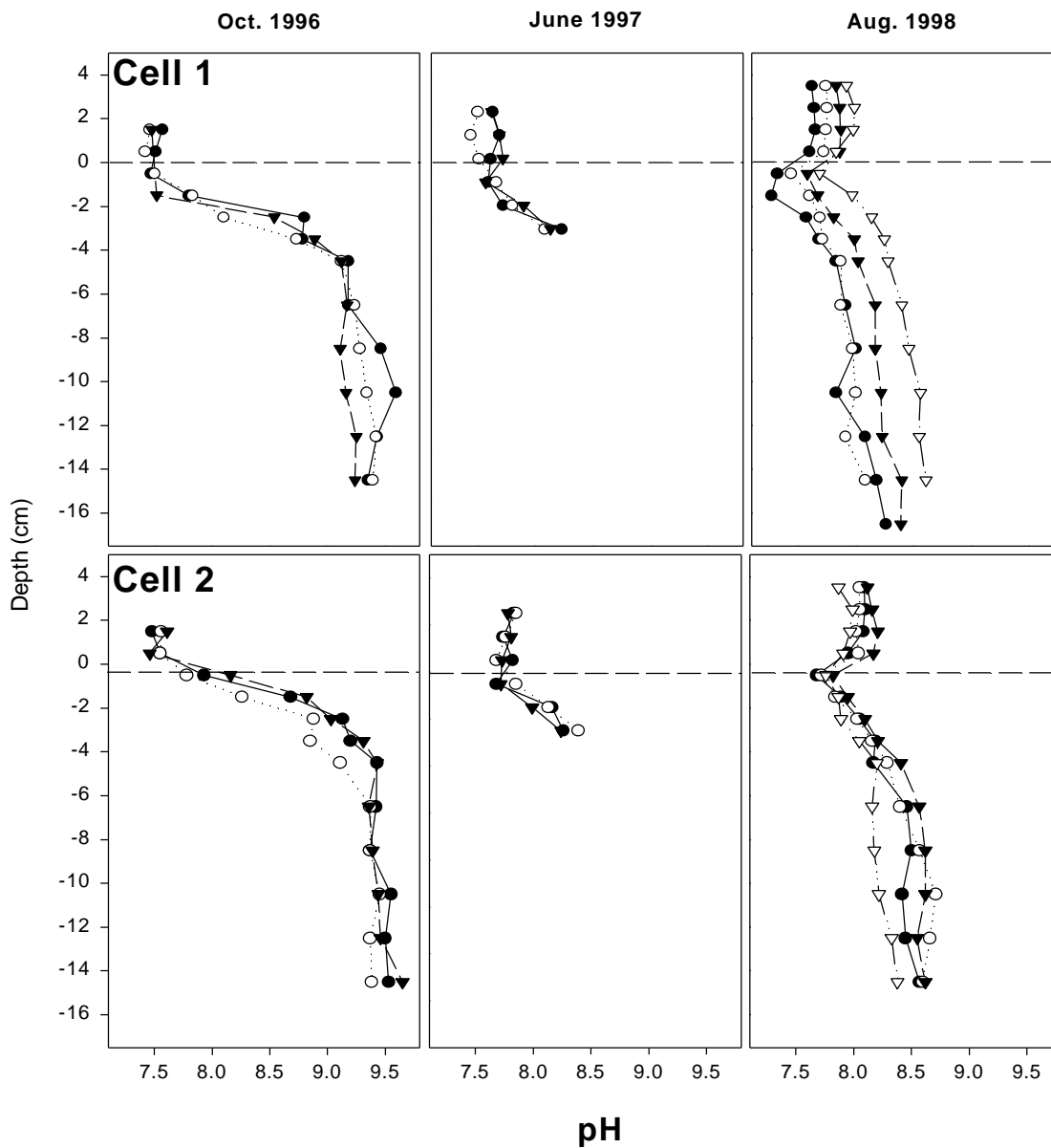


Figure 3. Porewater concentration profiles for (a) Cl^- (b) SO_4^{2-} and (c) CO_3^{2-} as sampled by *in situ* dialysis (1 cm vertical resolution). The horizontal broken line indicates the tailings – overlying water interface. Each curve is from an individual peeper inserted into the tailings in the experimental cell, $n = 3$ (1996 and 1997) and $n = 4$ (1998).

(a): Cl^-

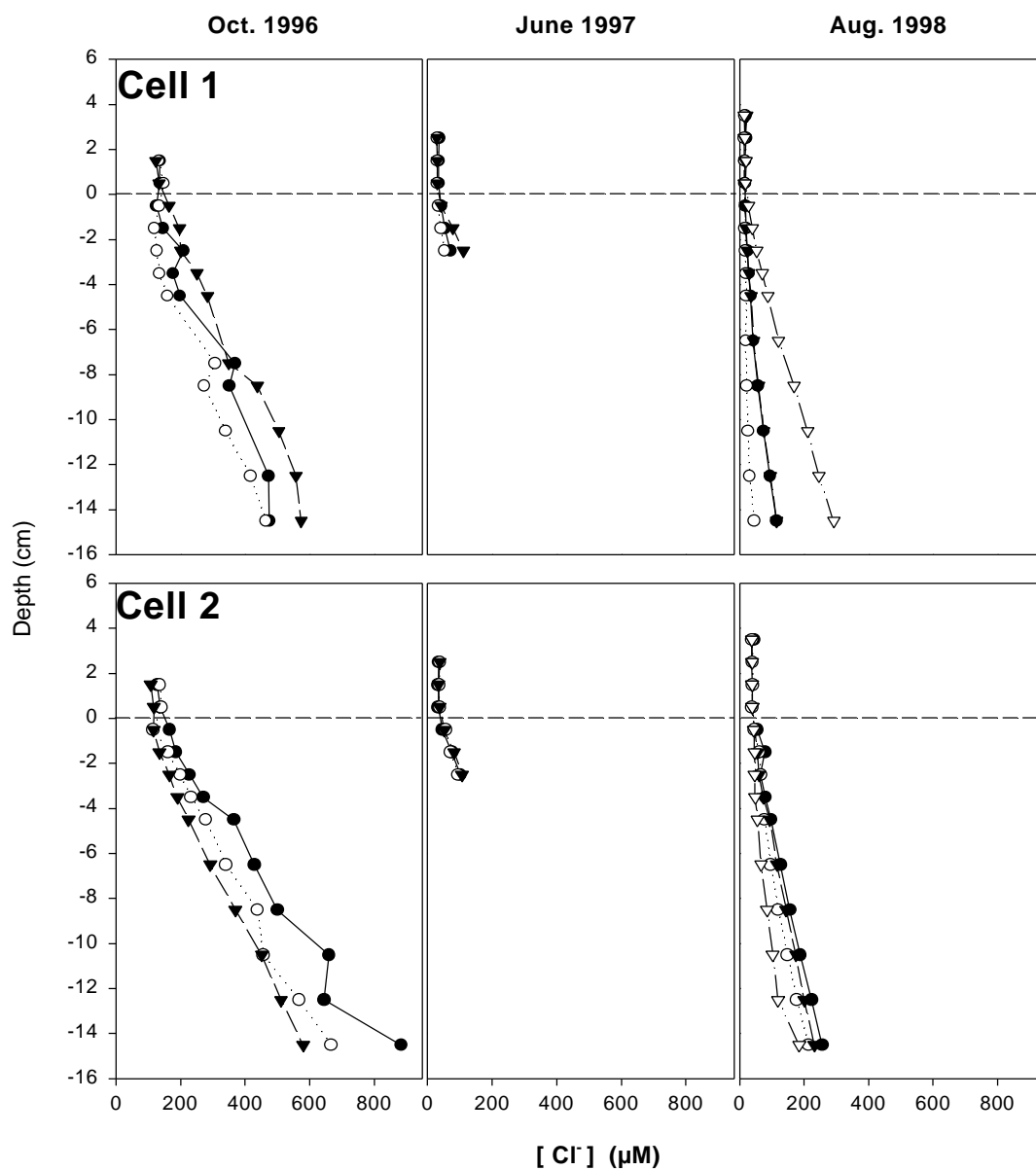


Figure 3 (continued)

