Mine Water and the Environment (2004) 23: 58–65 © IMWA Springer-Verlag 2004

Technical Article

Removal of Sulfate, Zinc, and Lead from Alkaline Mine Wastewater Using Pilot-scale Surface-Flow Wetlands at Tara Mines, Ireland

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Abstract. Passive treatment systems have primarily been used at abandoned mines to increase pH and remove metals from the drainage water. Two pilot-scale treatment wetlands were constructed and monitored at an active lead/zinc mine (Tara Mines) in Ireland to treat alkaline mine water with elevated sulfate and metal levels. Each system comprised three in-series surface-flow cells that contained spent mushroom compost substrate. Typically, aqueous concentrations of 900 mg L^{-1} sulfate, 0.15 mg L^{-1} lead, and 2.0 mg L^{-1} zinc flowed into the treatment wetlands at c. 1.5 L min^{-1}. During a two-year monitoring period, removal of sulfate (mean of 10.4 g m^{-2} day $^{-1}$ (31%), range of 0-42 g m^{-2} day $^{-1}$ (0-81%)), lead (mean of 1.9 mg m^{-2} day $^{-1}$ (32%), range of 0-6.6 mg m^{-2} day $^{-1}$ (0-64%)) and zinc (mean of 18.2 mg m^{-2} day $^{-1}$ (74%), range of 0-70 mg m^{-2} day $^{-1}$ (0-99%)) were achieved. These contaminants were somewhat associated with the vegetation roots but more significantly with the substrate. Communities of colonizing macroinvertebrates, macrophytes, algae, and microorganisms contributed to the development of a diverse ecosystem, which proved to be a successful alternative treatment process. The interacting processes within the wetland ecosystems responsible for wastewater decontamination are being further elucidated and quantified using a systems dynamic model.

Key Words: Ecology; iron; lead; zinc; mine water; passive treatment; sulfate reduction; vegetation

Introduction

Water quality of run-off and leachate from metalliferous mine tailings is generally not compliant with Irish (O'Leary 1996) or international (Allan 1995; Novotny 1995) discharge standards. It is characteristically elevated in metal and sulfate, since most zinc (sphlaerite), lead (galena), iron (marcasite, pyrite), and cadmium (greenockite) ore bodies contain high proportions of sulfur. Additionally, sulfuric acid used during extraction of these metals from the ore contributes to elevated sulfate levels in water discharged from the mine (Tara Mines 1996).

Since 1982, biological passive treatment technologies have developed as alternatives to conventional chemical applications (Gusek and Wildeman 2002; Nairn et al. 2000; Saunders et al. 1996; Stark et al. 1994). Typically, constructed wetlands are part of this treatment process. The self-renewing capabilities, good quality performance, and ecological benefits of using wetlands for mine waste remediation have been demonstrated (Beckett 1999; Debusk et al. 1996; O'Sullivan et al. 1999). Many different types of treatment wetlands are discussed in detail elsewhere (Gusek and Wildeman 2002; Mitsch and Gosselink 2000; Vymazal et al. 1999; Younger et al. 2002).

By comprehending the complex and dynamic biogeochemical properties of wetlands, the behavior of metal and sulfate contaminants in these ecosystems can be biotically and abiotically controlled (Dunbabin and Bowmer 1992; Fortin et al. 1995). In moderate climates (such as in Ireland) where temperatures do not reach extremes, anaerobic wetland substrates are conducive to year-round biological sulfate reduction (Equation 1) (Borden et al. 2001).

