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TECHNICAL ARTICLE

Field-scale demonstration of the potential for sewage to remediate acidic mine waters

C. D. McCullough · M. A. Lund · J. M. May

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Abstract Pit lake waters are often contaminated by acid mine drainage (AMD) from weathering of pyritic materials exposed by mining operations, leading to low pH, and high solute and heavy metal concentrations. Few cost-effective engineering solutions exist for large-scale environmental remediation of AMD-contaminated pit lakes. However, various studies have demonstrated that biological remediation strategies for remediating AMD-contaminated waters, including microbially-mediated sulphate reduction, show promise at the laboratory-scale. The addition of acidic mine water to raw sewage and workshop wastewaters in an evaporation pond provided an opportunity for a field-scale experiment as essentially a reversal of suggested in-situ treatment of acidic pit lakes by addition of organic carbon. The hyper-eutrophic evaporation pond initially contained high concentrations of nutrients, a pH > 8, high levels of sulphate (500 mg L^{-1}), and had regular algal blooms. Soon after the addition of the AMD pit water, the evaporation pond pH fell to 2.4, and electrical conductivity (EC) and most metal concentrations were elevated by one to two orders of magnitude. Over the following 18 months, the pH of the pond increased and the EC and metal concentrations decreased. After only 18 months of addition of AMD, pond water quality had returned to a level similar to that before AMD addition. These observations suggest that addition of low-grade organic materials shows promise for remediation of acid mine waters at field scale and warrants experimental investigation.

Introduction

Acid mine drainage (AMD) is the result of bacterial and oxidative processes on sulfidic minerals exposed by mining activities to water. In addition to low pH, AMD also mobilises metals and some metalloids (Banks et al. 1997). Environments receiving AMD typically show reduced environmental and social values due to direct toxicity from the low pH and elevated heavy metal and other solute concentrations. AMD continues to be the greatest environmental problem facing water management in the international mining industry (Gray 1997; Harries 1998).

Tuttle et al. (1969) were among the first to suggest the use of sulphate-reducing bacteria (SRB) for treatment of AMD. Sulphate-reducing bacteria can reverse AMD acidification by converting sulphates to sulphides in low redox environments when supplied with labile carbon sources, thus raising pH (Totsche et al. 2006). Dissolved metals then bind with sulphides to form insoluble precipitates or precipitate at higher pH as carbonates. Such *in-situ* neutralization via microbial sulphate reduction is expected to play a key role in the remediation of acidic mining pit lakes (Kleeberg 1998; McCullough 2007). For example, King et al. (1974) described the recovery of acidic mine lakes through the natural accumulation of organic matter. They advocated the acceleration of these naturally occurring sulphate reduction processes through additions of bulk organic matter such as sawdust, wheat straw, newspaper, manure, and wastewater sludge. However, most large-scale

C. D. McCullough (✉) · M. A. Lund
Centre for Ecosystem Management
and Centre of Excellence for Sustainable Mine Lakes,
Edith Cowan University, 100 Joondalup Dr,
Perth, WA 6027, Australia
e-mail: c.mccullough@ecu.edu.au

J. M. May
Xstrata Coal Queensland, Riverside Centre,
Brisbane, QLD 4000, Australia

demonstrations of AMD mine lake remediation approaches are ex-situ treatment systems such as bioreactors, anoxic limestone drains and successive alkalinity producing systems. Treatment of AMD-affected lentic water bodies by sulphate reduction is a new application of AMD mine lake remediation, with the majority of the experiments performed in microcosms (e.g. carboy vessels; Castro and Moore 1999; Fyson et al. 1998; Frömmichen et al. 2004; McCullough et al. 2006b), macrocosms (e.g. limnocorrals, Martin et al. 2003). To date, very few studies have been attempted at lake scale (e.g. Fisher and Lawrence 2006). Such up-scaling from microcosm to lake treatments is difficult as lake systems are open systems with a range of uncontrollable inputs and output (Castendyk et al. 2006), and practical considerations, such as sourcing sufficient organic matter, can be significant.

A review by Gibert et al. (2002) found that organic matter type was the prime determinant of the efficacy of SRB treatment systems, providing both a suitable redox environment and carbon source. Most published studies into the feasibility of SRB treatment systems have focused on highly labile, yet potentially expensive carbon substrates such as ethanol (Martin et al. 2003; Kolmert et al. 2001), sugar (Frömmichen et al. 2003, 2004; Pöhler et al. 2002), and cow manure (Drury 1999, 2000). However, many authors have now reported that the viability of this approach requires an organic matter source that is effective, economical, and locally available (Castro and Moore 1997; McCullough et al. 2006b). Several authors have suggested that sewage might be a useful organic matter source, as it is often readily available, economical, and rich in nutrients that can further enhance the rehabilitation processes (Costa and Duarte 2005; Davison et al. 1989; Decker and King 1973; McCullough et al. 2006b). In many remote mining locations around the world, the only bulk carbon sources available in large quantities may be green waste (a broad range of plant material collected through clearing of areas on the mine site or in towns from domestic and municipal lawns and gardens) and sewage from the site or support town (Lund et al. 2006; McCullough et al. 2006b).