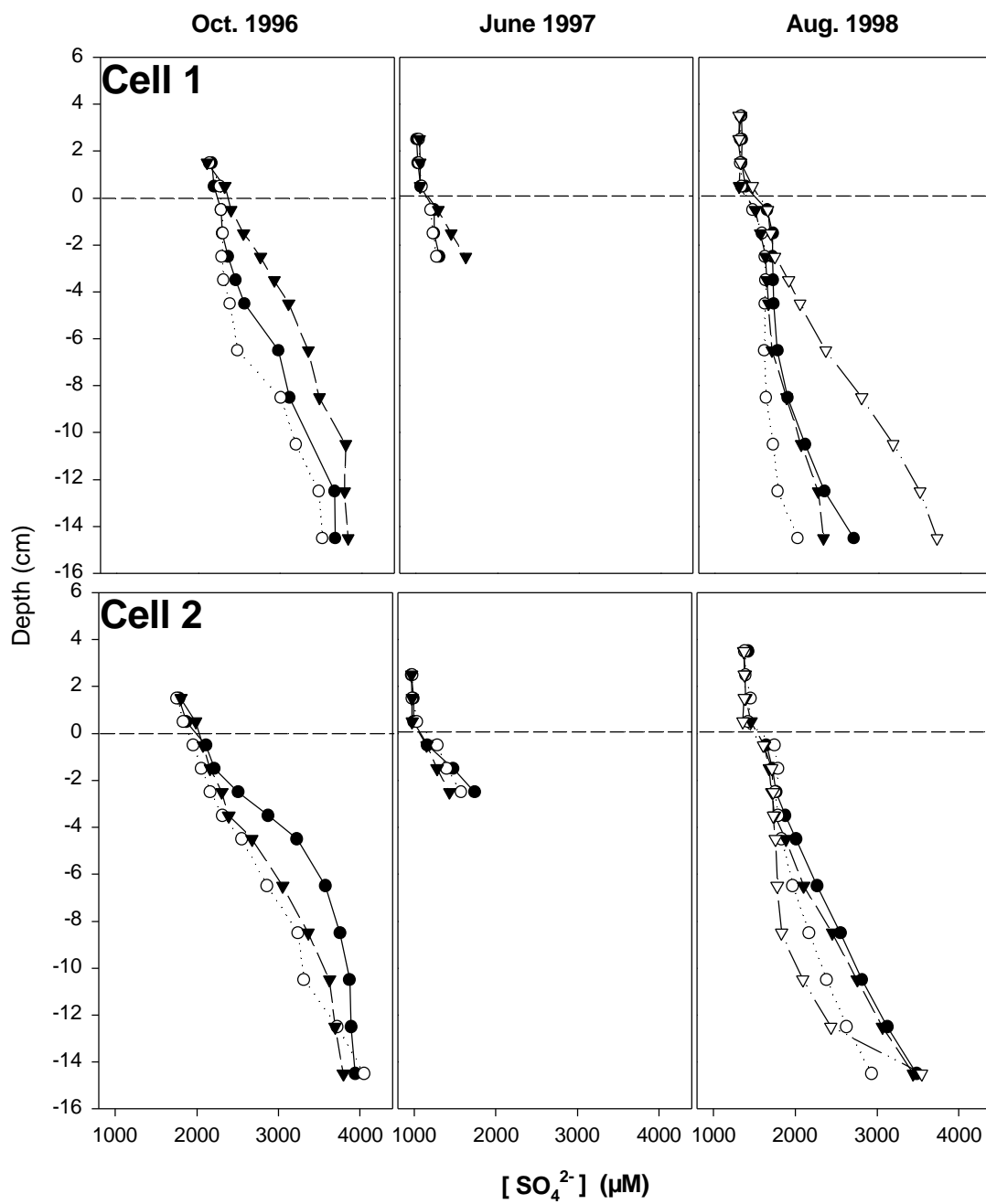
(b): SO₄

Figure 3 (continued)