Our research was conducted at Tara Mines Ireland (a subsidiary of Outokumpu-Zinc), which is the largest producer of zinc in Europe. Populations of sulfate-reducing bacteria (SRB) were believed to be indigenous; perhaps in micro-anaerobic zones within the spent mushroom compost substrate (SMS) used in the treatment wetlands. Four genera were isolated directly from the substrates (which had not been inoculated) and characterized as *Desulfobrio, Desulfotomaculum, Desulfoccus* and *Desulfobulbus* (O'Sullivan 2001). This substrate was also rich in organic material, which was simultaneously oxidized during microbial reduction of sulfate. Organic material was renewed cyclically through annual plant decomposition. Metal cations such as Zn and Pb can bind with sulfide anions under alkaline conditions to produce metal-sulfide precipitates, carbon-dioxide and water (Equation 2). Some studies have also shown that a closed-reaction system with calcite, elevated carbon dioxide, and a pH of c. 8.2 can also facilitate zinc precipitation as $ZnCO_3^0$ (Equation 3) (Nuttall and Younger 2000). The local geology of the mine near Navan, Co. Meath in Ireland comprises limestones of Lower Carboniferous age, which contain large quantities of both calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). These rocks buffer the wastewater discharged from the mine by carbonate dissolution (Equation 4) to a pH of approximately 7.8 (O'Leary 1996). Wastewater is stored in large tailings impoundment dams 5.6 km north of the mine (53º 42' N, 06º 43' W). Some of this wastewater is fed to the experimental treatment wetlands described here.

Simplified Equations:

$$2CH_2O + SO_4^{2-} = H_2S + 2HCO_3^- \qquad (1)$$

$$M^{2+} + H_2S + 2HCO_3^- = MS + 2H_2O + 2CO_2 \qquad (2)$$

(where M stands for a metal cation)

$$CaCO_3 + Zn^{2+} = Ca^{2+} + ZnCO_3^0 \qquad (3)$$

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \qquad (4)$$

Materials and Methods

Design Specifications and Experimental Set-up

Most treatment applications that employ microbes to remove contaminants from mine wastewater have focused initially on acidity and metal removal (Debusk et al. 1996; Dunbabin and Bowmer 1992; Hammack and Hedin 1995; Hedin et al. 1994; Nairn et al. 2000; Song et al. 1998; Stark et al. 1994; Younger et al. 1997). Although research has also been conducted on treating alkaline mine waters, particularly within the UK (Younger et al. 2002), this work has predominantly addressed abandoned mine waters. The research at the active Tara Mines has been concerned primarily with removing sulfate from alkaline mine water. Two experimental treatment systems were constructed at Tara Mines in 1997 to remove sulfate and metals from the wastewater. The systems received mine water from separate tailings ponds, each containing different loadings of metals. Each system comprised three 12 m^2 (2 m depth) in-series surface flow (SF) ponds: an inflow cell, a wetland cell, and an outflow cell in a 4:1 length to width ratio. Flow rates were measured flowing into the inflow cell and out of the outflow cell on each sampling date. These flows were then correlated and typically yielded a 0.97 coefficient. The margins of each pond provided for a slope of approximately 20º and were lined with a 2,000-gauge impervious, light insensitive liner. All ponds were filled with spent mushroom substrate and a fine inert grit (2.5 mm diameter).The volume ratio of grit to substrate was 1:6 in the inflow and outflow cells (50 cm total depth) and 1:3 in the wetland (1 m depth) (Figure 1). Water levels within inflow and outflow ponds were typically 1 m while the middle (vegetated) cells were approximately 0.6 m but dropped to as low as 0.4 m due to litter fall as the ponds matured. Hydraulic residence time was substantial and calculated to be in excess of 30 days for each system. Substrates remained net reduced shortly (3 months) after flooding and were usually highly reduced (– 300 mV), as determined by monthly redox potential measurements. Highly reduced substrate conditions coupled with extensive carbon supplies, provided conditions conducive for sustaining substantial sulfate reduction (Borden et al. 2001).

