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Long-term effects of submergence and wetland vegetation on metals in a 90-year old abandoned Pb–Zn mine tailings pond

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"Capsule": *Metal and acid-volatile sulfide concentrations were affected differently by flooding vegetation.*

Abstract

A Pb–Zn tailings pond, abandoned for approximately 90 years, has been naturally colonized by *Glyceria fluitans* and is an excellent example of long-term metal retention in tailings ponds under various water cover and vegetation conditions. Shallow/intermittently flooded areas (dry zone) were unvegetated and low in organic matter (OM) content. Permanently flooded areas were either unvegetated with low OM, contained dead vegetation and high OM, or living plants and high OM. It was expected that either water cover or high OM would result in enhanced reducing conditions and lower metal mobility, but live plants would increase metal mobility due to root radial oxygen loss. The flooded low OM tailings showed higher As and Fe mobility compared with dry low OM tailings. In the permanently flooded areas without live vegetation, the high OM content decreased Zn mobility and caused extremely high concentrations of acid-volatile sulfides (AVS). In areas with high OM, living plants significantly increased Zn mobility and decreased concentrations of AVS, indicating root induced sediment oxidation or decreased sulfate-reduction. This is the first study reporting the ability of wetland plants to affect the metal mobility and AVS in long-term (decades), unmanaged tailings ponds.

Keywords: Acid-volatile sulfides; *Glyceria fluitans*; Metal mobility; Tailings; Zinc

1. Introduction

Metal bioavailability and potential migration are important factors when considering the long-term storage of waste tailings from ore extraction operations. Tailings are fine-grained, rich in metals and low in organic matter, making them very different than true soils. Because of these characteristics, it presents special problems in terms of storage, stabilization and remediation. Storage of mine tailings under waterlogged conditions can inhibit metal mobility through coprecipitation with sulfides and subsequent sequestration in the soil (Bourg and Loch, 1995) as long as reducing conditions are maintained. Exposure of waterlogged tailings to air, particularly high-sulfide tailings, can result in oxidation reactions, acid-drainage and metal leaching, potentially creating severe environmental problems (Wong et al., 1998; Wen and Allen, 1999).

Organic matter (OM), derived from vegetation (senescence) can theoretically form an oxygen-consuming barrier over redox-sensitive metal sulfides. For this reason, researchers have promoted the establishment of wetlands on metal-rich sediments (e.g. Wilkinson et al., 1999). However, wetland plants influence sediment chemistry through processes other than solely providing organic matter. Wetland plant roots with aerenchyma may release oxygen into the rhizosphere through radial oxygen loss (ROL) (Armstrong et al., 2000). This oxygen diffusion may increase the redox potential (Eh) of

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local sediments (Wright and Otte, 1999), potentially oxidizing sulfides and releasing sulfide-bound metals (Holmer et al., 1998). Conversely, this ROL may remove metals from porewater via oxidation reactions (Roden and Wetzel, 1996) or through formation of iron plaques on the root surface (Mendelssohn et al., 1995). Additionally, plant presence can enhance leaching properties of metals, such as Zn, via release of rhizosphere organic ligands (Burckhard et al., 1995).

An abandoned tailings pond at Glendalough, County Wicklow, Ireland, supports a wetland of approximately 90-years old consisting of naturally established vegetation growing on Pb–Zn tailings of circumneutral pH. Numerous studies reported in the literature concern various aspects of water or vegetation cover on tailings, but lack the specific combination of factors described in the current investigation. For example, field studies have examined the metal mobility in flooded pre-oxidized tailings (Catalan et al., 2000, 3 years) or oxidized pre-flooded tailings (Simón et al., 2001, 3 months), but there was no vegetation and the duration of the studies was short-term. Other research has involved the effect of shallow water cover on tailings metals (Vigneault et al., 2001), but not compared with intermittent water cover or dry tailings. Constructed wetlands have been studied for their effect on mine waters (Lan et al., 1990), but these are not naturally developing wetland systems. McCabe and Otte (2000) investigated the growth of wetland plants on tailings, but did not address the effects of plants on the biogeochemistry of the sediments. Ye et al. (1999) studied the effects of organic matter on metal mobility and plant growth in mine tailings, but these were not wetland systems, nor did they address the effect of living roots on metal mobility. Banks et al. (1994) examined the effect of plants on metal leaching from tailings material, but this was also under dryland conditions. Wright and Otte (1999) showed evidence of wetland plant roots causing oxidation of tailings and increased metal mobility, but this was a short-term study (17 months). Two studies have assessed the long-term distribution of metal concentrations in abandoned mine tailings ponds with established wetland plant cover (Hamilton and Fraser, 1978, approximately 32 years; Sidle et al., 1991, approximately 50 years), but they did not investigate the specific effect of living roots on the tailings biogeochemistry, particularly acid-volatile sulfides. The Glendalough site provides a unique opportunity for the study of the long-term effects of both water cover and wetland plants on metal mobility in a natural, non-managed tailings pond system.