Although sewage alone was not very effective, seasoned green waste and a combined mixture of sewage and green waste was found to be effective in reducing acidity, metals, and sulphate concentrations of AMD in laboratory microcosm experiments (McCullough et al. 2006b). A mixture of sewage sludge and green waste (leaf mulch, woodchips, and sawdust) also had the highest rates of sulphate reduction in permeable reactive barriers, reducing 4,500 mg L^{-1} of sulphate to <25 mg L^{-1} in only 35 days (Waybrant et al. 1998). Sulphate reduction with a mixture of sewage sludge and plant material (fresh rye grass) was effective in laboratory bioreactors in increasing pH (2.3 to >3), and reducing acidity and divalent metal concentrations of AMD waters within 30 days (Harris and Ragusa 2000). This combined mixture also proved more effective in ameliorating pH and metal concentrations than either sewage sludge (little response) or fresh plant material (no response) (Harris and Ragusa 2000).

Potential limitations of bioremediation of AMD include Postgate's (1984) assertion that SRB activities only occur at a $pH > 5$. However since then, Herhily and Mills (1985) found SRB activity in a lake at pH 2.5, and Gyure et al. (1987) in a lake at pH 2.7. Other published studies have also reported SRB activity at $pH < 3$ in an acidic pit lake sediment (Koschorreck et al. 2003) and in pH 2–3 in mine tailings (Praharaj and Fortin 2004). It now appears that less acidic microenvironments are one feature that can allow SRB activity to occur in an acidic system, and that this activity sustains and increases the size of the microenvironment (Küsel and Dorsch 2000, Küsel et al. 2001). Nevertheless, Peine et al. (2000) found that that acidification in German pit lakes was maintained by the establishment of an acidity-driven Fe cycle. This cycle is dependant on the formation of the mineral schwertmannite, constant input of Fe^{2+}, and no SRB activity below pH of 5.5. If this model is broadly applicable, then the benefits of addition of organic matter to the sediment could eventually be overcome as this Fe cycle is established. Seasonal change in ambient temperatures has also been identified as limiting rates of sulphate reduction in some studies, with reduced rates of sulphate reduction occurring over cooler seasonal periods (Benner et al. 2002; Gammons et al. 2000; Praharaj and Fortin 2004). Most bioremediation research published to date has occurred in cool-temperate areas of Europe and North America (Benner et al. 2002; Frömmichen et al. 2004; Küsel et al. 2001; Totsche et al. 2006), where water bodies may freeze over winter, effectively ceasing remediative biochemical processes.

A framework for research leading to experimentation must begin with quantified observations (Underwood 1997). As such, this study made use of an opportunity for a natural mensurative experiment at a field-scale. Following additions of AMD into a sewage evaporation pond, both previously collected and post-mixing intensified monitoring data were analyzed to provide insight into likely mechanisms responsible for water quality improvements of AMD by sulphate reduction at a field-scale.

Methods

Study area

The Collinsville Coal Project (CCP) lease is located approximately 70 km inland from Bowen on the coast of

North Queensland, Australia (147.84° East, 20.55° South). Open-cut coal mining since the mid-1950s has resulted in a number of pit lakes, all of which are seriously affected by AMD (pH 1.8–2.5) (CCP unpublished data).

The CCP Workshop Evaporation Pond 2 (WEP2) is a shallow water body used to reduce volumes of low pH and/or high salinity surface water through evaporation. In early 2003, WEP2 received large quantities of low pH AMD pit water from the 'Blake-A' open-cut mine pit dewatering operations and was nearing storage capacity. To prevent an off-lease discharge, approximately 4 million L of this water from WEP2 was pumped into approximately 80 million litre of water in Workshop Evaporation Pond 1 (WEP1) in late May 2003. WEP1 is a hyper-eutrophic artificially constructed evaporation pond that continuously receives and reduces volumes of oxidation pond treated CCP sewage and workshop wastewaters.

Sampling

A surface water sample was collected from Blake-A open-cut pit lake in August 2002. Between January 2003 and December 2004, and at approximately monthly intervals after July 2003, WEP1 was sampled on 18 occasions. On each occasion, measurements of surface water pH, dissolved oxygen (DO, mg L^{-1} saturation), temperature, and electrical conductivity (EC) were made using either a Hydrolab Minisonde or Hach Sension 156 m.