Measurements and Analyses

Sulfate was measured by ion chromatography using Dionex instrumentation (QIC analyzer, automated sampler, and 4400 integrator) equipped with a separator column and conductivity cell. Vegetation and substrate samples were oven-dried at 60 ºC for 5 days, ground using a mortar and pestle, and sieved through a 2 mm aluminum sieve. Samples were then digested overnight in strong acid under high temperature, using Teflon™ bombs, as described by Beining and Otte (1996), in order to extract total concentrations (solid-phase forms of metals and sulfate were characterized as mostly residual, e.g. metal-sulfides, and is documented in extensive detail in O'Sullivan et al. 2004). Lead, zinc, and iron were analyzed in the vegetation and substrate extracts and in water using a Unicam 929 atomic absorption spectrophotometer supporting SOLAAR ATI software. Concentrations were log-transformed to obtain homogeneity of variance. Data were analyzed using SAS (v 6.1) to test for significant differences by conducting a series of ANOVAs.

Results

Water Characteristics

Water quality discharged from Tara Mines was generally comparable with other lead/zinc alkaline wastewaters (Allan 1995; Gao and Bradshaw 1995). However, concentrations of metals supplied to the treatment wetlands were typically lower than at other mines. This is probably due to metal precipitation within the storage tailings dam, perhaps as zinc-carbonates (due to alkalinity), as has been reported elsewhere (Finnegan 1998; Song et al. 1998).

Sulfate mass removal

Sulfate removal in the water was calculated from a rate perspective (Table 1, equation 5). Sulfate removal in system 2 ranged between 1-29 g m^{-2} day^{-1}, and between 1-18 g m^{-2} day^{-1} (with the exception of 42 g m^{-2} day^{-1} in September 1998) in system 1. A negative value (e.g., 16 Sept. 1998 for system 2) indicates that there was a net export of sulfate from the system. The treatment systems reached equilibration