The aims of this research were (1) to asses the effects of long-term metal retention in Pb–Zn tailings under variously submerged conditions and (2) to determine if the presence of wetland plants affects As, Fe and Zn porewater and sediment concentrations. There were four general areas within the tailings pond as follows: a shallow/intermittently flooded zone with low OM, and three permanently flooded zones with either low OM and bare tailings, high OM (dead plants) or high OM and living plants. It was expected that metal mobility (as shown by porewater concentrations) would be lower in permanently flooded zones, as a result of consistent reducing conditions, compared with the shallow or intermittently flooded zone. It was also expected that metal mobility would decrease in sediments with organic matter, compared with bare soils, due to formation of highly reducing conditions and sulfide precipitation. Due to reversal of these highly reducing conditions via ROL, the zones with living roots would show higher metal mobility than in the zones of dead plants. Whereas many studies extrapolate from relatively short-term investigations, this study yielded important real-time information into the long-term behaviour of metals in mine tailings impoundments and wetlands designed for tailings stabilization and/or remediation.

2. Materials and methods

The tailings pond is located in the Wicklow Mountains National Park in the Valley of Glendalough (6° 23′ W, 53°00′ N, grid reference T 095 962), Co. Wicklow, Ireland. Built in approximately 1910, the 45×55 m^2 pond contains crushed ore materials. It is adjacent to a sorting floor and mine spoil heaps remaining from Pb–Zn mining activities, which peaked during the late 1800s. See Beining and Otte (1996) for a detailed site description. Runoff from the spoil heap enters the pond and exits into an adjacent marsh. The tailings pond was divided into four zones as follows: (1) an unvegetated, intermittently dry or shallow zone with low OM (S, shallow) and three permanently flooded zones; (2) bare tailings with no evidence of plants and low OM (B, bare), (3) a zone with live vegetation and high OM (L, living), and (4) a zone with dead, degraded root material, no aboveground biomass and high OM (D, dead) (Fig. 1). The S zone was the shallowest, submerged in winter or during heavy rain and becoming dry and exposed during the summer. The tailings here were more consolidated than in the other zones and showed easily distinguishable layers containing orange particles, probably iron oxides. The B zone was constantly submerged and the tailings in this zone were less compact. The L and D zones were interspersed (patches of either vegetation or exposed tailings surface) in areas of permanently flooded soil, and the samples were taken in the centre of the patch (1 m minimum distance from another patch). *Glyceria fluitans* (L.) R. Br. exclusively had naturally colonized the marsh and grew vigorously in clumps in the L zones (McCabe and Otte, 2000). The D tailings contained remnants of dead

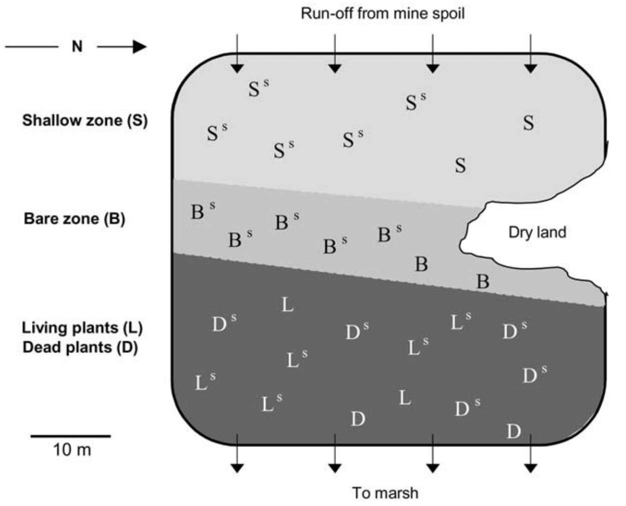

Fig. 1. Glendalough tailings pond sampling sites within the four zones S, the shallow or intermittently flooded zone; and three permanently flooded zones: B, with bare soil (no evidence of plants); D, with dead plants and degraded organic matter; and L, with living plants. Large letters indicate approximate porewater sampling locations and 's' in superscript indicates location of sediment samples. Run-off from spoil heaps along the western edge moves through the pond to exit into a marsh to the east.

roots from previous years, but no currently live plants and thus no visible aboveground biomass.