On seven of these occasions, at approximately three-month intervals, an ad hoc surface water sample was also collected for analysis of a suite of selected nutrients and metals that often differed between sampling times. Each water sample from WEP1 was split into a 250 ml filtered (0.5 µm Pal Metrigard) and unfiltered aliquot. All aliquots were stored frozen prior to analysis. A filtered aliquot was analyzed for SO_4^{2-} on an ion chromatograph (Metrohm model 7961). Filtered samples were analyzed for ammonium, NO_2^-/NO_3^- (NO_x), and filterable reactive phosphate (FRP) on a Skalar Autoanalyser, using methods adapted from APHA (1998). The remaining filtered sample was then acidified with reagent grade HCl and selected metals/metalloids analyzed by inductively coupled plasma atomic emission spectrophotometry (ICP-AES; Ca, Fe, Na) or mass spectrometry (ICP-MS; Al, Ba, Be, Cd, Cr, Co, Cu, Mn, Ni, Sb, Sn, and V). Unfiltered samples were digested using a per sulphate digestion and then analyzed as per FRP and NO_x on a Skalar Autoanalyser to determine total P and total N, respectively, according to APHA (1998). Due to confounding by high Fe concentrations, limits of detection were calculated separately for different sampling times.

In April and November 2004, a vertical profile (at 1 m intervals) of the water column was taken in the centre of WEP1. At each interval, a water sample was collected using a Kemmerer bottle, and treated as the surface water samples described above. Temperature, pH, DO, turbidity, oxidation reduction potential (*E*H) and EC were measured at each interval using a Hydrolab Datasonde 4a (April 2004) and a Hydrolab Quanta (Nov. 2004).

In November 2004, a known volume of surface water was filtered (0.5 µm Pal Metrigard). The filter paper was frozen, and following extraction with dimethylformamide (DMF) (Speziale et al. 1984), chlorophyll *a* was measured with a Schimadzu UV-1201 spectrophotometer.

Faaecal coliform abundances were determined from a single surface water sample in April 2003, four replicate samples in May 2003, and two replicates in Sept. 2004. Most Probable Numbers (MPN) were calculated for the two initial occasions and Colony Forming Units (CFU) were determined for the September sample.

On 28 September 2005, three intact sediment cores from random locations around WEP1 were also collected to the depth of the clay pond liner ($\approx$0.2 m) using a Wildco K-B Corer. Cores were divided into three different horizontal strata (upper, middle, bottom) based on sediment horizon colour and texture. Strata with identical colour and texture were pooled from the replicate cores and homogenized under helium and stored at 1.5°C. Subsamples were then taken for determination of sediment mineralogy by X-ray diffraction. To minimize exposure to air, each sample was run one at a time as both wet and dry samples from 3–70° 2θ using Cu-radiation. Counting time was weighed against the likelihood of sample oxidation with overall measurement time (ca. 30 min). Sediment subsamples were also dried for 24 h at 105°C, and then ashed for 24 h at 550°C to calculate the proportion of ash remaining. Another subsample was dried (80°C to constant dry weight) and then digested with $HNO_3/H_2O_2/HCl$ as per USEPA (2004) and analyzed with ICP-AES for the same metal/metalloid suite as for water samples.

Results

Prior to the addition of AMD water, WEP1 had water quality typical of a sewage evaporation pond, with moderate EC (0.9–1.0 mS cm^{-1}), moderately-high pH (8.4), many metal (Al, As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, V) concentrations below detection (<0.005 mg L^{-1}), and low levels of B (0.07–0.10 mg L^{-1}), Ba (0.016 mg L^{-1}), Fe (0.1 mg L^{-1}), Mn (0.2 mg L^{-1}) and Zn (0.008–0.01 mg L^{-1}) (Table 1). Concentrations of sulphate were high at 500 mg L^{-1} (Table 2) with NO_x concentrations below detection levels (<0.5 mg L^{-1}, high limit-of-detection due to confounding by high Fe concentrations) but total P at 2.4 mg L^{-1}, and a sustained algal bloom (pers.

obs.). Faecal coliforms in the water were highly variable ranging from means 800 to 8,800 MPN 100 ml^{-1} in April and May 2003, respectively.

Blake-A open-cut pit dewatering water had a low pH of 2.5, high EC 8 mS cm^{-1}, sulphate concentrations of 6,000 mg L^{-1}, high metal concentrations (in mg L^{-1}; Al = 260, Cu = 0.7, Fe = 1 200, Ni = 9, and Zn = 36) and $NO_x < 0.5$ mg L^{-1} (Collinsville Coal Project, unpublished data). This water was discharged into WEP2 until that was full; then it was transferred directly into WEP1.