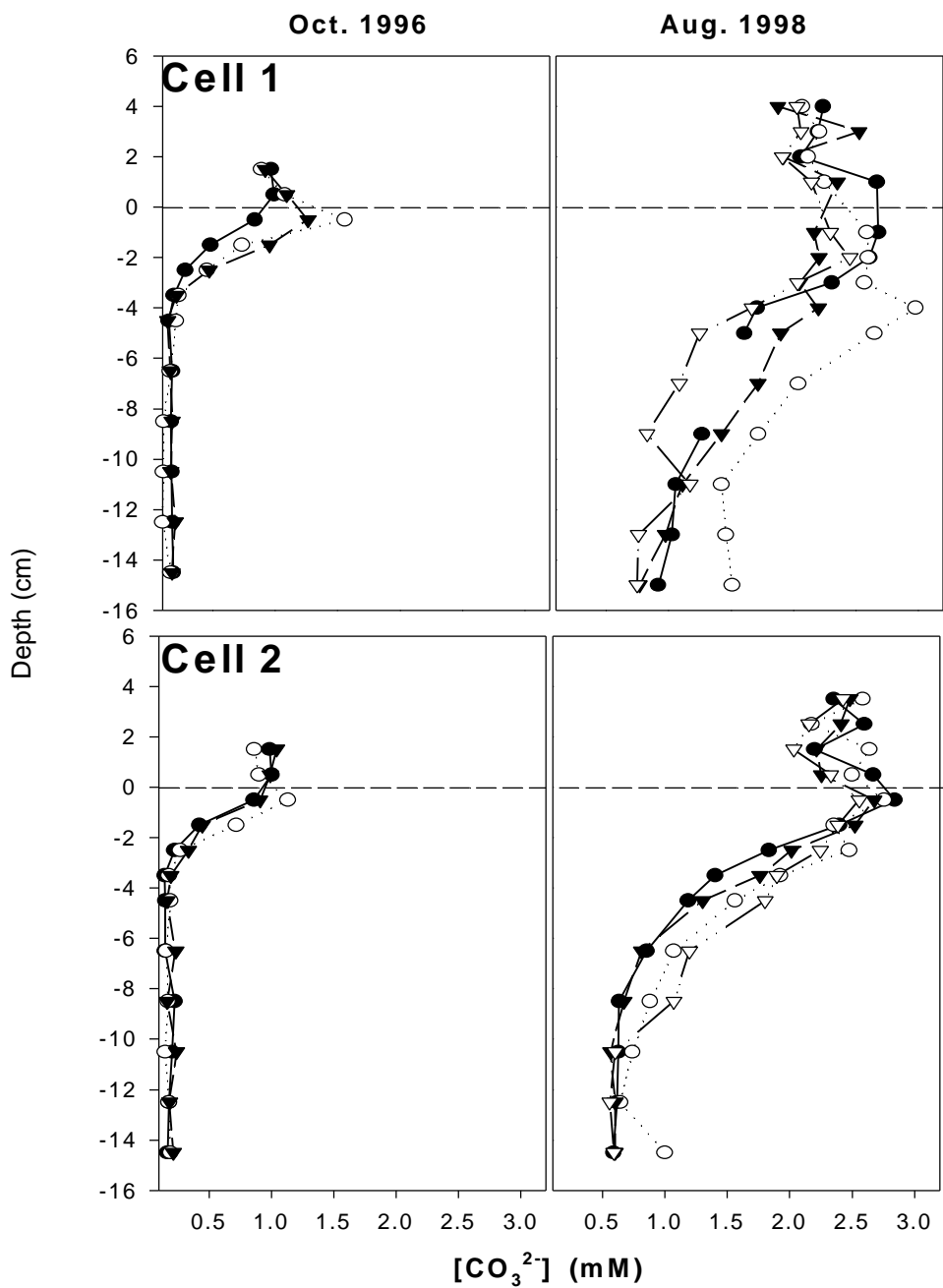
(c): CO_3 

Figure 4. Porewater SH_2S concentrations profiles sampled by *in situ* dialysis (1 cm vertical resolution, detection limit = 0.004 μM). The horizontal broken line indicates the tailings – overlying water interface. Each curve is from an individual peeper inserted into the tailings in the experimental cell, $n = 3$ (1996 and 1997) and $n = 4$ (1998).

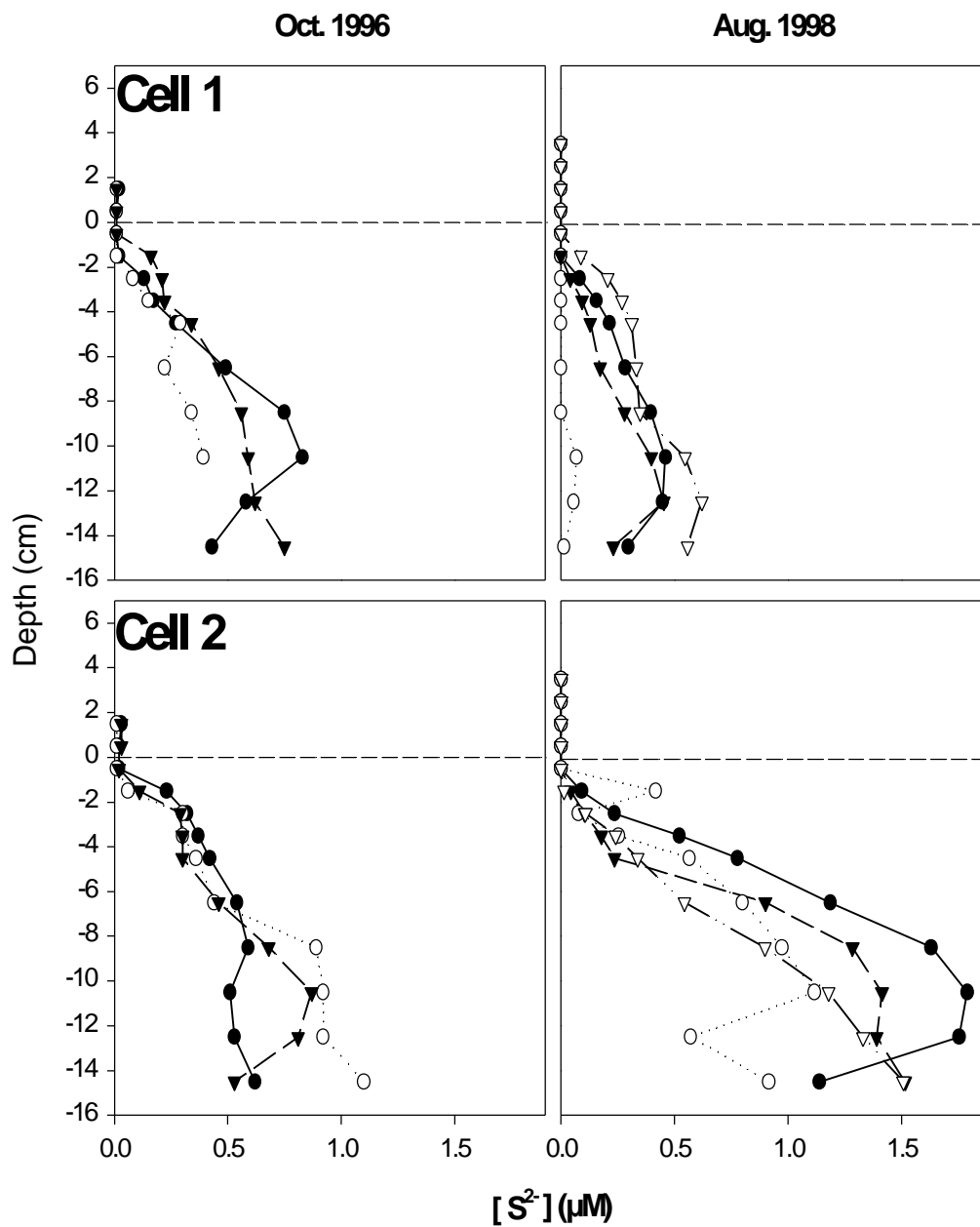


Figure 5. Porewater dissolved iron (a) and dissolved manganese (b) concentrations profiles sampled by *in situ* dialysis (1 cm vertical resolution, detection limits = 0.2 μM and 0.05 μM for Fe and Mn respectively). The horizontal broken line indicates the tailings – overlying water interface. Each curve is from an individual peeper inserted into the tailings in the experimental cell, $n = 3$ (1996 and 1997) and $n = 4$ (1998). In 1998, one aberrant data point for both Fe and Mn, presumably resulting from contamination, was not included in their respective profiles.