The tailings porewater was sampled at approximately 3-month intervals from July 2000 to October 2001. Seven dialysis vials, consisting of 20 ml plastic scintillation vials covered with 20-μm Nytal® mesh, were buried at a depth of 10 cm in each of the four zones. On subsequent sampling dates, the dialysis vials were removed from the pond and replaced with new vials filled with distilled water. Some vials disappeared or had been disturbed during the sampling interval, especially in the S zone (no water samples retrieved July 2001). Before the dialysis vials were removed from the tailings, the Eh [portable Eh meter, standard reference calomel electrode and platinum electrode calibrated after Bohn (1971)] and temperature of the sediments were measured at each dialysis vial (10 cm), as was the depth of the water cover (from the tailings surface). Upon vial retrieval, unfiltered subsamples were fixed for alkalinity analysis (see below) before the remainder of the sample was filtered through a 0.45-μm Gelman® syringe filter. Subsamples were then fixed for sulfide and Fe^{2+} analyses (see below). The samples were transported back to the laboratory where the alkalinity, sulfide and Fe^{2+} subsamples were immediately analysed. The remainder of the sample was stored at 4 °C overnight until pH was measured. Then the samples were acidified with concentrated HNO_3 and stored at 4 °C until analysed for total As, Fe and Zn concentrations within 2 weeks.

The porewater was analysed using various methods. Total Alkalinity was measured using the method of Podda and Michard (1994) and Sarazin et al. (1999). This method uses a colorimetric technique with Gran-titrated standards. Immediately after collection, 1.5 ml of unfiltered water sample was added to 1.5 ml of the coloured reagent (0.1 B formic acid and bromophenol blue solution). Absorbance was measured at 590 nm on a Shimadzu UV Mini 1240 UV–vis spectrophotometer. The total alkalinity was calculated from a standard absorbance curve, which was titrated by the Gran titration method as in Talling (1973). Alkalinity data for January 2000 are not available due to analytical difficulties. Iron and zinc were analysed via air-acetylene flame spectrometry on a Unicam 929 atomic absorption spectrometer (AAS) with Unicam Limited SOLAAR Data Station Software version 5.25 program. Arsenic was determined on the AAS using the hydride generation technique. Sulfide was measured following a modified method (Otte and Morris, 1994) after Cline (1969). Immediately after sample collection and filtration, a 1.5 ml subsample was added to 1.5 ml ZnAc (2.2 g l^{-1}). In the laboratory, 2 ml of the fixed sample or standard was added to 0.16 ml dye (2 g *N*,*N*-dimethyl-p-phenelynediamine sulfate and 3 g ferric chloride ($FeCl_3.6H_2O$) in 500 ml cold 6 B HCl). Standards were made up from a stock solution $Na_2S\cdot 9H_2O$ in ZnAc. Absorbance was measured at 670 nm. Porewater Fe^{2+} was determined after a FerroZine® method by Roden and Wetzel (1996).

Five randomly selected sediment samples from each zone were collected in October 2001 at 10 cm depth with PVC cores placed adjacent to the corresponding dialysis vial (Fig. 1). The pH was measured by inserting the pH electrode directly into the tailings after transport to the laboratory the same day. As a measure of organic matter content, loss-on-ignition (LOI) was determined by heating the tailings at 500 °C. Ferrous iron in fresh tailings was measured following Roden and Wetzel (1996). Total As, Fe and Zn were determined using a hot acid digestion as follows: a known quantity of dried tailings was transferred to Teflon bombs with 2 ml acid digestion mixture (HNO_3:HCl 4:1), heated at 140 °C for 7 h, 8 ml distilled water was added after cooling, the solution then filtered (0.45 μm) and stored. Iron and zinc were analysed via AAS. Arsenic was determined on the AAS using the hydride generation technique.

