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GEOCHEMICAL CHANGES IN SULFIDIC MINE TAILINGS STORED UNDER A SHALLOW WATER COVER

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Abstract—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 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, mobilization of Cu from tailings was less evident. Unlike previous reports, which suggested that submerged tailings were effectively inert, our results show alteration of the superficial layer over time.
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Key words—pyrite, sulfide, oxidation, sediment, *in situ* dialysis, pH, DO

INTRODUCTION

Acid mine drainage (AMD) is a major environmental concern for the mining industry worldwide. Many of the ores exploited contain a large proportion of sulfides, present mainly as pyrite (FeS_2). Pyrite-containing tailings produced by mining 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 $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$, which is catalyzed by microorganisms (Singer and Stumm, 1970). The resulting acidic solution can leach metals from the tailings, constituting a threat to the receiving environment (Geller *et al.*, 1998).

Several techniques have been developed for the treatment of AMD, 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 involved and the open-ended nature of the operation, which could potentially last for centuries after the original mining operation has stopped. Accordingly, considerable effort has been expended to develop techniques for the prevention of AMD (Filion *et al.*, 1990). These prevention techniques are based on processes such as the inhibition of the activity of Fe-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 AMD has also been considered (MEND, 1989).

Underwater disposal attenuates the input of DO to tailings, given the low diffusion coefficient and solubility of oxygen in overlying and interstitial water. In addition, anoxic conditions should inhibit the microbial catalysis associated with the oxidation process (Kleinmann and Crerar, 1979). Pedersen and co-workers (Pedersen, 1983; Pedersen and Losher, 1988; Pedersen *et al.*, 1991; 1993) studied the chemistry of pore waters, overlying water and solid phases (sediment and deposited tailings) in two lakes that had previously received mine tailings. They concluded that the submerged tailings were not

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releasing Cd, Cu or Zn to the overlying water, but were acting as a sink for metals that reached the lake water from AMD in the catchment.

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 *et al.*) raises environmental conservation issues. The use of engineered water covers has been suggested, but there are legitimate concerns regarding the long-term stability of man-made reservoirs and the need for dike maintenance. To reduce the initial engineering costs, and to minimize the chances of dike failure, a shallow water cover depth would be desirable. However, tailings under shallow water covers (e.g., <1 m) may be affected by fluctuating 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 shallow water depth, DO concentrations will remain high in the overlying water. In addition, the higher amount of light reaching the tailings surface will favor the establishment of a periphyton layer, the photosynthetic activity of which would constitute a localized source of DO. These potential perturbations of the tailings raise justifiable questions regarding the effectiveness of shallow water covers in preventing the development of AMD. The present investigation was thus designed to assess the effectiveness of a shallow water cover (0.3 m) in a man-made reservoir for the prevention of the oxidation of sulfidic mine tailings.

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 DO 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.

MATERIALS AND METHODS

Site description/sampling

The fresh tailings were obtained from an underground Cu/Zn mine located near Val d'Or, Québec, Canada. After separation of Cu and Zn concentrates by flotation, most of

the residual tailings are used as underground back fill (60%); the remaining 40% is disposed of underwater in a man-made 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).

To evaluate the effectiveness of the shallow water cover, two field test cells (21 × 21 × 3 m deep) were constructed adjacent to the main reservoir. These two 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 two days longer to fill than did cell #2; during this additional time, the mine's flotation plant changed from a Cu and Zn recovery mode to a Cu-only recovery procedure. As a result, the upper layer of tailings was enriched in Zn (and was less homogeneous) in cell #1 compared to cell #2. Nevertheless, the geochemical behavior of the tailings in the two cells proved similar. For simplicity, we have emphasized results from cell #2, where the total metal concentrations in the tailings were somewhat lower and the surface layer was more homogenous.

A floating sampling deck was installed in the center of each cell to facilitate sampling. Water levels were controlled with V-notched weirs. Water inputs into the cells occurred largely by direct precipitation onto their water surface, with some minor surface runoff from the small raised area surrounding the cells. In the event of insufficient inputs from precipitation and drainage waters, the cells were topped up periodically by pumping from an adjacent pond. From the third week of May to the first week of November (i.e., the ice-free season), outflow and temperature were automatically recorded at 1 h intervals in 1997 and at 2 h intervals in 1998.

After the filling of the cells and decantation of the excess process water, the tailings were covered by 0.3 m of water, pumped from the adjacent pond, at the end of August 1996. The tailings were allowed to settle/consolidate for six weeks after filling, before the first sampling campaign in October 1996. Sampling was also carried out on three subsequent occasions — June 1997, August 1998 and June 1999.