(a): Fe

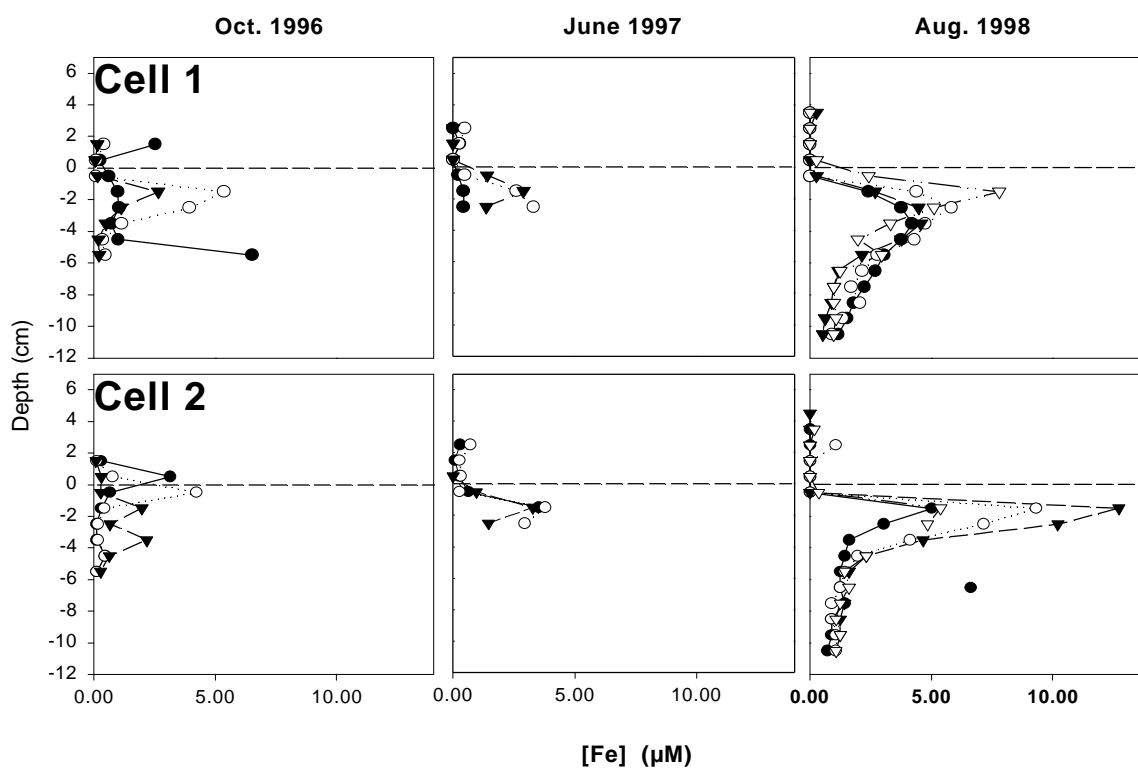


Figure 5 (continued)

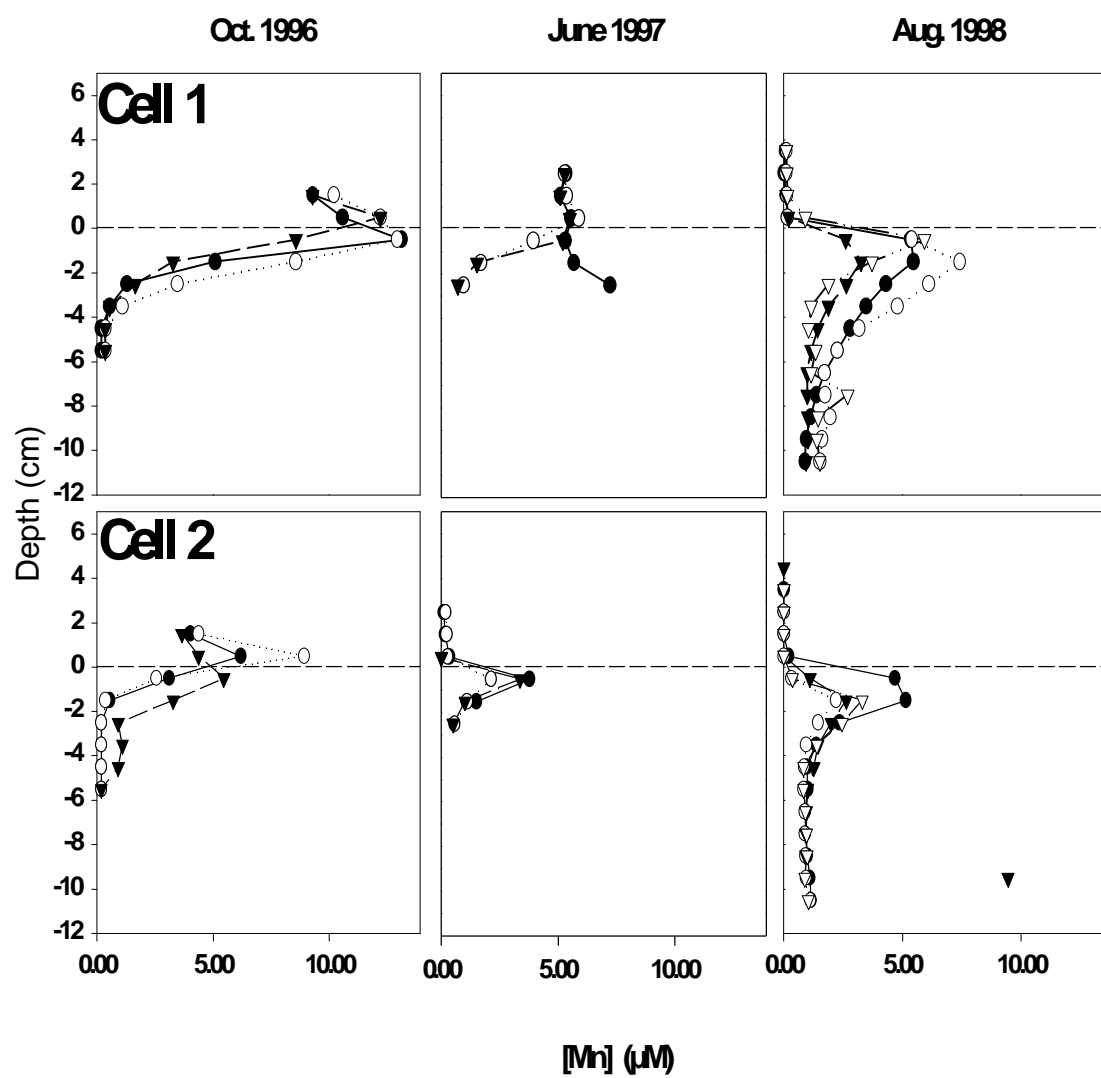