Acid-volatile sulfide (AVS) was measured using a method modified from Allen et al. (1993). Three reaction vessels in series, the last two containing 0.15 l each ZnAc solution, were purged with N_2 gas prior to addition of the sample. Immediately after the sediment cores were opened, a known weight of fresh sample was quickly inserted into the first vessel followed by injection of 50 ml 6 M HCl. The sediment–acid solution was stirred constantly, and the released H_2S gas was bubbled through the ZnAc solutions at approximately 0.3 l min^{-1} with N_2 gas. After 30 min, an equal quantity of ZnAc was removed from each of the two gas-collection vessels, combined and analysed for sulfide as for porewater. The acid solution was filtered (0.45 μm) and stored until analysis of simultaneously-extracted metals (SE-M) including Zn (SE-Zn), Fe (SE-Fe) and As (SE-As) via AAS.

Percentage values for sediment concentrations (the proportion of a metal fraction to the total metal concentration) were determined where appropriate. Data were log transformed (concentrations) and arcsine transformed (fractions) according to Sokal and Rohlf (1981). For sediment samples ($n = 5$), Eh, temperature, water cover depth and porewater variables ($n = 7$, individual sampling dates), the zones were compared with a one-way analysis of variance (ANOVA) using GenStat 5th ed. (Release 4.21 PC/Windows 98© 2001, Lawes Agricultural Trust, Rothamsted Experimental Station). This was followed by two-tailed *t*-test to determine *P* values between specific zones in the three relevant comparisons as follows: to determine the effect of water cover (S vs. B), the effect of organic matter in flooded tailings (B vs. D), and the effect of live vegetation (D vs. L). Pearson correlations (linear) were run on Minitab Statistical Software (Release 13.2® 2000 Minitab Inc.).

3. Results

3.1. Water cover, temperature and Eh

The water cover depth (Fig. 2a) in the S zone (mean range 0–15.9 cm) was significantly lower compared with the B zone throughout the experiment, but the three flooded zones were similar to each other (mean ranges of 17.5–43.7 for B, 23.8–44.9 for D and 18.9–42.9 cm for L). The temperature of the sediment (Fig. 2b) varied from 2.0 to 17.5 °C with peaks in July and the lowest temperatures in January with no consistent significant differences between the zones. For Eh (Fig. 2c), the S zone, with a mean range of 269–436 mV, was significantly higher than the B zone for all sampling dates, but there were no consistent significant differences between the flooded zones (mean ranges 95–196 mV for B, 65–219 mV for D and 146–202 mV for L).

3.2. Porewater components

Alkalinity in the tailings pond ranged from a mean of zero to 3.7 meq l^{-1} (overall mean values for each zone: S 1.3, B 2.7, D 2.6 and L 3.0 meq l^{-1}). The S zone had a significantly lower alkalinity than the B zone, while the flooded zones were not different from each other. The pH (Fig. 2d) of the S zone (mean range 6.7–7.3) was generally significantly higher than the B zone (6.4–7.2), but there were no consistent differences for the other comparisons (mean ranges 6.4–6.8 for D and 6.4–6.7 for L). The S zone showed significantly lower concentrations of As (Fig. 2e), with a mean range of 0–4.4 nmol l^{-1}, but there were no consistent differences between the three flooded zones (mean ranges 11.4–177.0 for B, 6.0–97.7 for D and 8.9–165.1 nmol l^{-1} for l). The sulfide concentrations (Fig. 2f) showed a mean range of 0–0.9 μmol l^{-1} and there were no differences between the zones. For Fe, the concentrations in the S zone (Fig. 2g, mean range 2–6 μmol l^{-1}) were significantly lower than B, but there were no consistent differences between the flooded zones (mean ranges 133–706 for B, 204–666 for D and 244–878 μmol l^{-1} for l). There were no Zn concentrations (Fig. 2h) in the S zone (mean range 104–233 μmol l^{-1}) were not consistently different than B (mean range 72–115 μmol l^{-1}), but both B and L (mean range 45–64 μmol l^{-1}) were significantly higher than D (mean range 73–128 μmol l^{-1}) for three of five sampling dates. For porewater Fe^{2+} there were no consistent significant differences between the flooded zones (mean range 77–735 for B, 165–652 for D and 83–989 μmol l^{-1} for l), but all three showed higher concentrations than the S zone (mean range 0–4 μmol l^{-1}).