DO and pH micro-profiles

A submersible micro-manipulator, consisting of a hand-operated micrometer attached to a tripod support inserted into the tailings, was used to displace the DO 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. DO micro-profiles were measured *in situ* using Clark-type DO micro-electrodes with a guard cathode (Diamond General Corporation; type 737-GC; tip size 15–35 µm; response time < 1 s; signal drift < 1% h⁻¹; linear response over a range of 0–100% air saturation). A two-point calibration was made between an air-saturated solution and anoxic sediment. 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 DO 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 micro-profiles that were measured at night. The micro-manipulator was deployed at different

points adjacent to the sampling deck, allowing us to obtain several micro-profiles within each cell.

Interstitial water sampling and 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 a 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 this period.

After the equilibration period, the peepers were retrieved, rinsed with the overlying water from the cell and sampled immediately. 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 $\text{N,N}'$ -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°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-} analysis. 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. 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 flame 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).

Diffusive fluxes across the tailings–overlying water interface

Porewater advection was considered to be negligible, and diffusive fluxes of species “i” across the tailings–water

interface, J_i , were calculated according to Fick’s law:

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

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 DO concentration gradients were calculated from the slope of the micro-profiles in the tailings. DO diffusivity was obtained from Broecker and Peng (1974) and corrected for temperature according to Zhang and Davison (1995); the mean temperature over the DO measurement period was used ($23 \pm 2^\circ\text{C}$).

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, i.e., $19 \pm 3^\circ\text{C}$ in June 1997 and $17 \pm 3^\circ\text{C}$ 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, $8.1 \pm 0.8^\circ\text{C}$. 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.

Solid-phase analysis

In October 1996 and August 1998, cores were collected close to the peeper sampling sites with Plexiglas coring tubes (9 cm 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 and only the uppermost 0.5 cm layer was kept 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 $12,000 \times g$ for 30 min to remove excess water. Metals were analyzed as previously described in the (Interstitial water sampling and analysis) section. Metals in the sediment (Cd, Cu, Zn and Fe) were partitioned into operationally defined fractions by extracting the sediment sample sequentially (Tessier *et al.*, 1989). For oxic lake sediments, these fractions have been associated with certain geochemical phases (e.g., Campbell and Tessier, 1996), but in the case of tailings, it is clear that metals extracted with a given reagent cannot be ascribed to a specific geochemical phase. The results do, however, reflect changes in metal partitioning that occurred over time.

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; DO) 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.

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, for data from 1996, 1997 and 1998 (Jandel Scientific, Sigmapstat 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’ correction) and the Levene median test, respectively.

RESULTS

pH and DO micro-profiles

The DO micro-profiles showed the disappearance of oxygen within only a few mm of the tailings–water interface (Fig. 1). The first measurements, carried out in June 1997, revealed a sharp decrease in the DO concentration in the tailings, with anoxic conditions

appearing 3–4 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 we attribute its daytime presence to the photosynthetic production of DO by a periphyton layer on the surface of the tailings. This green layer was visually observed at the interface in 1998 and 1999. 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 changed over time as the tailings aged (Fig. 2). In 1997, a slight acidification had developed immediately beneath the interface, but the pH then 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 (0–3 mm), and only at greater depths did

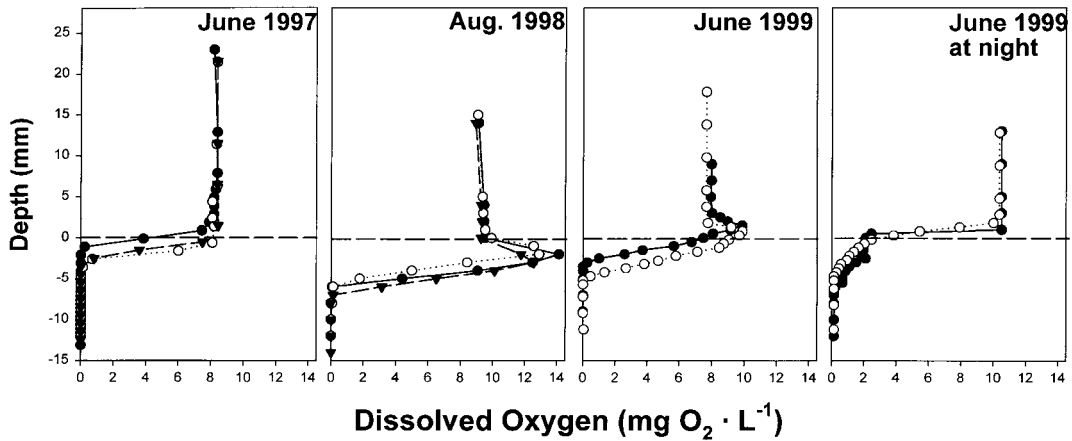


Fig. 1. Typical porewater DO concentration micro-profiles as measured with micro-electrodes inserted into the tailings (1 mm vertical resolution). The horizontal broken line indicates the tailings – overlying water interface. Each curve is from different insertions of the micro-electrode at locations adjacent to the sampling deck, *n* = 3 (1997 and 1998) and *n* = 2 (1999).