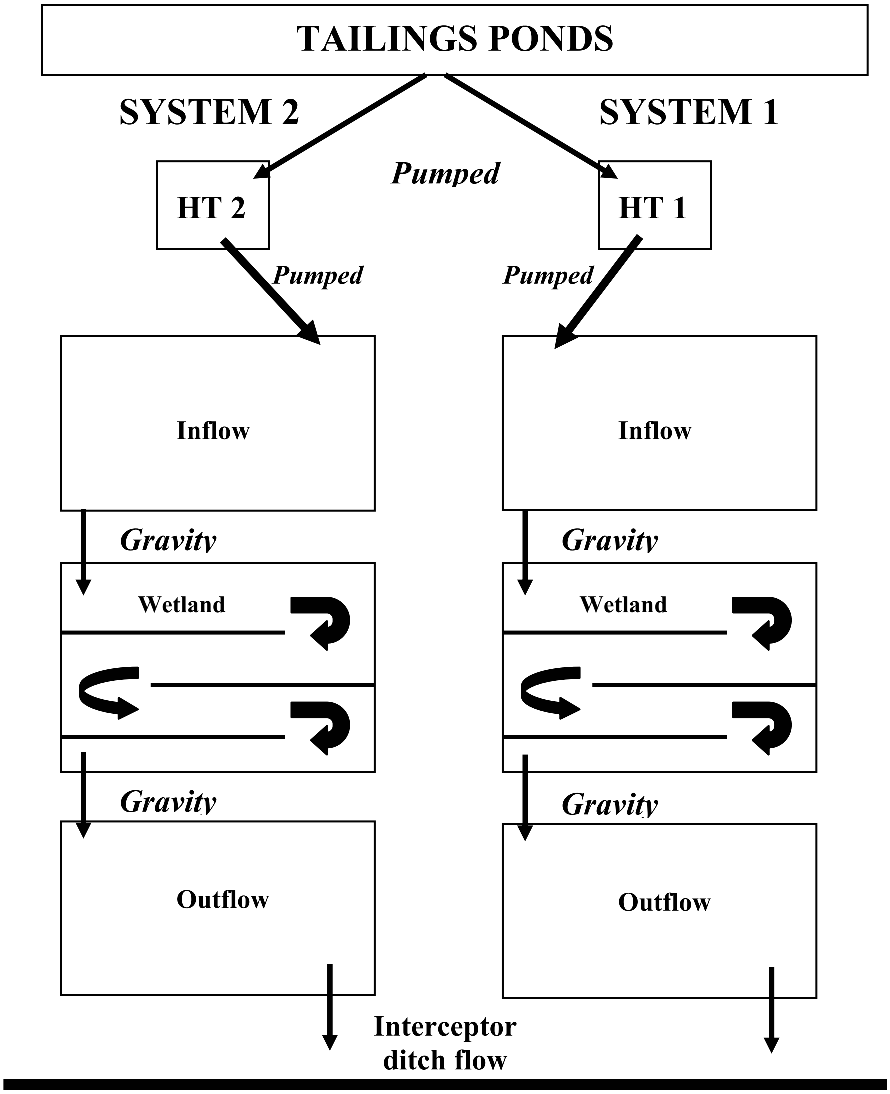

Figure 1. Schematic representation of the experimental treatment systems at Tara Mines, Ireland; arrows indicate the flow path of the water, which was pumped from the storage tailings ponds to the header tanks (HT 1 and HT 2) and subsequently to the inflow cells of each system. From there, water traveling between cells was gravity fed (by head differences between cells) to the vegetated wetland cells and then finally to the outflow cells. Horizontal baffles in the wetland cells served to increase the flow path of the water in the limited treatment space available (used with permission from John Wiley and Sons Publishers, "Encyclopedia of Water," which will be published in 2004).

by October 1998 (determined from preliminary data), approximately 1 year following construction. These data (Nov. 1997 - Oct. 1998) are discussed in more detail elsewhere (O'Sullivan et al. 1999; O'Sullivan 2001) but are also included within the context of this paper to highlight differences in operation of the systems before and after equilibration. Typically, more sulfate was removed following equilibration of the treatment systems. Reduction in sulfate concentrations was significant in both systems at the $p<0.001$ level. Furthermore, differences in concentration as a function of sampling date were also significant for system 1 ($p<0.01$) and for system 2 ($p<0.001$).

$$SO_{4REM} = \frac{(SO_{4ENT} - SO_{4EXIT})*(\text{Daily rate})*(\text{Mol. mass})}{(\text{Area of wetland})}$$

$$g\ m^{-2}\ day^{-1} = ([mol\ SO_4\ removed\ min^{-1}]*1440*96)/36 \quad \textbf{(5)}$$

where: SO_{4REM} is the mass removal of sulfate, SO_{4ENT} is the sulfate load entering in mol min^{-1}, SO_{4EXIT} is the sulfate load exiting in mol min^{-1}, daily rate is 60 minutes*24 hours (= *1440 minutes), and the area of the wetland is 36 m^2.

Metal Mass Removal

Metal concentrations in the water entering the constructed wetlands were determined in millimoles per liter and thus their removal rates are expressed as

Table 1. Sulfate removal rate (g m^{-2} day^{-1}) calculated from differences in concentration between water entering and exiting the treatment systems as a function of the average flow rate (1.5 L min^{-1}), n = 5. Equivalent percentage removals are also given; – implies net export of sulfate.

SAMPLING	**SYSTEM 1**		**SYSTEM 2**	
	g m^{-2} day^{-1}	% equivalent	g m^{-2} day^{-1}	% equivalent
01 Feb. 1998	0	2	1	4
31 Aug. 1998	12	24	6	6
16 Sep. 1998	42	81	-1	-
POST-EQUILIBRATION				
05 Oct. 1998	0	0	10	34
19 Oct. 1998	5	14	4	11
16 Nov. 1998	18	62	13	45
21 Dec. 1998	11	38	29	69
01 Feb. 1999	9	36	7	37
22 Feb. 1999	5	21	20	62
29 Mar. 1999	14	42	8	30
08 Jun. 1999	1	4	8	24
08 Nov. 1999	8	34	19	60