Approximately 4 months after the addition of mine water to WEP1, the EC was substantially elevated at 2.4 mS cm^{-1}, while pH had decreased to 2.4 (Fig. 1). Metal concentrations were also typically one to two orders of magnitude higher for Al (15 mg L^{-1}; 5/4/04), Be (0.051 mg L^{-1}), Co (0.97 mg L^{-1}), Fe (78 mg L^{-1}), Mn (15 mg L^{-1}), Ni (1.6 mg L^{-1}) and Zn (4.6 mg L^{-1}). Boron (0.16 mg L^{-1}), Ba (0.023 mg L^{-1}), Cu (0.009 mg L^{-1}), and Se (0.008 mg L^{-1}) showed only an approximate doubling in concentration. Molybdenum showed a minor decrease in concentration, to 0.008 mg L^{-1}.

Table 2 Sulphate and nutrient concentrations (mg L^{-1}) in surface waters of WEP1 pre- and post-addition of mine water from WEP2

Date	SO_4	NH_4^+	NO_x	Total N	FRP	Total P
16/01/03	500	–	<0.5	–	–	–
07/04/03	–	–	–	–	–	2.4
03/10/03	1,900	–	11	–	–	1.3
09/01/04	1,300	–	4.4	–	–	0.4
05/04/04	690	–	1.2	–	–	0.3
23/04/04[a]	877	10.23	0.1	–	0.02	0.12
03/07/04	814	–	30.7	–	–	–
06/10/04	733	–	0.34	7.3	–	3.0
12/11/04[a]	665	0.16	0.05	1.6	3.63	6.01

– No data collected, dark line indicates when mine water was added

[a] Data taken from the centre of the lake, during vertical profiles

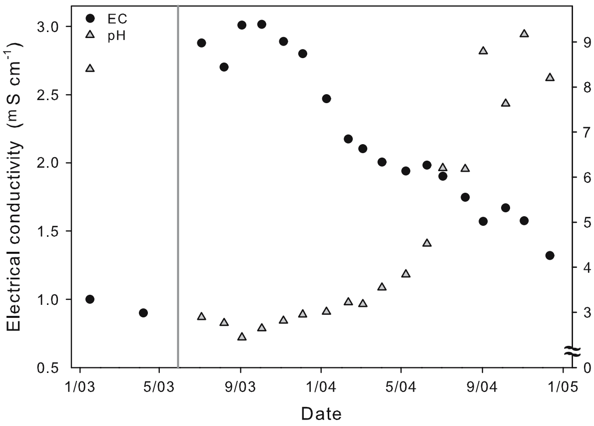

Fig. 1 Electrical Conductivity (EC) and pH of surface water from WEP1 pre- and post-addition of mine water from WEP2. *Dark grey line* indicates date of addition of pit AMD water to WEP1

In the 18 months after addition of AMD, water quality dramatically improved in WEP1. WEP1 pH rose from 2.4 to 7.9, increasing at a greater rate once pH 4 was reached (Fig. 1). Concomitantly with pH increase, EC declined from 2.4 to 1.5 mS cm^{-1}. Although there is limited data for the conservative elements Ca, K, Mg, and Na; concentrations did not appear to change in the 11 months post-addition (mean ± standard error in mg L^{-1}; Ca 133 ± 6.7, K 15 ± 0.3, Mg 85 ± 7.3, Na 127 ± 6.7 mg L^{-1}). Concentrations of Sb, Cd, Cr (0.006 mg L^{-1} on 5/4/04), Pb (0.02 mg L^{-1} on 5/4/04), all decreased. Sn and V remained generally <0.005 mg L^{-1} both pre- and post-addition. Arsenic also was generally below detection at <0.001 mg L^{-1}, except on 5/4/04 when As reached a concentration of 0.011 mg L^{-1}. By November 2004, other metal concentrations had decreased by around an order of magnitude of immediate post-addition concentrations with 0.05 mg L^{-1} for Al, 0.001 mg L^{-1} for Be (23/4/04), 0.023 mg L^{-1} for Ni, and 0.004 mg L^{-1} for Zn. Cu had

Table 1 Metals and metalloid concentrations (mg L^{-1}) in surface waters of WEP1 pre- and post-addition of mine water from WEP2

Date	Al	Ca	Ba	Be	Co	Cu	Fe	Mn	Na	Ni	Zn
16/01/03	<0.005	90		<0.005	–	<0.005	0.1	–	–	<0.005	0.01
07/04/03	–	–	0.016	<0.005	<0.005	<0.005	–	0.2	–	<0.005	0.008
03/10/03	–	140	0.023	0.051	0.97	0.009	78	15	120	1.60	4.60
09/01/04	–	120	0.024	0.038	0.76	0.011	12	12	120	1.10	3.70
05/04/04	15.0	140	–	–	0.47	0.015	3.5	10	140	0.77	1.60
23/04/04[a]	7.3	120	–	0.001	0.30	0.002	1.6	6.9	–	0.49	0.93
03/07/04	0.42	–	–	–	0.21	0.002	0.7	6.6	–	0.36	0.56
06/10/04	0.01	–	–	–	–	–	–	–	–	–	–
12/11/04[a]	0.05	74	–	–	0.003	<0.001	6.9	–	–	0.023	0.004