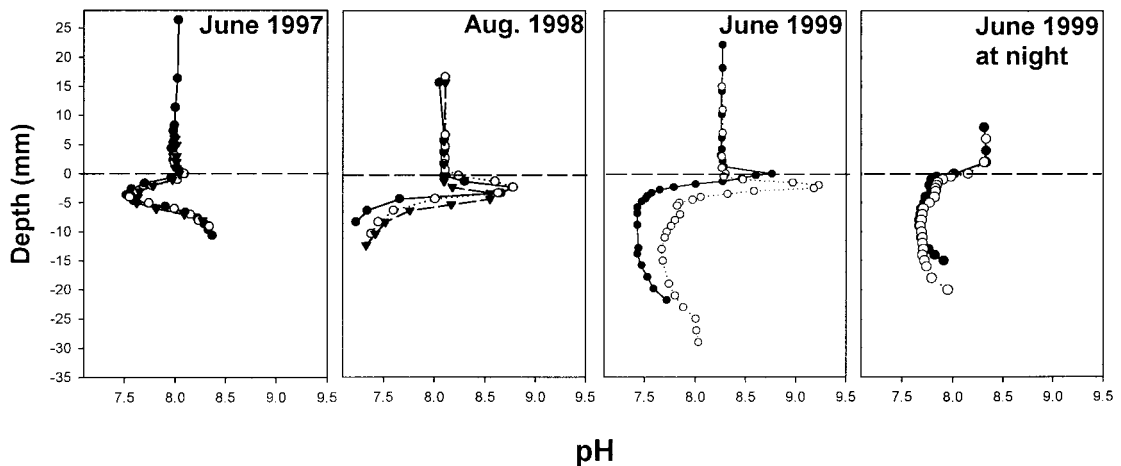


Fig. 2. Typical porewater pH micro-profiles as measured with micro-electrodes inserted into the tailings (1 mm vertical resolution). The horizontal broken line indicates the tailings – overlying water interface. Each curve is from different insertions of the micro-electrode at locations adjacent to the sampling deck, *n* = 3 (1997 and 1998) and *n* = 2 (1999).

acidification become evident. The pH increase just below the interface, coincident with the increase in 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 DO 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 DO concentration and pH.

Interstitial water analysis (peepers) – vertical variation of pH, anions, Fe, Mn

One month after the filling of the experimental cells, pH profiles showed a marked increase in pH with increasing depth in the tailings (Fig. 3), 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 micro-electrode (Fig. 2) also appeared in the pH profile obtained by *in situ* dialysis (Fig. 3), but with a much lower resolution. For both 1997 and 1998, the pH values obtained from the peeper samples at –0.5 cm were close to the average pH measured with the micro-electrode over the first cm, 7.74 and 7.84, respectively. The pH at depths > 6 cm decreased from 9.5 in 1996 to 8.5 in 1998.

Initial concentrations of both Cl^- and SO_4^{2-} were much higher in the tailings than in the overlying water (Fig. 4), which resulted in the diffusion of both anions from the tailings to the overlying water. As

can be seen by comparing profiles for the two complete dialysis campaigns (1996 and 1998), the concentrations of both anions and their concentration gradients decreased with time over the 16 cm depth interval sampled. The relative decrease over time was greater for Cl^- than for SO_4^{2-} , for two reasons: Cl^- has a higher diffusion coefficient than SO_4^{2-} (Li and Gregory, 1974), and, in contrast to SO_4^{2-} , Cl^- does not participate in diagenetic reactions. Sulfate profiles in 1998 showed bulges just below the tailings–water interface, suggesting localized production of SO_4^{2-} as a result of the oxidation of sulfide minerals.

The presence of $\Sigma\text{H}_2\text{S}$ in pore waters sampled > 1.5 cm below the tailings–water interface (Fig. 5) was consistent with the existence of anoxic conditions at these depths. The Fe(II) and Mn(II) peaks observed a few cm below the interface in 1997 and 1998 (Fig. 6) were also consistent with anoxia; the pH at these depths was relatively high (≥ 7.5) and oxidation of Fe(II) would have been rapid had traces of DO been present (Stumm and Morgan, 1995). These peaks for reduced Fe and Mn likely correspond to the dissolution of Fe- and Mn-containing carbonates, such as ankerite and magnesian siderite, which are present in the tailings material. 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 was 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.