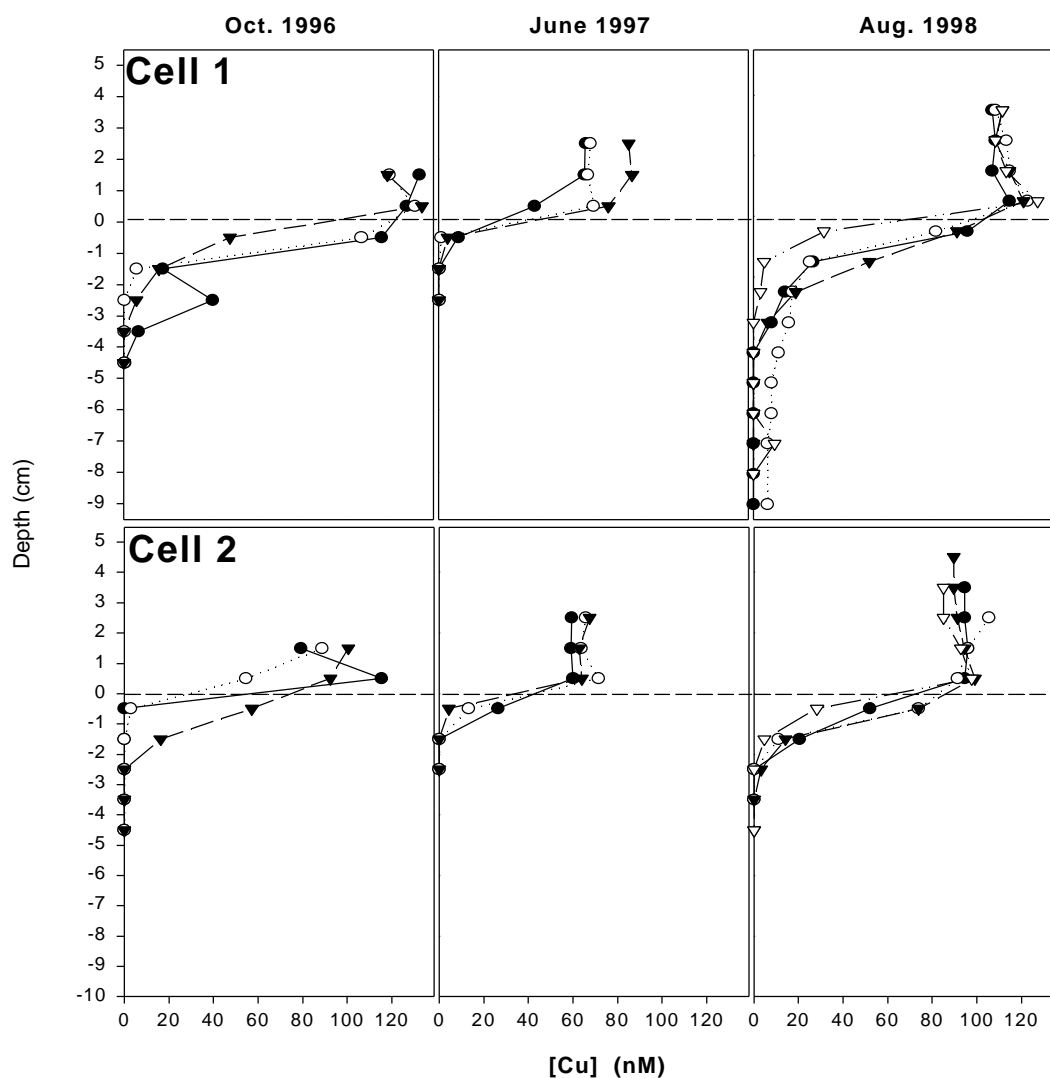
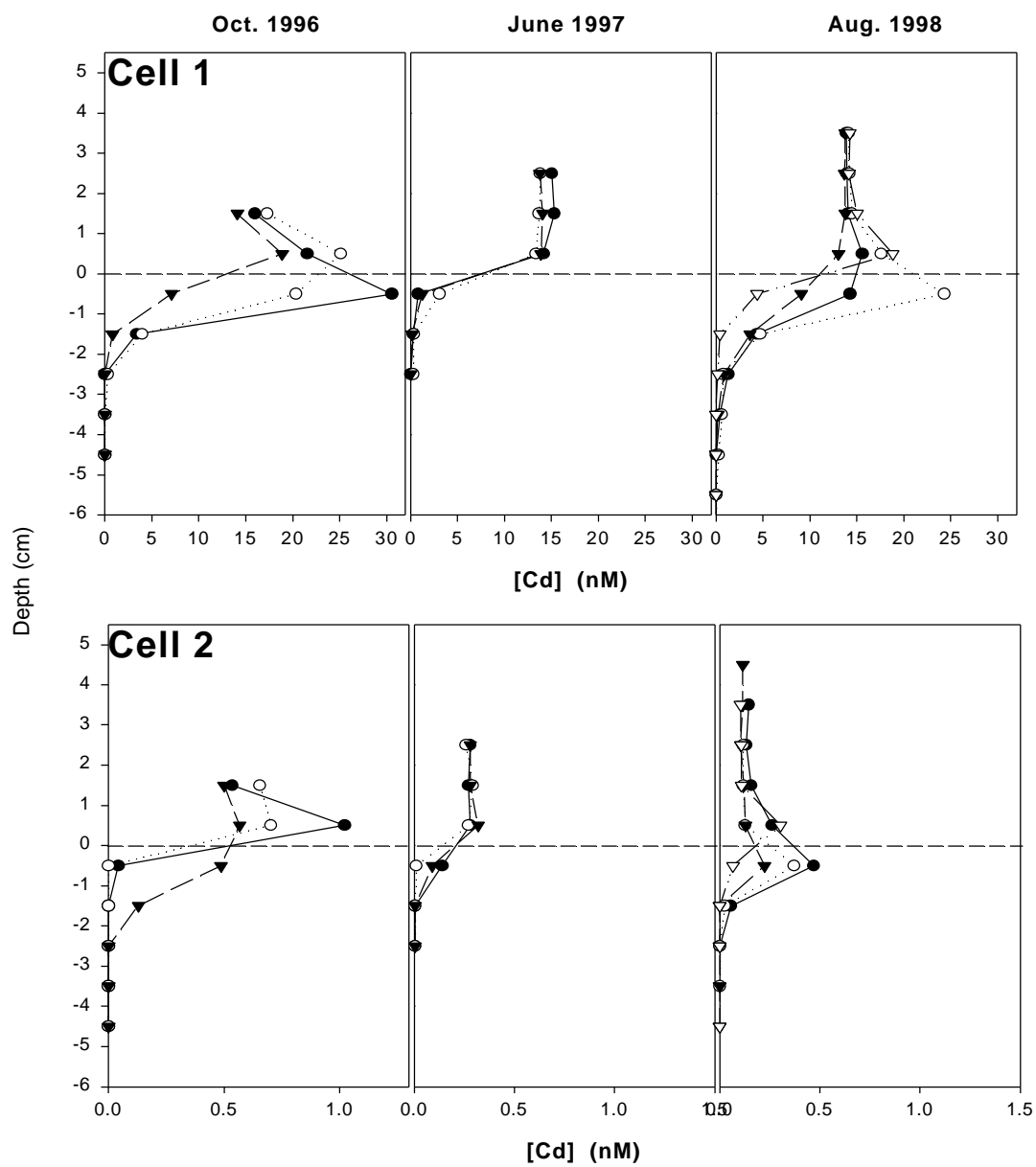
(b): Mn