mg per m^2 per day to reflect this. Generally, zinc and lead removal was greater following the equilibration phase, while comparisons cannot be made for iron due to insufficient data (Table 2). Zinc loadings entering system 2 were always higher than those entering system 1 (O'Sullivan 2001), as the systems received different sources of mine drainage, which was controlled by mining operations on-site. Removal of Zn in system 2 ranged between 0.5-70 mg m^{-2} day^{-1}, while for system 1, lower removal rates of 0.3-5.7 mg m^{-2} day^{-1} were calculated. Lead removal ranged up to 6.6 mg m^{-2} day^{-1} in system 2 and 5.8 mg m^{-2} day^{-1} in system 1. For iron, up to 2.5 mg m^{-2} day^{-1} was removed. The calculation is summarized below using Zn as an example (Equation 6). Negative values indicate that the metal loading was higher in water exiting, compared to water entering, on the same sampling date. Metal removal rate, as a function of the metal loading, showed strong correlation coefficients for Zn ($r^2 = 0.99$) and Pb ($r^2 = 0.97$) (O'Sullivan 2001).

$$M^{2+}_{REM} = \frac{(M^{2+}_{ENT} - M^{2+}_{EXIT})*(\text{Daily rate})*(\text{Mol. mass})}{(\text{Area of wetland})}$$

$$\text{mg } m^{-2}\ day^{-1} = ([\text{mmol } M^{2+} \text{ removed } min^{-1}]*1440*65)/36 \quad \textbf{(6)}$$

where: M^{2+}_{REM} is the mass removal of the metal, M^{2+}_{ENT} is the metal load entering in mmol min^{-1}, M^{2+}_{EXIT} is the metal load exiting in mmol min^{-1}, daily rate is 60 minutes*24 hours =*1440 minutes, the molecular mass of zinc is 65 g, and the area of the wetland is 36 m^2.

Fate of Contaminants

A contaminant budget was calculated for each treatment system based on averaging all concentrations of metals and of sulfur in the substrates, plant shoots, and algae over the 29-month monitoring period (O'Sullivan 2001). Averaged concentrations in each media for each treatment system were expressed as a fraction of the (averaged) amount of contaminant removed, in order to assess how much was retained in each media. For example, in system 2, 96% of the zinc was removed from the water but only 0.3% of this was measured in plant shoots and 0.1% in the algae tissues, while 94% was retained in the substrate (the difference of 1.6% between the total amount removed from the water and that measured in these media was attributed to sampling error). Similarly, on average, 38% of the sulfate was removed from the water in system 2, of which plant shoots accumulated <1% while substrates retained more than 30% of it (the 7% difference between the total amount removed from the water and that measured in these media may have accumulated in algae but is more likely due to sampling error). When these substrates were characterized in more detail following sequential chemical extraction and X-ray diffraction techniques, it was found that the majority of metals and sulfur were retained in immobile residual forms, principally as metal-sulfides (O'Sullivan et al. 2004).

Ecological Success and Productivity

The treatment systems also demonstrated ecological success through provision of food webs and nesting niches (Table 3). Both systems were voluntarily colonized by microorganisms, algae, angiosperms, macroinvertebrates, and a variety of birds (including *Gallinula chlorpus* chicks). Organic matter contribution to the wetlands during the monitoring period (June 1997 - June 2000) was substantial, particularly by *Typha latifolia*, which averaged 700 g biomass m-2 yr-1 (O'Sullivan 2001). This vegetation additionally afforded refuge to visiting wildlife.