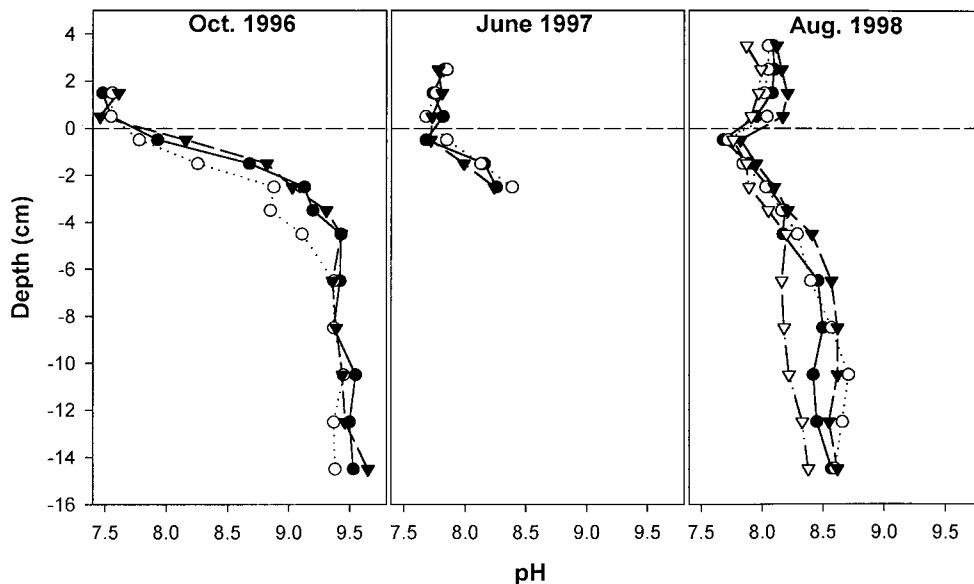


Fig. 3. Porewater pH profiles as sampled by *in situ* dialysis (1 cm vertical resolution). The horizontal broken line indicates the tailings–overlying water interface. Each curve is from an individual peeper inserted into the tailings and allowed to equilibrate for 2 weeks; $n = 3$ (1996 and 1997) or $n = 4$ (1998).