– No data collected, dark line indicates when mine water was added

[a] Data taken from the centre of the lake, during vertical profiles

decreased to below detection levels by November 2004. Fe concentrations had declined to 1.6 mg L^{-1} on 23/4/04 (still an order of magnitude higher than pre-addition), but in November 2004 had risen again to 6.9 mg L^{-1}. Sulphate concentrations decreased to 665 mg L^{-1}, which was only marginally higher than the pre-addition concentrations. Following AMD addition, NO_x concentrations showed an initial increase from <0.5 to 11 mg L^{-1}, but then declined to 0.1 mg L^{-1} by late April 2004. On 3/7/04, NO_x peaked at 31 mg L^{-1} but by November 2004 had decreased to 0.05 mg L^{-1}. This peak in NO_x occurred approximately two months after high ammonium levels (10.2 mg L^{-1}) were recorded in WEP1, suggesting that it might be the result of nitrification. Post-addition FRP concentrations were moderate in April 2004 (0.02 mg L^{-1}) before reaching very high levels in November 2004 (3.63 mg L^{-1}). Total P declined initially to 1.3 mg L^{-1} post addition and had decreased to 0.12 mg L^{-1} by April 2004, before reaching 6.06 mg L^{-1} in November 2004. FRP showed a similar pattern to total P.

After addition of mine water, rushes around the edge of the pond died. The water cleared as the algal bloom ceased, an orange precipitate (presumably FeOOH) covered all surfaces, and dissolved oxygen concentrations were at 1.3 mg L^{-1}. Phytoplankton blooms returned to WEP1 (pers. obs.) in April 2004 (turbidity around 11 NTU) and reached a hyper-eutrophic chlorophyll *a* of 50 µg L^{-1} in November 2004. Faecal coliforms in WEP1 in September 2004 were 210 CFU 100 ml^{-1}, which indicate a reduction in faecal coliforms due to toxicity, low pH, or changes in inflows.

Water temperature profiles taken on 23/4/04 showed stratification (3°C change over 1 m); with a hypolimnion beginning 0.5 m above the sediment surface (Fig. 2a). Dissolved oxygen levels were lower immediately below the epilimnion around 1.2 mg L^{-1}. Thermal stratification was less pronounced on November 2004, possibly due to lower water levels. However, the epibenthic water was hypoxic. On 23/4/04, the surface water was supersaturated with DO (9.1 mg L^{-1}) while on November 2004, there was only 5.9 mg L^{-1}. On both occasions, *E*H decreased from >500 mV at the pond surface to <200 mV near the benthos; on 23/4/04, this drop was only seen in the hypolimnion (Fig. 2b). A strong sulphide smell was observed on both hypolimnion sampling events. Furthermore, the pH on 23/4/04 increased from 3.6 at the surface to ≈6 in the hypolimnion (Fig. 2b). Although most hypolimnion dissolved metal concentrations differed little from the epilimnion. In the hypolimnion Al was an order of magnitude lower, Zn was lower, and Fe was an order of magnitude higher (Table 3). EC was 7% lower in the hypolimnion than in the epilimnion (1.84 and 1.97 mS cm^{-1}, respectively). Sulphate concentrations varied through the profile but hypolimnetic concentrations were very similar to surface concentrations (Table 4). On November 2004, pH decreased slightly with depth (from ≈8 to ≈7) and EC was unchanged throughout the profile. The decline in nitrogen compound concentrations between April and November 2004 is likely due to denitrification in the hypolimnion and sediment. The bottom waters on both occasions also contained elevated concentrations of total P and FRP concentrations (Table 4), probably through redox mediated release from Fe compounds. Although N concentrations changed little with depth, NO_x showed a slight increase at the bottom in November. This increase was contrary to expectations of denitrification in the reducing hypolimnion environment.