Figure 6. Porewater dissolved copper (a) dissolved cadmium (b) and dissolved zinc (c) concentrations profiles sampled by *in situ* dialysis (1 cm vertical resolution, detection limits = 3 nM, 0.1 nM and 0.08 μ M for Cu, Cd and Zn respectively). The horizontal broken line indicates the tailings – overlying water interface. Each curve is from an individual peeper inserted into the tailings in the experimental cell, n = 3 (1996 and 1997) and n = 4 (1998).

(a): Cu



(b): Cd

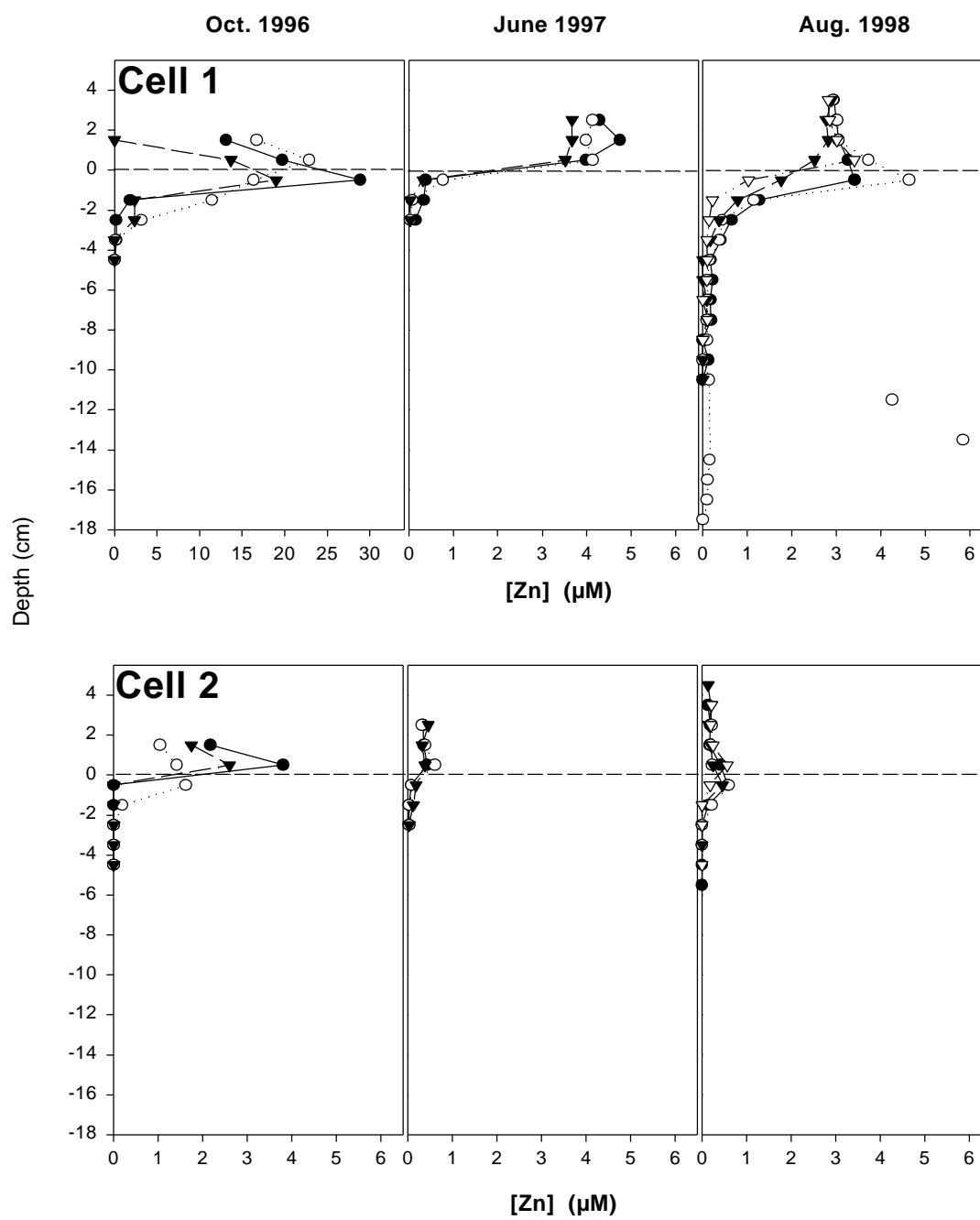
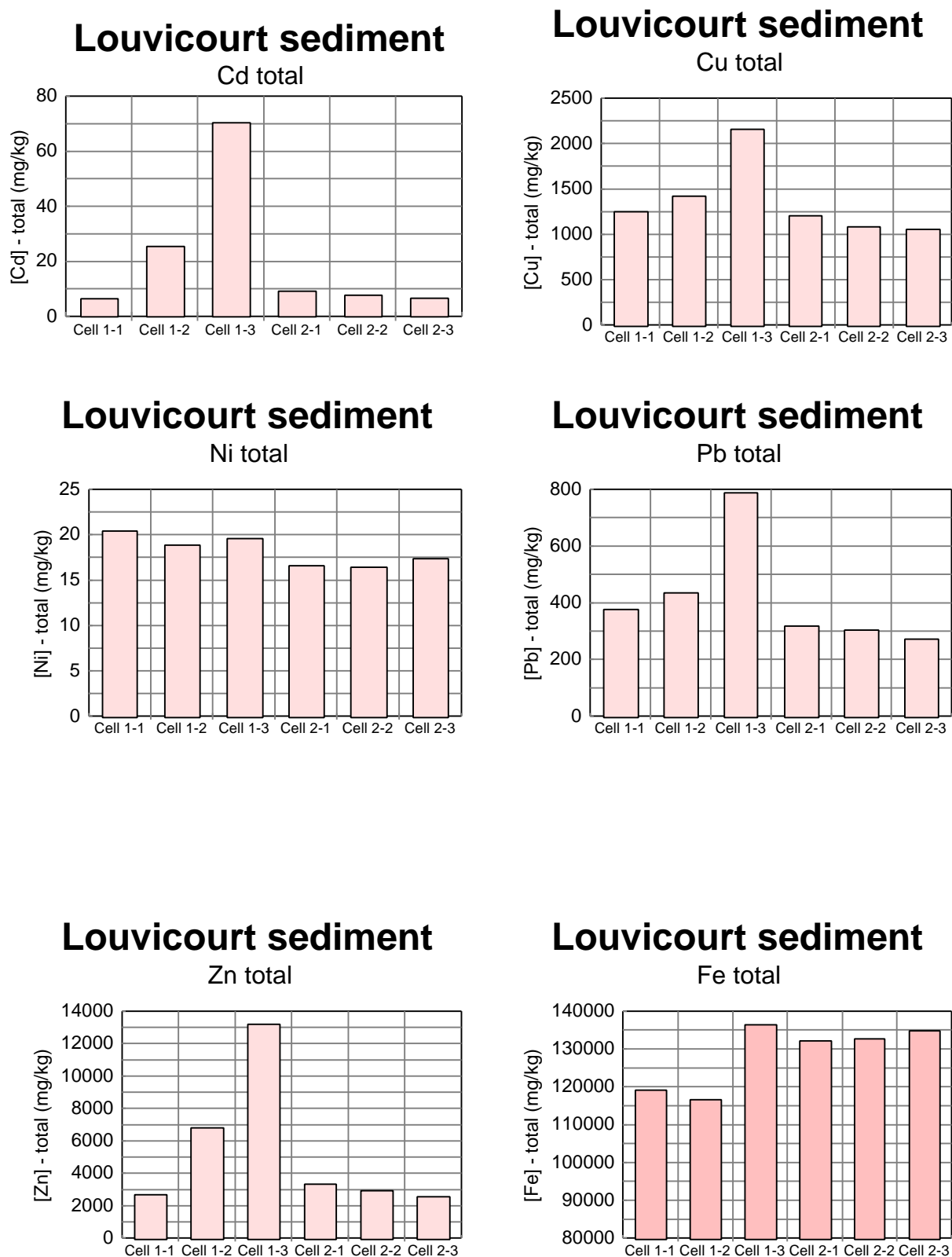
(c): Zn

Figure 7. Total metal concentrations (Cd, Cu, Ni, Pb, Zn, Fe) in surface layer of tailings in Cells 1 and 2. (a) October 1996 sampling; (b) June 1997 sampling. Note heterogeneity for Cd, Cu, Pb and Zn in Cell 1.

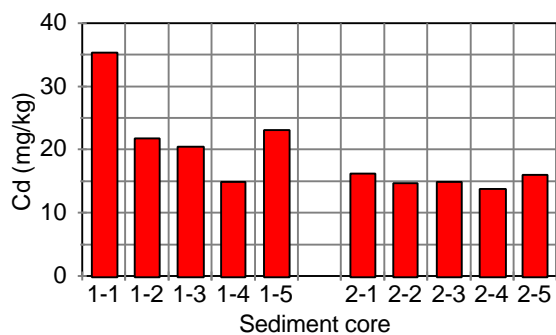
(a):



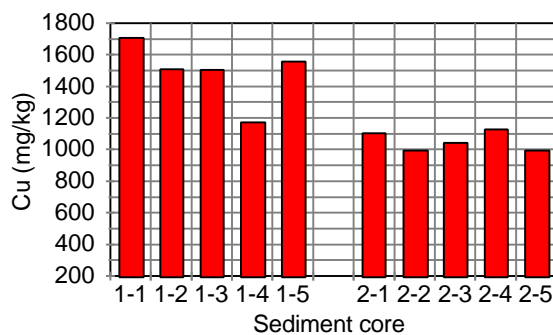
(b):