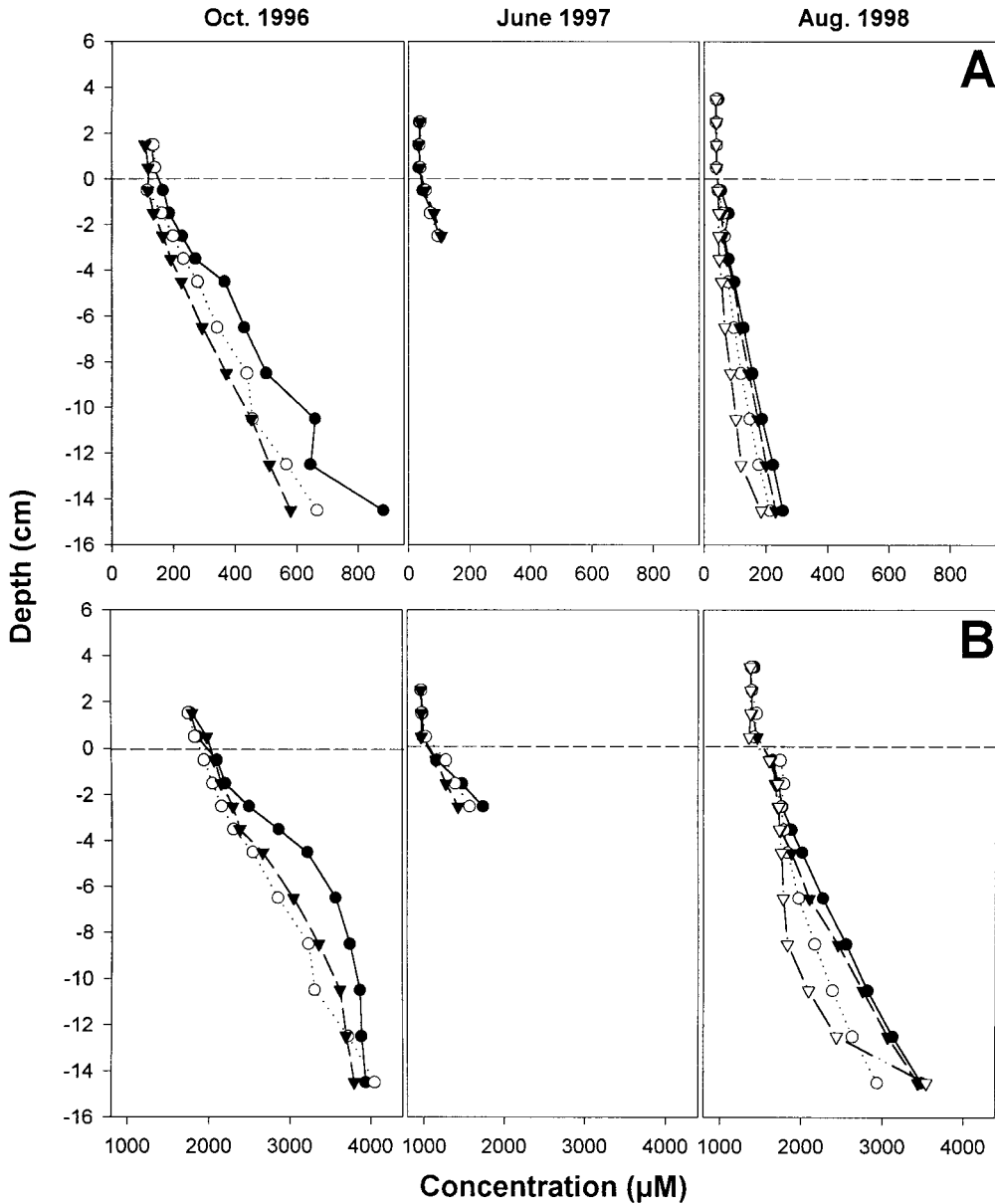


Fig. 4. Porewater Cl^- (A) and SO_4^{2-} (B) concentration profiles as sampled by *in situ* dialysis (1 cm vertical resolution). The horizontal broken line indicates the tailings–overlying water interface. Curves as in Fig. 3.

Interstitial water analysis – vertical variation of trace metals

Dissolved Cu, Cd and Zn concentrations all decreased sharply below the tailings–water interface, attaining levels of a few nM or less (Fig. 7). This decrease presumably reflects precipitation of the metals as sulfides. Early in the experiment (1996 and 1997 profiles), trace metal concentrations (Cu, Cd, Zn) in the interstitial water close to the interface tended to be lower than those in the overlying water (Fig. 7). This trend persisted for Cu in the 1998 profiles, with the exception of some

profiles in which 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, clearly indicating some mobilization of these metals and their diffusion toward the overlying water.

Solid-phase analysis

The apparent increase in dissolved metal concentrations just below the tailings–water interface was associated with marked modifications in their

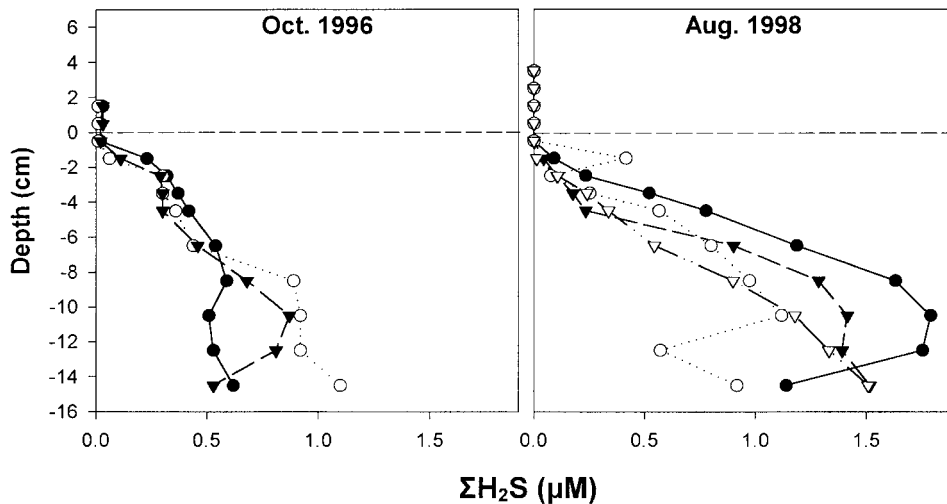


Fig. 5. Porewater $\Sigma\text{H}_2\text{S}$ concentration profiles as sampled by *in situ* dialysis (1 cm vertical resolution, detection limit = $0.004\ \mu\text{M}$). The horizontal broken line indicates the tailings-overlying water interface. Curves as in Fig. 3.