3.3. Sediment components

LOI values were significantly lower in the unvegetated S zone and higher in the L and D zones (Table 1). There were no significant differences between the zones for the total solid-phase concentrations of As (mean range 4.6–7.1 nmol g^{-1} dry soil), Fe (194–259 μmol g^{-1} dry soil) and Zn (377–643 μmol g^{-1} dry soil). However, AVS concentrations in the sediments were very different between the zones (Table 1) with S showing the lowest concentration and D the highest. There were no significant differences for SE-As and SE-Fe, but SE-Zn showed clear differences between the zones. Mean SE-Zn and %SE-Zn in the D zone were significantly higher than B and L. In the D zone, the %SE-Zn was above 100% due to the non-sequential nature of these analyses. However, because the difference between the %SE-Zn and total Zn concentrations was not significant (two-way ANOVA, factors being zone and concentration), this anomaly was therefore coincidental. For the D zone only, Eh showed a significant negative correlation with LOI ($P = 0.028$) and with AVS ($P = 0.027$) (Fig. 3a and b) while there were significant positive correlations between SE-Zn and AVS ($P = 0.045$, Fig. 4) and between %SE-Zn and LOI ($P = 0.002$).

4. Discussion

The tailings at Glendalough had very high concentrations of total Fe and Zn, but were not contaminated with As. The total As values were similar to concentrations seen in freshwater soils (Aggett and O'Brien, 1985). The total Fe concentrations were approximately 50 times to several orders of magnitude higher than