Discussion

Sulfate removal

Sulfate removal was calculated from a rate perspective in accordance with Hedin et al. (1994); the equivalent percent removals are also given for comparison. Initially, it was not expected that substantial sulfate would be removed from the water in the first (inflow) cell, so water sampling was not conducted in the storage header tanks and inflow pipes. However, when preliminary data showed that substantial sulfate was being removed in these inflow cells, sampling regimes were modified to include sampling for sulfate in all locations throughout the water cycle (see Figure 1). Sulfate removal was quite substantial at times, though similar removals have been reported elsewhere (Borden et al. 2002; Van Hille et al. 1999). Lower sulfate removal prior to October 1998 may be explained in part by the initial biogeochemical changes occurring in the systems, which is typical of newly created wetlands (Mitsch and Gosselink 2000). These changes would have ultimately affected the redox status and therefore the chemistry of the wetland substrates, particularly sulfate dynamics (Engler and Patrick 1973; Lefroy et al. 1993). After the systems had equilibrated (Oct. 1998), sulfate was consistently, although not completely, removed from the water. Post-equilibration, sulfate was removed less in the spring (22nd Feb. for system 1 and 29th March for system 2) and summer (8th June) of 1999 than on other dates. Apparently, less sulfate was removed during the plant-growing seasons than in the non-growing seasons. It is possible that the proliferation

Table 2. Metal removal rates (mg m^{-2} day^{-1}) calculated from differences in concentrations between water entering and exiting the treatment systems as a function of the average flow rate (1.5 L min^{-1}), n = 5. Equivalent percentage removals are also given, – implies net export of metal.

SAMPLING	SYSTEM 1		SYSTEM 2	
Zinc	mg m^{-2} day^{-1}	% equivalent	mg m^{-2} day^{-1}	% equivalent
Oct. 1997	0	0	1.82	47
Nov. 1997	4.9	95	0.52	67
Jan. 1998	0.3	50	0.52	67
		POST-EQUILIBRATION		
Nov. 1998	-0.3	-	61	98
Jan. 1999	1.3	99	34	94
Jun. 1999	1.3	71	8.9	98
Mar. 2000	5.7	67	70	99
Lead	mg m^{-2} day^{-1}	% equivalent	mg m^{-2} day^{-1}	% equivalent
Oct. 1997	-0.8	-	-0.8	-
Nov. 1997	0.8	33	0	0
Jan. 1998	-0.8	-	-0.8	-
		POST-EQUILIBRATION		
Nov. 1998	-3.5	-	0.8	25
Jan. 1999	1.6	48	2.5	60
Jun. 1999	5.8	64	5.8	47
Mar. 2000	1.1	26	6.6	50
IRON	mg m^{-2} day^{-1}	% equivalent	mg m^{-2} day^{-1}	% equivalent
Nov. 1997	2.5	85	2.0	82
Jan. 1998	0.2	99	0.2	98
		POST-EQUILIBRATION		
Nov. 1998	0.4	29	2.5	52
Jan. 1999	0.4	29	2.1	99

Table 3. Vegetation, macroinvertebrate, and bird species, as a function of their colonization time, post-completion of the systems, illustrating the degree of ecological diversity attracted to the wetland systems. Sulfate reducing bacteria (SRB) were isolated from the substrates both directly and through lab cultures. For inventories of all colonizing species, see O'Sullivan et al. (2003).

Type	# Species (Identified)	Months Post -Completion
Angiosperms	5	15
Algae	3	18
Moss	1	12
Avians	3	20
Macroinvertebrates	34 (21 Families)	15
Other Fauna	Frogs (From Spawn), Rabbits, Foxes, Shrews	11
S. R. B.	4	12

of new plant shoots/roots during growing seasons had a negative impact on, as substrates were locally, albeit temporarily, oxygenated. Oxygen leakage to rhizospheres by wetland plants such as *Typha* and *Phragmites* is well documented, particularly by young shoots (Brix and Schierup 1990; Wright and Otte 1999). The activity of SRB was not apparently inhibited during winter, possibly due to the mild temperatures characteristic of the Irish Atlantic climate. Reduced substrates resulting from biological processes, coupled with increased organic material renewal (O'Sullivan 2001), may account for generally more favorable sulfate removal rates in non-growing seasons (Borden et al. 2001).