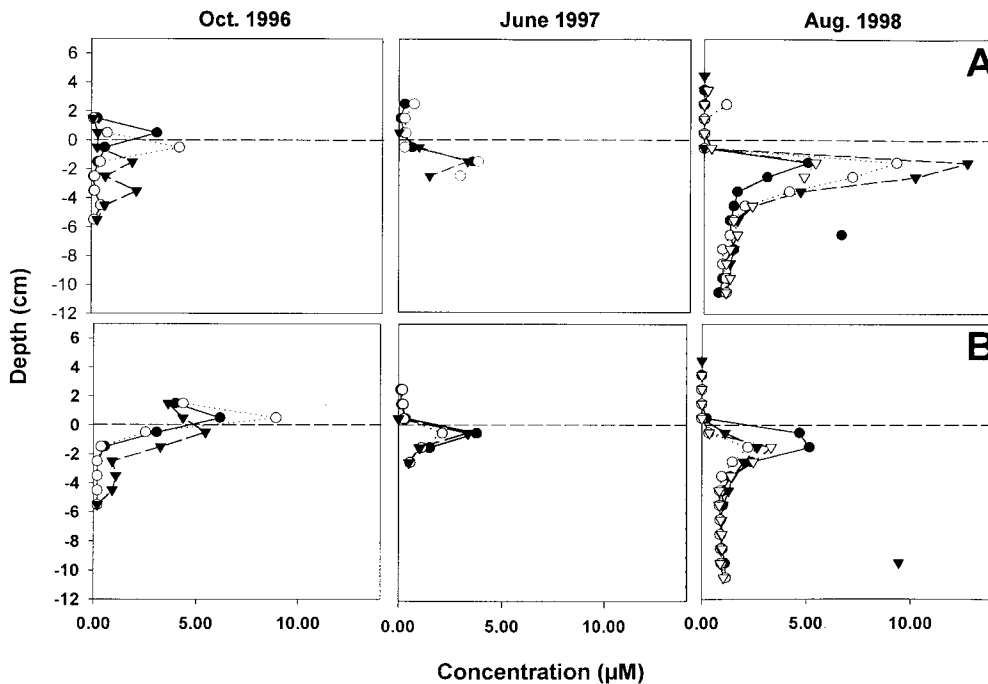


Fig. 6. Porewater dissolved Fe (A) and Mn (B) concentration profiles as sampled by *in situ* dialysis (1 cm vertical resolution, detection limits = 0.2 and $0.05\ \mu\text{M}$ for Fe and Mn, respectively). Curves as in Fig. 3. The horizontal broken line indicates the tailings-overlying water interface. In 1998, one aberrant data-point for both Fe and Mn, presumably resulting from contamination, was not included in their respective profiles.

partitioning in the solid phase of the surficial tailings (Table 1). As mentioned earlier, the Fe, Mn and DO profiles were all consistent with a precipitation of diagenetic Fe- and Mn-oxyhydroxides in this tailings layer. Cd and Zn showed a clear tendency to shift from residual and oxidizable fractions (fractions 5 and 6 in Table 1, which can probably be attributed to

the sulfide minerals in the tailings) to the acid-exchangeable or reducible fractions (fractions 2–4 in Table 1, which largely reflect metals bound to amorphous Fe- and Mn-oxyhydroxides). For example, over the 2-yr interval the proportion of Cd in fractions 5 and 6 decreased from 66 to 25%, whereas Cd concentrations in the other more labile fractions