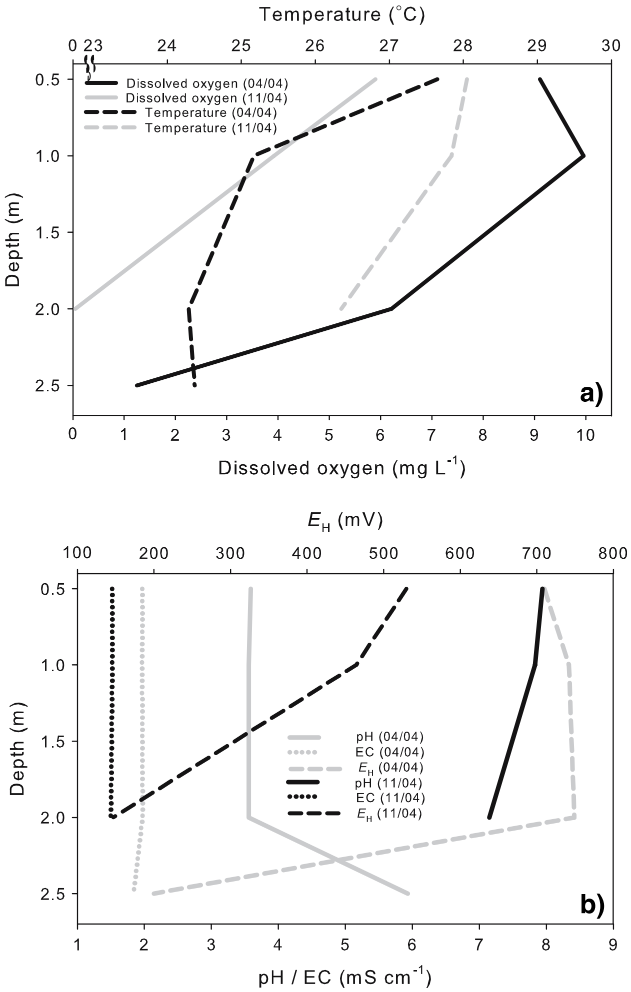

Fig. 2 Vertical profile **a** temperature and DO and **b**. *E*H, pH, and electrical conductivity (*EC*) in WEP1 on 23 April (04/04) and 12 November 2004

The WEP1 sediment mineral composition 2 years post-addition (September 2005) is shown in Fig. 3; metal concentrations are provided in Table 5. Se concentrations were below detection and K concentrations were similar in all

Table 3 Vertical profile of selected ion concentrations (mg L^{-1}) 11 months (April 2004) and 18 months (November 2004) after addition of mine water to WEP1

Depth (m)	Al		Cd		Co		Cu		Fe		Mn		Ni		Zn	
	Apr	Nov	Apr	Nov	Apr	Nov	Apr	Nov	Apr	Nov	Apr	Nov	Apr	Nov	Apr	Nov
0.0	7.30	0.05	0.001	<0.001	0.3	0.003	0.002	<0.001	1.6	6.90	6.9	0.520	0.49	0.049	0.93	0.004
1.0	6.40	<0.01	0.003	<0.001	0.26	0.003	0.005	<0.001	2.2	0.19	6.0	0.027	0.43	0.021	0.92	0.002
2.0	5.10	<0.01	0.001	<0.001	0.2	0.003	0.001	<0.001	1.2	0.01	4.7	0.480	0.34	0.023	0.64	<0.002
2.5	0.66		0.007		0.19		0.002		12		6.3		0.42		0.39	

Table 4 Vertical profile in the water column of nutrient concentrations (mg L^{-1}) in WEP1 11 months (April 2004) and 18 months (November 2004) after the addition of mine water (*FE* high concentrations of Fe raised detection total N limits too high to permit determination of these total N concentrations)

Depth (m)	SO_4		NH_4^+		NO_x		Total N		FRP		Total P	
	Apr	Nov	Apr	Nov	Apr	Nov	Apr	Nov	Apr	Nov	Apr	Nov
0.0	877	665	10.2	0.16	0.10	0.05	FE	1.6	0.02	3.6	0.12	6.06
1.0	1,032	661	13.0	0.06	0.11	0.05	FE	1.5	0.02	3.9	0.13	5.82
2.0	817	619	10.7	0.14	0.11	0.08	FE	4.9	0.02	11	0.23	18.3
2.5	906		13.8		0.10		16.9		0.08		0.83	

strata. Cd concentrations were low, but still an order of magnitude higher in the lowest strata. Cu concentrations increased with depth in the sediment. The lower B concentrations in the upper strata might be due to release from the sediments, which could account for the increasing concentrations seen in the overlying water. Considering the continuous inputs of sewage, WEP1 sediment samples contained only moderate amounts of organic material (27.5, 24.5 and 6.7% for upper, middle and bottom strata, respectively). All sediment samples showed a significant amorphous mineral peak, even after drying. The mineralogy of all sediments was dominated by alpha quartz and kaolinite ($Al_2Si_2O_5(OH)_4$) (Fig. 3). Kandite group minerals, mainly dickite and kaolinite, possibly some nacrite, and some zeolite and goethite were present in the bottom strata. Al concentrations were similar in the upper and middle strata (22 and 27 g kg^{-1}, respectively) but declined in the lowest strata to 15 g kg^{-1}. The distribution of Al is very similar to the distribution of the major Al minerals, kaolinite and muscovite ($KAl_2(AlSi_3O_{10})(F, OH)_2$)) which declined as a proportion in the bottom strata. Ca concentrations were similar in upper and middle strata (11 615 and 10 108 mg kg^{-1}, respectively) but increased substantially in bottom strata to 77,536 mg kg^{-1}, consistent with distribution of gypsum ($CaSO_4.2H_2O$) which was only recorded in the bottom strata (12%) (Fig. 3). Although the sulphur mineralogy present was generally very poorly crystalline, pyrite (FeS_2) was present in the bottom strata, however pyrite was mainly found in the upper and middle strata (4, 9, and 1%, respectively, for upper, middle, and bottom strata) (Fig. 3). Sulphur increased significantly with depth (17–68 g kg^{-1}), while Fe was highest in the middle strata and lowest in the bottom strata (36, 58, and 17 g kg^{-1} for upper, middle, and bottom strata, respectively), reflecting pyrite and poorly crystalline minerals in the upper and middle strata and gypsum and poorly crystalline minerals in the bottom strata. It appears that the upper and middle strata were laid down after the mine water addition, when the increased availability of Fe led to the preferential formation of pyrite instead of gypsum. As pyrite is an end product of