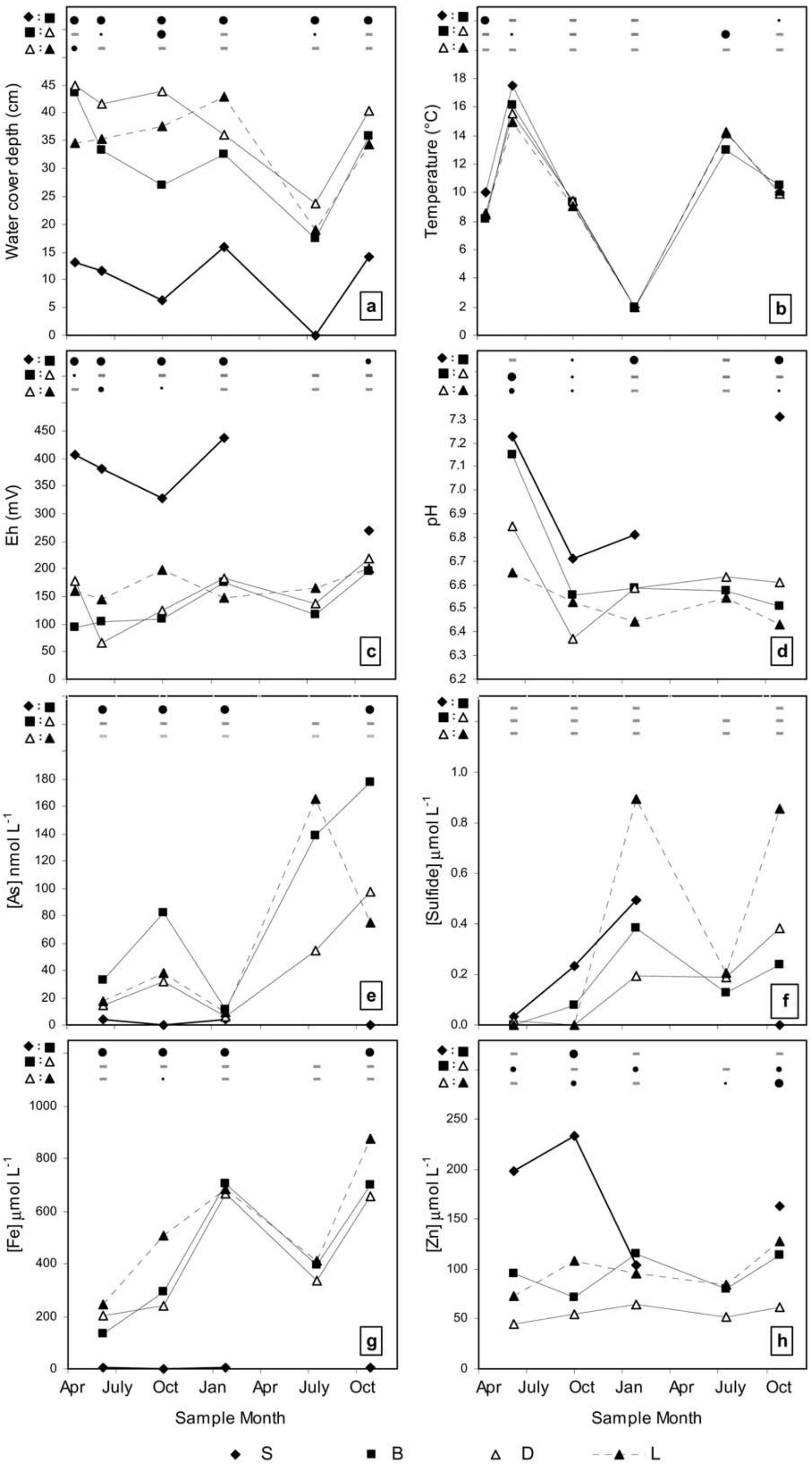

Fig. 2. Water cover depth (a), sediment temperature (b), Eh (c), pH (d), and porewater concentrations of As (e), sulfide (f), Fe (g) and Zn (h) over the course of the experiment (from April 2000 to October 2001) from the four zones as in Fig. 1. Statistical significance of each relevant comparison (the effect of water cover, S zone vs. B zone; the effect of organic matter, B vs. D; and the effect of living plants, D vs. L) for individual sampling dates is indicated at the top of each graph. The size of the circle corresponds to the level of significance as follows: small = $0.05 \geq P > 0.01$, medium = $0.01 \geq P > 0.001$, large = $P \leq 0.001$. Example: for water cover depth on the first sampling date, April 2000, the depth of the S zone is significantly lower than the B zone to the 0.1% significance level. There is no difference between the B zone and D. The depth of the L zone is significantly lower than D to the 1% level.

Table 1
Mean pH, LOI, Fe(II), acid-volatile sulfide (AVS) and simultaneously-extracted Zn (SE-Zn) concentrations (and percentages relative to total concentrations for Fe(II) and SE-Zn) for sediment factors in the four zones as in Fig. 1. Matching letters, in rows only, indicate no significant differences (one-way ANOVA and two-tailed *t*-test, $n = 5$ at $P \leqslant 0.05$

Sediment factors		Zones							
		S		B		D		L	
pH	Mean	7.0	a	6.4	b	6.1	b	6.2	b
LOI g 100 g^{-1}	Mean	3.2	a	6.5	b	14.7	c	19.7	c
Fe(II) µmol g^{-1} dry soil	Mean	17.9	a	37.8	b	87.1	b	80.4	b
	%	9.2	a	17.2	a	37.3	b	31.1	a
AVS µmol g^{-1} dry soil	Mean	0.1	a	1.0	b	1412	d	50	c
SE-Zn µmol g^{-1} dry soil	Mean	319	a	305.2	a	775.9	b	317.4	a
	%	67.7	a	47.5	a	>100.0	b	84.1	a

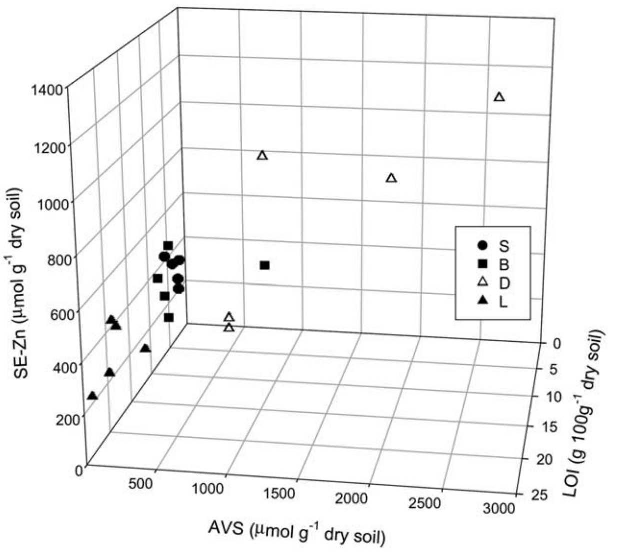

Fig. 4. Three-dimensional correlation between AVS, LOI and SE-Zn for the zones as in Fig. 1.

unpolluted freshwater systems (Moore et al., 1994; van den Berg et al., 1999). McCabe and Otte (2000) reported that total Fe concentrations in a nearby, unpolluted lake (Lough Dan, Co. Wicklow) were of the same magnitude as Glendalough, but Zn concentrations were approximately 100 times lower. This implies that Fe is ubiquitous and the high Zn concentrations are a result of mining operations in the Glendalough Valley.