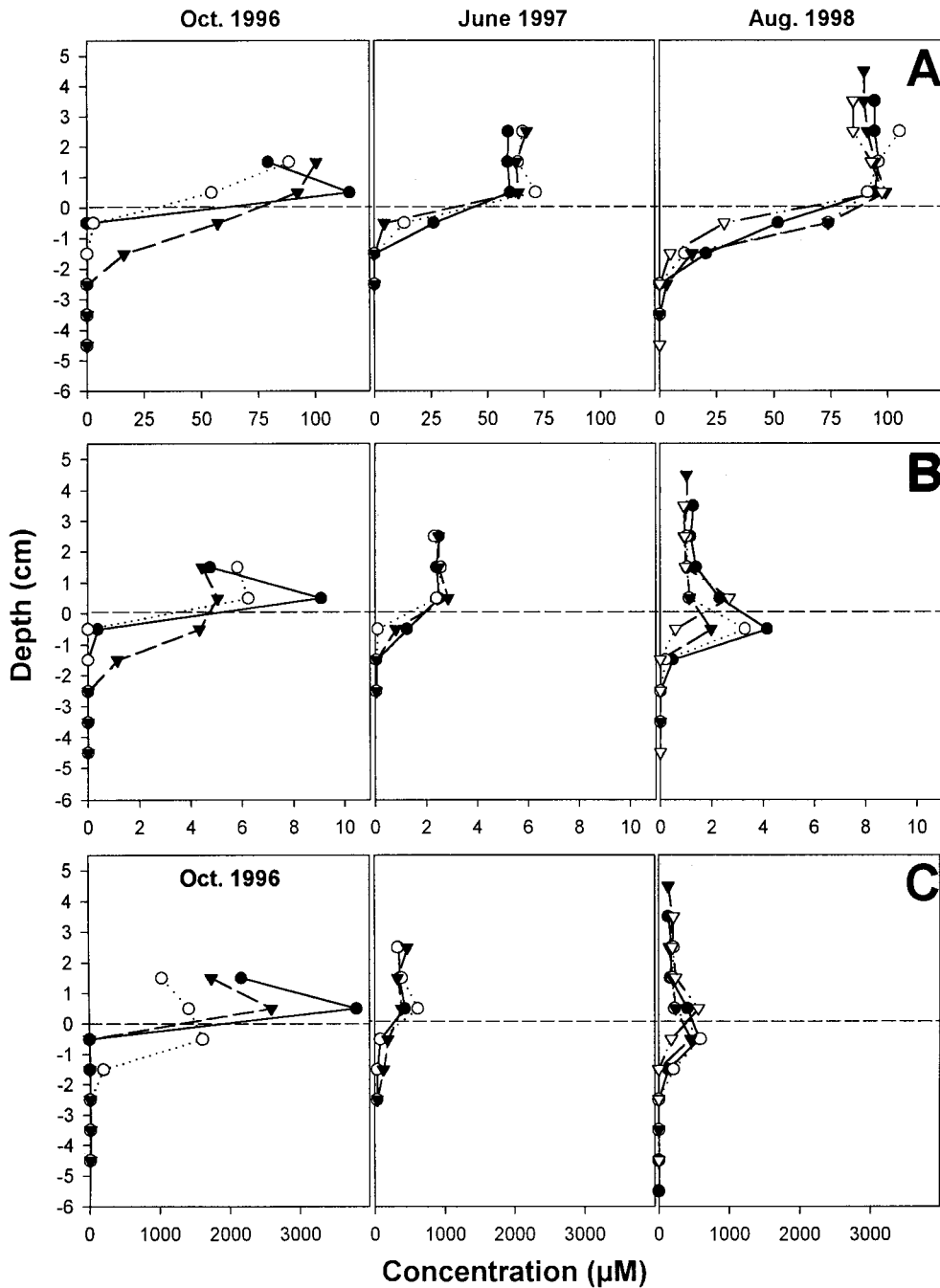


Fig. 7. Porewater dissolved Cu (A), Cd (B) and Zn (C) concentration profiles as sampled by *in situ* dialysis (1 cm vertical resolution; detection limits = 3 nM, 0.1 nM and 0.08 µM for Cu, Cd and Zn, respectively). The horizontal broken line indicates the tailings-overlying water interface. Curves as in Fig. 3.

increased — in 1998, 75% of the Cd was either specifically adsorbed to, or associated with Fe- and Mn-oxyhydroxides (fractions 2-4), and 10% was found in the exchangeable fraction, this being the highest proportion observed for any metal in fraction 1. Zn also shifted from oxidizable fractions over the 2-yr study period but to a lesser extent, passing from 52 to 33%.

DISCUSSION

DO consumption by the submerged tailings

The shallow water cover (0.3 m) in the experimental cells clearly limited the oxidation process. The DO flux into the tailings, as calculated from the micro-profiles obtained in June 1997 in cells #1 and #2, where no significant periphyton

Table 1. Changes in metal partitioning in the uppermost 0.5 cm layer of the submerged tailings in cell 2, between 1996 and 1998. Value are means \pm SD, $n = 3$ (1996) and $n = 4$ (1998). The relative contribution of each fraction (%) is given in parentheses after each concentration

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

^a Fractions (1–6) correspond to successive extractions 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. See Tessier *et al.* (1989) for details.

photosynthetic activity was observed, was 1.7 (± 0.2) $\times 10^{-3}$ nmol cm⁻² s⁻¹. This DO consumption was about 2000 times lower than the O₂ consumption observed for the tailings in humidity test cells, 3.6 nmol cm⁻² 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 (Fig. 1). In this respect, the tailings were behaving like normal fine-grained lake sediments, where the oxic surface layer is normally ≤ 10 mm in thickness (Rasmussen and Jorgensen, 1992; Berg *et al.*, 1998). However, the DO sink in the present case (sulfidic minerals) differs from that in normal aquatic sediments (organic matter). Clearly tailings lying more than 10 mm below the tailings–water interface were not exposed to DO during this study.