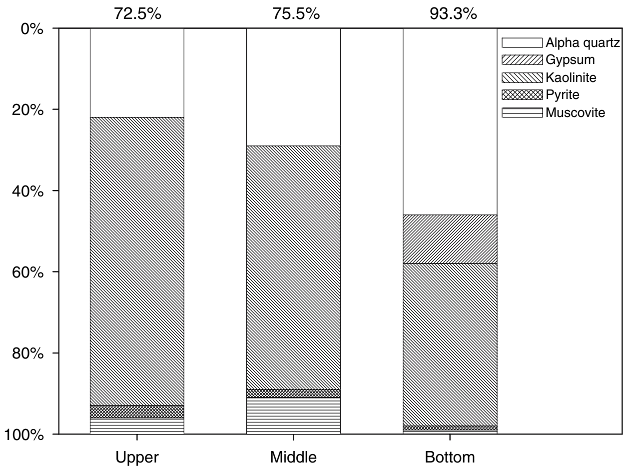

Fig. 3 Mineral composition of strata from WEP1 sediments (as a proportion of %Ash) collected in September 2005 (% ash shown on top of each column)

Table 5 Sediment concentrations (mg kg^{-1}) of selected analytes from strata (upper, middle, or bottom) at WEP1

Element	Upper	Middle	Bottom
Al	22,352	26,605	15,013
Ca	11,615	10,108	77,536
Cd	0.2	0.1	1.8
Co	73	68	2
Cr	15	11	5
Cu	27	63	102
Fe	35,498	58,087	17,451
Mn	825	628	52
Na	973	629	242
Ni	126	106	4
Pb	20	26	12
S	17,371	41,496	67,757
Zn	632	378	194

sulphate reduction, this is evidence that sulphate reduction is the process most likely responsible for the overall improvement in post-addition water quality. Declines in the water column concentrations of As, Co, Cr, Mg, Na, Ni, Pb, and Zn over time are reflected in their accumulation in the upper and middle strata, presumably as metal sulphides.

Discussion

This project observed an addition of AMD waters to a hypertrophic water body as essentially a reversal of suggested in-situ treatment of acidic pit lakes by the addition of organic carbon. In approximately 18 months, hypertrophic 80 million literes WEP1 remediated 4 million literes of highly acidic and contaminated mine waters to a condition comparable to that found in WEP1 pre-addition. Sulphate (and, to a lesser extent, nitrate) reduction in WEP1 appears to have been responsible for the remediation of water quality.

Given that the function of the pond was to evapo-concentrate the water, a general trend towards increased concentrations of these solutes and increasing EC was expected. Adding mine water also raised EC and solute concentrations substantially, and so an increase in EC or solute concentrations was expected over the study. Nevertheless, over the monitoring period, there was a substantial reduction in water concentrations of solutes, and differences in metal concentrations and mineralogy of new sediments overlying older WEP1 sediments.

Metal and sulphate concentrations decreased with *E*H down the water column profile, suggesting increased sulphate reduction rates at hypoxic deeper lake depths. Concomitant decreases in metal and sulphate concentrations over time provide evidence for biologically mediated sulphate reduction as the process removing metals and sulphate with most of the metals likely precipitated as insoluble sulphides (Frömmichen et al. 2004; Totsche et al. 2006). Although hypolimnion waters were low in both DO and *E*H, it is likely that SRB activity would still have been greatest in benthic sediments where lower *E*H conditions existed. Given the high pH achieved, most of the remaining metals are likely to have been precipitated as insoluble oxyhydroxides or as amorphous sulphur minerals (probably metal monosulphides (Suits and Wilkin 1998) in the upper and middle sediment strata. The middle strata contained moderate amounts of pyrite, which was probably derived from secondary mineralisation of the amorphous minerals (Frömmichen et al. 2003; Praharaj and Fortin 2004). The presence of gypsum as the main sulphur mineral in the bottom strata may suggest that this stratum was laid down prior to the mine water addition, when the lower Fe concentrations in the water would have favoured gypsum rather than pyrite formation. However, the dramatic and rapid decrease in sulphate concentrations between October 2003 and April 2004 (Table 2), well before hypolimnion conditions favoured sulphate reduction, indicates that addition of AMD suddenly increased sulphate concentrations, causing pond water to be saturated for gypsum ($CaSO_4$) at higher pH. This common ion interpretation is also supported by reduced calcium concentrations in November relative to earlier pre- and post-filling sampling times. The presence of a small proportion of pyrite in the bottom strata reveals that sulphate reduction was occurring prior to AMD addition and may have been limited by sulphate availability prior to AMD addition.