4.1. Effect of water cover (S zone vs. B zone)

Due to shallow or intermittent water cover, the S zone has undergone long-term oxidation. This conclusion is supported by evidence of significantly higher Eh and lower AVS and sediment Fe(II) concentrations. The alkalinity in the S zone was lower and the pH higher than in the flooded zones, probably as a result of alkalinity depletion due to pH neutralization (Blowes et al., 1998). In alkaline Pb-Zn tailings, limestone or dolomite may be a large source of carbonate minerals, which can undergo dissolution and neutralize the acid produced from oxidation reactions (Bertorino et al., 1995). The high pH in the S zone may be maintained, even with continued Fe-oxidation, by saturation of dissolved carbonate minerals near the sediment surface (Blowes et al., 1998).

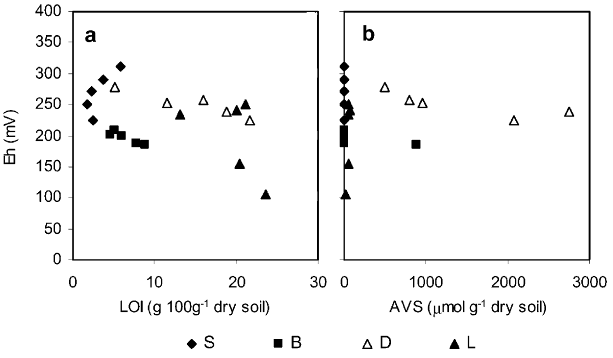

Fig. 3. Correlations between Eh and LOI (a) or AVS (b) for the four zones as in Fig. 1.

Contrary to expectations, the flooded zones showed higher metal mobility than the dryer zone. The pore-water concentrations of Fe in the S zone were all below or near the detection limits while the flooded B zone showed significantly higher concentrations. The lower Fe values in the S zone coincided with increased Eh, and higher pH conditions, all of which would facilitate metal precipitation. Arsenic concentrations were higher in B probably due to the influence of Eh and pH conditions, since As solubility is controlled by these two factors; it can be mobile under reducing conditions and at neutral pH (Smedley and Kinniburgh, 2002), due to dissolution of As bound to iron oxides (Aggett and O'Brien, 1985; Huerta-Diaz et al., 1998). The zinc concentrations in the S and B zones were not significantly different and seem to have been independent of water cover and iron mobility. Several studies have shown both Zn and As to be affected by the behaviour of Fe (Aggett and O'Brien, 1985; Huerta-Diaz et al., 1998), but in this study, pore-water Zn showed a very different behaviour relative to Fe and may be more affected by organic matter in this system.

4.2. Effect of organic matter (B zone vs. D zone)

Wetlands are thought to be sinks for metals because the organic matter provided from dead biomass facilitates the microbial reduction of the sediment and subsequent metal removal from the interstitial water via sulfide–precipitation reaction (Pedersen et al., 1993). The significantly higher LOI in the D zone clearly showed that the presence of plants was the primary source of organic matter in the substrate (Table 1). The significant negative correlation between Eh and LOI in the D zone indicated enhanced reducing conditions with organic matter (Fig. 3a), and this is supported by the significantly higher concentrations of AVS compared with the B zone with its lack of organic matter. Contrary to expectations, there was no consistently significant effect of organic matter on porewater or sediment Fe and As concentrations. There were also no clear differences in pH or sulfide.

The extremely high AVS values in the Glendalough tailings resulted from the high organic matter content and possibly, in part, from the sediment being composed of unprocessed, partially oxidized sulfidic ore particles. Some high AVS values reported in literature are up to 60 μmol g^{-1} dry soil in freshwater systems (van den Berg et al., 1999) or up to 120 μmol in polluted estuarine soils (Simpson et al., 1998). In the Glendalough tailings, the AVS concentrations in the high organic matter zones (D and L) showed mean values up to 1412 μmol g^{-1} dry soil (Table 1). The very high AVS concentrations seen in the D zone, up to 1400 times higher than B, may have resulted from more decomposing organic matter and lower Eh (Fig. 4). Van den Berg et al. (1998) noted that the degradation of roots covered with iron plaque (Fe-oxides) might result in conversion of the plaques to reduced metal-sulfides and subsequent in situ replacement of cell structures, and this may occur at a gradual pace as the roots die and degrade. Marnette et al. (1993) observed evidence of rapidly formed pyrite associated with reduced microsites in organic matter. They found framboidal pyrite crystals in decomposing freshwater plant tissue and determined that these tissues inhibited oxygen penetration, resulting in localized highly reduced conditions.