Note, however, that our small test cells (21 \times 21 m) clearly did not allow simulation of storm-induced resuspension events, such as may occur in the main tailings pond with its much longer fetch. This question remains of concern regarding the effectiveness of shallow water covers. Li and St-Arnaud (2000) addressed the question of storm-induced resuspension of tailings by modeling the subaqueous tailings oxidation rate; they concluded that oxidation due to tailings resuspension would be directly proportional to the duration of the resuspension event and the thickness of the tailings layer resuspended.

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. Diagenesis/oxidation does occur close to the overlying water–tailings interface. Oxidation of the tailings is demonstrated by the decrease in pH observed in the pH micro-profiles just below the tailings surface (Fig. 2), by the shoulder in the SO₄²⁻ porewater profiles

observed at the same depth (Fig. 4b), as well as by the mobilization of trace metals (Fig. 7).

The increase in size of the pH depression observed between 1996 and 1999, whether in the pH micro-profiles or in the lower-resolution profiles obtained by *in situ* dialysis, is an unambiguous indication of the oxidation of pyritic material. As indicated by the pH micro-profiles measured during daytime and night (Fig. 2), 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 relatively constant throughout the ice-free period at a value of about 8 from June 1997 to June 1999 (data not shown). Overall, H⁺ fluxes across the tailings–water interface did not affect the pH of the overlying water greatly, given the buffering capacity of the overlying water and the dilution from input water.

The SO₄²⁻ porewater profiles are also indicative of sulfide oxidation process occurring near the surface of the tailings. We attribute the weak SO₄²⁻ peak below the interface in 1998 to the production of SO₄²⁻ by oxidation of the tailings. Diagenetic SO₄²⁻ production is also suggested by a comparison of the Cl⁻ and SO₄²⁻ fluxes across the interface. Whereas the Cl⁻ flux (nmol cm⁻² s⁻¹) decreased from $(-2.1 \pm 0.3) \times 10^{-5}$ in 1997 to $(-8.1 \pm 0.9) \times 10^{-6}$ in 1998 (*t*-test, $n = 3$, $P = 0.003$), the SO₄²⁻ flux (nmol cm⁻² s⁻¹) remained unchanged, $(-1.4 \pm 0.3) \times 10^{-4}$ in 1997 and $(-1.7 \pm 0.5) \times 10^{-4}$ in 1998 (*t*-test, $n = 3$, $P = 0.54$), presumably due to the production of SO₄²⁻ just below the tailings–water interface.

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.

The Cd and Zn concentration profiles measured in 1998 by *in situ* dialysis suggest a mobilization of these metals from the tailings to the overlying water. These profiles were obtained with a vertical spatial resolution of 1 cm. The pH and DO micro-profiles showed that diagenetic reactions at the tailings–water interface were occurring at the mm scale, i.e. well below the vertical scale sampled by the porewater peepers. Sharp dissolved metal peaks and steep metal concentration gradients would not be detected by the peepers. Nevertheless, 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 to more labile fractions.

Taken at face value, the dissolved Cu profiles suggest that Cu was diffusing from the overlying water into the tailings and that the magnitude of the Cu flux was unchanged from 1996 to 1998 (one-way ANOVA, $n = 3$ (1996 and 1997), $n = 4$ (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 (Cu \neq Cd, Zn). 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, it is possible that Cu was also mobilized from the tailings (e.g., from the uppermost tailings layer) but that the peepers “missed” the subsurface maximum in Cu concentration.

Pedersen *et al.* (1993) concluded that Cu and Zn were not diffusing out of the submerged tailings in Anderson Lake. Similar observations were made for Cd, Cu and Zn in Buttle Lake (Pedersen, 1983; Pedersen *et al.*, 1991). These 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 the concentrations in the overlying water were not determined at the same time as the porewater measurements. Note, too, that metal concentrations in their lake water columns were higher than in our experimental cells. Both of their lakes were affected by AMD so that metal concentrations in the overlying water were higher than in the present study. Bottom water concentrations in Buttle Lake were $2.6 \mu\text{M}$ Zn, 9.9 nM Cd and 173 nM Cu (Pedersen, 1983), and up to $6.6 \mu\text{M}$ Zn and $690 \mu\text{M}$ Cu were reported for Anderson Lake (Pedersen *et al.*, 1993).

CONCLUSIONS

- A 0.3 m water cover 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 moist tailings samples exposed to air in humidity test cells.
- Progressive oxidation of tailings does occur. Evidence for this oxidation comes from the increase in interstitial water acidity and from indications of SO_4^{2-} production just below the interface. The pH and DO micro-profiles demonstrate that this oxidation occurs at the mm scale beneath the tailings–overlying water interface.
- Two years after underwater tailings disposal, 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). Evidence for Cu mobilization from tailings to the overlying water was less clear.

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