Metal Removal

As was done for sulfate, metal removal was calculated from both a rate and percent removal perspective. Zinc concentrations in water supplied to the treatment systems were higher than background levels but considerably lower than typical mine effluent (Gao and Bradshaw 1995), probably due to substantial precipitation in the tailings storage dam. Additionally, metal concentrations in the water varied considerably, depending on the mine operations, although water supplied to system 1 was always lower in metal concentrations than that supplied to system 2 (O’Sullivan 2001). Removal of zinc and lead generally improved after the equilibration phase, presumably due to biogeochemical stabilization and maturation of the treatment wetlands. Removal was greater in system 2 than in system 1 for all metals, as would be expected given the higher loading of metals in system 2. Metal removal, as a function of sampling date, was significant for Zn (system 1; $p<0.05$, system 2; $p<0.001$) and Pb (systems 1 and 2; $p<0.001$), but this was most likely due to variable metal loading rather than seasonal effects. This explanation is supported by the strong correlation between metal loading and removal seen for Zn and Pb. It seems that the efficacy of these treatment systems to remove metals such as zinc and lead was not maximized since greater metal loading resulted in greater metal removal efficiencies. It is also possible that lead concentrations may not have been accurately measured due to insufficient detection capabilities of the instrumentation employed for measuring lead at these low concentrations.

Contaminant Fate

In all of the cells, concentrations of metals accumulating over time were significantly greater in the upper 10 cm of the substrates than at greater depth (O’Sullivan 2001) and metal sulfides were the dominant form of precipitates, as documented by O’Sullivan et al. (2004). Other studies have reported similar results (Hammack and Hedin 1995; Sobolewski 1996). Metal concentrations in below-ground biomass were significantly higher (> three-fold) than in above-ground biomass in the monocotyledons planted (O’Sullivan 2001); this is not a new phenomenon. Predominantly, it was the substrates that served as a sink for contaminant removal. However, precipitation and related processes are highly dependent on vegetation (Dunbabin and Bowmer 1992), and thus plant and substrate processes worked concurrently in removing sulfate and metals from the wastewater.

Ecological Function

Wetlands are increasingly recognized for their multi-functional roles, including habitat amenities, landscape restoration, flood control, recreational areas, and water quality enhancement via their filtering capacity (Catallo 1993; Mitsch and Gosselink 2000). The systems at Tara Mines, although initially designed, were allowed to evolve naturally. Roots and rhizomes stabilized the substrate and vegetation afforded refuge to macroinvertebrate and avian communities as well as opportunities for microbial niche establishment. Vegetation also contributed substantial amounts of carbon, renewed annually through plant die-back.

Conclusions

It is apparent that the wetland systems did not reach their treatment capacity (at least for metals) during the course of this monitoring, since an increase in metal levels exiting the systems would have otherwise been expected over time (Mays and Edwards 2001). This may have been due to insufficient metal loading (nutrient loading and removal are also correlated in the literature). Additionally, hydrogen sulfide was frequently evolved from the treatment systems (O’Sullivan 2001), indicative of metal exhaustion and/or insufficient metal loading rates in reduced systems (Hammack and Hedin 1991). Consequently, long-term treatment of sulfate in these systems may be jeopardized since substantial metal cations are required to precipitate high levels of sulfide anions. Despite substantial removal of sulfate from the wastewater, exiting sulfate concentrations were not compliant with the discharge levels (250 mg L^{-1}) stipulated in national and EU legislation.

It is reported that the performance of ecosystems increases proportionally with ecosystem complexity, hence diversity (Naeem et al. 1994; Wackernagel et al. 2002). It is reasonable to suggest that the level of diversity provided by the complex array of vegetation, macroinvertebrates, and microbes in the constructed wetlands documented here is moderately high. Furthermore, it may be speculated that successful treatment of the wastewater in these wetland ecosystems could have been influenced, in part, by the diversity developed within them.

Acknowledgements

This research was conducted at University College Dublin, Ireland. Financial support was provided by Outokumpu-Zinc Tara Mines Ireland and Enterprise Ireland. Graduate colleagues assisted during the construction of the treatment systems.

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Submitted May 9, 2003; revised manuscript submitted May 23, 2004; accepted May 25, 2004