Louvicourt sediment

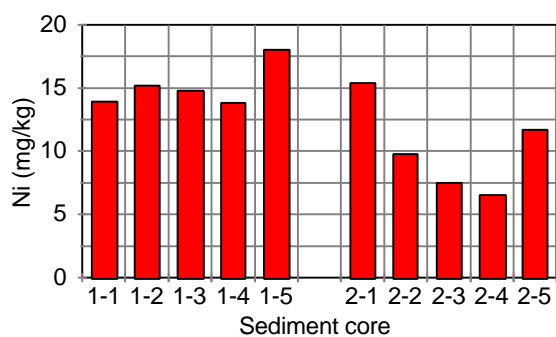
Cd total (June 1997)

**Louvicourt sediment**

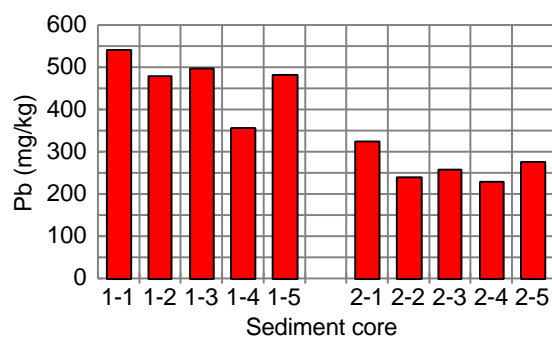
Cu total (June 1997)

**Louvicourt sediment**

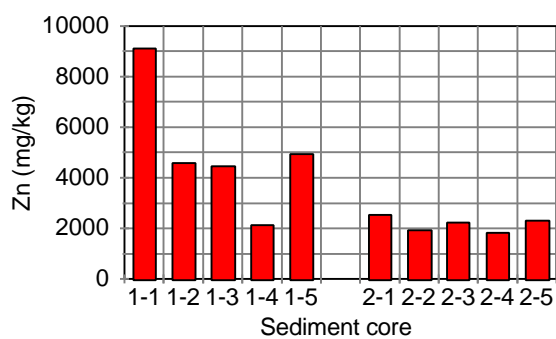
Ni total (June 1997)

**Louvicourt sediment**

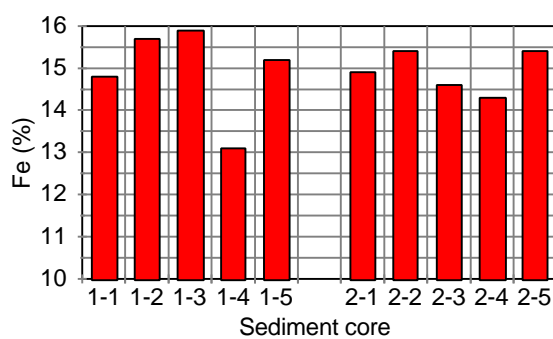
Pb total (June 1997)

**Louvicourt sediment**

Zn total (June 1997)

**Louvicourt sediment**

Fe total (June 1997)



Appendix 1

Summary of findings from October 1996 sampling.

1. *In situ* dialysis

- a) The peepers showed no signs of subsidence after the two week equilibration period (we had feared that they might simply sink into the un-consolidated tailings).
- b) Rinsing the peepers, to remove the tailings that physically adhered to the plastic assembly, proved easier than anticipated.
- c) Based on our overall comparison of the results from the October 1996 peeper analyses ...
 - for any given variable, agreement among the individual peepers in a particular cell was generally good;
 - for any given variable, vertical profiles in the two cells generally showed similar patterns;
 - but, the absolute values for some variables (notably the trace metals) differed markedly between the two cells.
- d) In both cells and in all peepers, the pH increased markedly with depth (e.g. from 7.5 in the overlying water to 9.5 at a depth of 10 cm), presumably reflecting the addition of lime to mine waste stream.
- e) In both cells and all peepers, SO_4^{2-} and Cl^- values increased markedly with depth. SO_4^{2-} concentrations in the overlying waters were slightly higher in Cell 1 (2.2 mM) than in Cell 2 (1.9 mM); concentrations increased almost linearly with depth, attaining values from 3.5 to 4.0 mM at the maximum sampled depth of 15 cm. Cl^- concentrations also increased steadily with depth, attaining values in the range 0.5-0.6 mM in Cell 1, 0.6-0.9 mM in Cell 2. These profiles indicate the presence of a "deep" source of dissolved SO_4^{2-} and dissolved Cl^- , leading to a steady diffusive flux out of the tailings into the overlying water.
- f) In contrast, in both cells and in all peepers, carbonate concentrations decreased rapidly with depth. Concentrations in the overlying water ranged from 0.9 to 1.1 mM, but at depths as shallow as 3 cm concentrations decreased to about 0.2 mM and remained at this level all the way down to 15 cm. Such profiles suggest that the original porewater present in the tailings was carbonate-poor (and/or that there is a sink for carbonate at depth), and that atmospheric CO_2 is diffusing downwards from the overlying water.
- g) In both cells and in all peepers, SH_2S concentrations were undetectable in the overlying waters and at the first sampled depth within the sediment (1 cm). However, at depths > 2 cm SH_2S was detectable and indeed concentrations increased from 2 cm down to 10-12 cm, attaining values ranging from 0.5 to 0.9 : M (i.e., $\ll \text{SO}_4^{2-}$ concentrations).

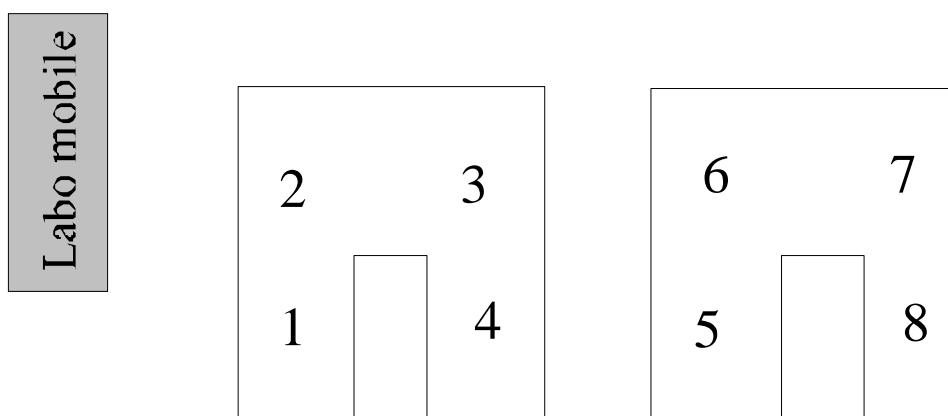
- h) Consistent with the appearance of SH_2S , and with the increase in pH, in both cells and in all peepers, trace metal concentrations decreased with depth. At depths > 2-3 cm, metal concentrations were consistently below the analytical detection limit.
- i) In both cells, concentrations of zinc in the overlying water were much greater for the other metals (100-1000x).
- j) In both cells, the measured lead concentrations varied erratically and failed to meet the criteria of "geochemical consistency" - we suspect random contamination of the samples during the porewater sampling.
- k) For Zn, Cd and Ni there were indications of a maximum in the porewater close to the tailings-water interface (e.g., at about 1 cm above or below the tailings-water interface) with concentrations decreasing upwards and downwards from this point. Such profiles would be consistent with the presence of a surface source for these metals (e.g., sulfide oxidation). However, the maximum concentration in these vertical profiles was not always found below the apparent sediment-water interface (e.g., in the -1 cm stratum); in some cases the maximum concentration value occurred in the first sample above interface. We suspect that the peepers may have moved slightly, in the vertical plane, towards the end of their deployment.
- l) As alluded to under point c above, although the four trace metals (Zn, Cd, Cu, Ni) all showed similar vertical profiles, the absolute concentrations measured in the overlying water of the two cells differed quite markedly. For example, the mean [Zn] in the overlying water of Cell 1 (1.1"0.2 mg/L) was about 8 times higher than in Cell 2 (0.14"0.06 mg/L). Differences for the other metals were less important but nevertheless worrying.