Zn concentrations in the tailings were clearly influenced by organic matter and sulfides. Zn porewater concentrations were significantly lower in the D zone, coinciding with high concentrations of SE-Zn and AVS, indicating that the Zn was precipitating with reactive sulfides. The %SE-Zn was significantly higher in the D zone compared with B, indicating that more of the Zn in the sediments was bound in potentially labile phases. The positive correlation between %SE-Zn and LOI ($P=0.002$, Fig. 3) and SE-Zn and AVS ($P=0.045$, Fig. 4) confirms that there was a relationship with sulfides and this may have been a major controlling factor in Zn retention in the sediment. In the Glendalough tailings, where the maximum total Zn concentrations were 867 and Fe reached 379 μmol g^{-1} dry soil, the prevalence of Zn may have induced direct formation of metastable ZnS precipitates in reduced organic microsites. Luther et al. (1980) found precipitation of Zn sulfide crystals in estuarine sediments containing high total Zn concentrations (cited as 15.3 μmol g^{-1} dry soil), still much lower than Glendalough.

4.3. *Effect of plants (D zone vs. L zone)*

The presence of active, living roots significantly increased the Zn mobility in the tailings relative to zones with only dead roots, but similar levels of organic matter. The D zone showed clear correlations between AVS and Eh (Fig. 3) and SE-Zn (Fig. 4), but these relationships did not emerge in the L zone. This indicates there must be some activity associated with live plants that suppresses accumulation of AVS and sulfide-associated Zn, even with similar levels of Eh and organic matter in the substrate. This difference between the D and L zones is especially clear in Fig. 4. The lower concentrations of AVS in the L zone would have reduced the capacity for Zn precipitation with the sulfides, as reflected by lower concentrations of SE-Zn, thus causing significantly higher concentrations of porewater Zn. The living plants in the L zone may have directly oxidized metastable Zn-sulfides to an oxidizeable form, or prevented their formation through ROL (Holmer et al., 1998).

If plants were oxidizing their rhizospheres via ROL, we would have expected higher Eh in the L zone compared with the D zone, at least during the growing season. The similar Eh between the two zones, but the lack of correlation between Eh and LOI in L, as seen in the D zone, may indicate that the presence of live roots did affect the sediment Eh, but not in a consistent, linear manner. Ratering and Schnell (2000) report simultaneous oxidation and reduction in the rhizosphere of wetland plants and this may account for the variability seen in the L zone. Also, the effect of living roots on sediment chemistry can be variable depending upon the specific conditions of the soil (Jacob and Otte, 2003). However, the L zone did show significantly lower %Fe(II) than D, possibly resulting from oxidation of Fe-sulfides to sulfate and Fe(III), and subsequent precipitation as root iron plaque, as has been observed in Fe-rich soils (Lucassen et al., 2000).

5. Conclusions

The results from this study show real-time conditions of vegetated mine tailings ponds after decades whereas most studies extrapolate to a longer time scale from experiments that are relatively short-term.

- In shallow/intermittently flooded tailings, development of high pH conditions resulting from carbonate buffering decreased mobility of As and Fe.
- Accumulation of organic matter caused retention of metals in the sediments via reducing conditions and sulfide precipitation, but this was seen only for Zn and not for Fe and As.
- The presence of living roots reversed these reducing conditions in the root zone enough to either limit

the formation or reverse the accumulation of reduced sulfides and thus increase Zn mobility. On the whole, after the wetland has become established, the proportion of living roots to degraded organic matter would decrease, potentially limiting the rhizosphere effect. However, because organic matter degradation can be slow in tailings sediments (Ritcey, 1989), if the plants continue to colonize or re-colonize these reduced zones, the rhizosphere could continue to limit Zn retention for an indefinite time.

It is also important to note that the conditions seen in this tailings pond could be altered relatively easily and are not in a steady-state condition. Metal mobility was restricted by the lack of water cover in the dry zone, but this could be reversed through dissolution reactions if this zone becomes permanently flooded. The precipitated Zn-sulfides in the D zone could be mobilized if oxidized during a period of drought or via ROL from encroaching living roots. Any metals coprecipitated with iron-plaque on the surface of living roots could be reduced and mobilized when the plants die and ROL ceases. Knowledge of these variables and long-term metal behaviour is important for mine closure plans that strive for minimal maintenance and for predictions of the effects of planted wetlands on these substrates.

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