	Cell 1	Cell 2
Zn	1.13 " 0.24 mg/L	0.14 " 0.06 mg/L
Cd	2.1 " 0.4 : g/L	0.66 " 0.17 : g/L
Cu	8.1 " 0.4 : g/L	5.6 " 1.2 : g/L
Ni	3.0 " 0.6 : g/L	1.6 " 0.5 : g/L

2. Sediment analysis:

- Three 3 mini-cores were taken in each cell and the surface tailings (top 0.5 cm) were extruded, suspended in water from the parent cell, and then frozen until analysis (sequential extractions). Extracts were analyzed for Fe, Mn; Cd, Cu, Ni, Pb, Zn.
- In Cell 2, the surface sediments from the 3 cores were geochemically similar; in Cell 1, however, surface sediments from the 3 cores differed geochemically (most notably for Zn and Cd).
- Metal concentrations in 2 of 3 cores from Cell 1 were markedly higher than in the cores from Cell 2 (particularly for Cd and Zn; less so for Pb, Cu; not for Ni). This difference is in the same direction as the differences in dissolved metal levels in the overlying water in the two cells.
- For Cd and Zn, the sequential extraction results show that the differences among the three sites in Cell 1 are largely due to differences in metal levels in fractions F4 (extracted with H_2O_2 , an oxidizing agent) and F5 (residual fraction), i.e. likely due to differences in the sulfide fractions.

Sketch of the sampling points in the two experimental cells:



Appendix 2

Summary of findings from June 1997 sampling.

1. *In situ* dialysis

- Porewater analysis for the major anions (Cl^- and SO_4^{2-}) indicated that one of the four peepers had shifted in each cell (i.e., a gap persisted between the peeper cells and the tailings material, permitting free circulation of the overlying water). The results from this one peeper in each cell were discarded.
- The gradients noted in October 1996 for Cl^- , SO_4^{2-} and pH (i.e., concentrations increasing with depth) were still present in June 1997, but the gradients were less steep. See Figs. 13-15. The absolute concentrations of Cl^- and SO_4^{2-} in the overlying water were lower in June 1997 than in October 1998, presumably reflecting the dilution effect of the spring snowmelt.
- Absolute concentrations of Zn and Cd were also lower than in October 1996, but the previously noted differences between the two cells were still present in June 1997.

	<i>Cell 1</i>	<i>Cell 2</i>
Zn	265 " 27 $\mu\text{g/L}$	25 " 7 $\mu\text{g/L}$
Cd	1.6 " 0.06 : g/L	0.28 " 0.02 : g/L
Cu	3.7 " 0.6 : g/L	4.0 " 0.3 : g/L

2. Sediment analysis

- The total metal analyses (Fe, Mn; Cd, Cu, Ni, Pb and Zn), determined on the five samples of surface tailings collected from each cell, confirmed the relative homogeneity of Cell 2 and the heterogeneity of Cell 1.
- This heterogeneity in Cell 1 was most marked for Zn ($[\]_{\text{max}} : [\]_{\text{min}}$ ratio of 4.3) and Cd (ratio of 2.4) - see Table below.
- In general, the metal levels observed in the June 1997 sampling were similar to those measured in October 1996. The only apparent exception to this generalization concerns total Cd, for which the values in the surface tailings in Cell 2 in 1997 are greater than in 1996 (roughly $8 \text{ mg}\cdot\text{kg}^{-1}$ in 1996 and $15 \text{ mg}\cdot\text{kg}^{-1}$ in 1997). This difference is difficult to explain. If it were simply due to the heterogeneity of the tailings, then we would have expected to see similar differences for some of the other metals – no such differences are observed (compare Figure 7(a) and 7(b) for the metals other than Cd). In the sequential extraction experiments, we performed a mass balance and added up the metal extracted in each fraction. As indicated in Table 1, the total Cd concentration remained effectively unchanged in Cell 2: $8\pm 1 \text{ mg}\cdot\text{kg}^{-1}$ in 1996 and $7\pm 1 \text{ mg}\cdot\text{kg}^{-1}$ in 1998. Note that the $8\pm 1 \text{ mg}\cdot\text{kg}^{-1}$ value for 1996 agrees well with

the total Cd value determined independently (Figure 7(a)). Thus the total Cd values for 1997 in Cell 2 ($15 \text{ mg}\cdot\text{kg}^{-1}$) appear abnormally high; we suspect an analytical bias, resulting from measurements made with an older ICP-AES apparatus at Cd levels close to the detection limit. Since the 1997 sediment sampling was done only to confirm the heterogeneity that had been observed in Cell 1 in 1996, these analyses were not repeated with more sensitive methods.

		<i>Cd</i>	<i>Cu</i>	<i>Fe</i>	<i>Mn</i>	<i>Ni</i>	<i>Pb</i>	<i>Zn</i>
		<u>mg/kg</u>	<u>mg/kg</u>	<u>%</u>	<u>mg/kg</u>	<u>mg/kg</u>	<u>mg/kg</u>	<u>mg/kg</u>
Cell 1	core 1	35.3	1705	14.8	2546	13.9	541	9105
	core 2	21.8	1508	15.7	2638	15.2	479	4590
	core 3	20.5	1503	15.9	2762	14.8	497	4455
	core 4	14.9	1173	13.1	1987	13.8	356	2136
	core 5	23.1	1555	15.2	2571	18	482	4945

		<i>Cd</i>	<i>Cu</i>	<i>Fe</i>	<i>Mn</i>	<i>Ni</i>	<i>Pb</i>	<i>Zn</i>
		<u>mg/kg</u>	<u>mg/kg</u>	<u>%</u>	<u>mg/kg</u>	<u>mg/kg</u>	<u>mg/kg</u>	<u>mg/kg</u>
Cell 2	core 1	16.2	1102	14.9	2255	15.4	325	2525
	core 2	14.7	996	15.4	2332	9.8	239	1914
	core 3	14.9	1044	14.6	2345	7.5	257	2243
	core 4	13.8	1127	14.3	2416	6.5	229	1812
	core 5	16.0	993	15.4	2277	11.7	275	2313

3. Electrochemical profiles

- Profiles were determined in both cells, using the floating quays as the support for the electrochemical instrumentation and installing the micromanipulator close to the quay. Once the tripod had been installed, the electrode assembly could be displaced both vertically (to obtain the profiles) and horizontally (to compare separate profiles at points several cm apart in a lateral direction).
- In both cells and at all sites, the DO profiles indicated that the tailings interstitial water was anoxic within 5 mm of the tailings-water interface.
- In both cells, and at some sites, the pH profiles showed evidence of a source of protons (i.e., acidification) very close to the tailings-water interface; this pH depression presumably reflects some localized SH_2S oxidation at the oxic-anoxic boundary.