Following AMD addition in May 2003, decaying algal matter may have stripped metals from the water column (McCullough 2007). The biochemical oxygen demand of algal and sewage decay would further made the hypolimnion anoxic and produced added alkalinity through denitrification (Abril and Frankignoulle 2001), further contributing to overall water quality remediation. The algal bloom in April 2004 occurred despite high concentrations of Al (7.3 mg L^{-1}) and Fe (1.6 mg L^{-1}) in the water (ANZECC/ARMCANZ, 2000), both of which are strongly bound by P (Kopacek et al. 2000). Concentrations of Al and Fe subsequently declined, which likely further reduced binding of P, allowing more algal growth (Kleeberg 1998).

In November 2004 (18 months post-addition), water column concentrations of Al, Cd, Cu, Fe (except for a single high surface result), Mn, and Zn were all below national environmental protection guideline values for neutral pH waters of moderate hardness (ANZECC/ARMCANZ 2000). Reduction of Mn may also have contributed in a small part to alkalinity generation (Abril and Frankignoulle 2001). The single high surface water concentration of iron was likely due to rapid oxidation of amorphous Fe monosulphide following increased oxygen concentrations resulting from algal blooms (Simpson et al. 1998). Only Ni concentrations exceeded the guidelines, in the epilimnion by five times, and by only twice in the hypolimnion.

One explanation for high rates of SRB activity at the low pH of this study is the likely existence of alkaline microenvironments (Miller et al. 1996) in the hypertrophic WEP1 benthic sediments prior to AMD addition. SRB generation of alkalinity within these microenvironments would be expected to have maintained and expanded these higher pH regions, resulting in successful SRB activity even at low overlying water pH (Küsel and Dorsch 2000; Küsel et al. 2001). Nevertheless, accelerated rates of sulphate reduction above pH 4 have also been observed and are thought to be due to reductions in buffering of acidity as aluminium was hydrolyzed and precipitated (King et al. 1974).

The high rate of sulphate reduction encountered with bulk materials in this tropical clime study may be due to elevated sulphate reducing bacteria activity at higher maximum and mean temperatures (Praharaj and Fortin 2004). Consequently, the higher temperatures at Collinsville, even during the Dry season (20–28°C; Commonwealth of Australia Bureau of Meteorology, 09/02/2005) are likely to have increased overall biochemical rates of sulphate reduction compared with temperate Europe and North America. For example, at a mean ambient Dry season temperature of 20°C, McCullough et al. (2006) found that municipal green waste and a mixture of semi-dried green waste and sewage sludge were equally effective at remediating highly acidic AMD water of metals, with pH increases to circum-neutral in only 5 months.

Financially viable treatment by biological remediation using bulk materials may provide lasting solutions to AMD water quality issues in even remote mining areas. Indeed, a viable end use for remediated mine water may involve its use in mining operations, such as for dust suppression, where only a low quality is required (McCullough and Lund 2006). To this end, further research into sulphate reduction and other biological remediation strategies is likely to be of increasing interest and application to mining companies, regulatory authorities, and regional stakeholders.

Overdosing with organic material, leading to hypereutrophication, remains an important consideration for ad hoc applications of this technology when a treatment aim is for high water quality (King et al. 1974). However, this study demonstrates that the corrective measures for very acidic, hard-water mining lakes are likely to differ greatly from those used for eutrophication control (Klapper 2003). Consequently, both researchers and regulatory agencies need to maintain an open mind about these novel passive AMD treatment options.

In conclusion, the remediation of the low pH and high heavy metal concentrations in the mine waters added to WEP1 indicates that the general approach is feasible. While biological remediation processes are complex and still poorly understood (Klapper and Geller 2002), hypotheses drawn from these observations suggest: (1) warmer tropical climates than encountered in previous studies may have led to a synergistic effect upon remediation rates, (2) readily available and cheap bulk organic materials (such as sewage) show potential for field-scale AMD remediation, and (3) contrary to much literature, $\mathrm{pH} < 5$ do not appear to have prevented effective sulphate reduction and other remediation reactions in this study. This study suggests that sulphate reduction remediation may prove useful as an in situ treatment for AMD pit lakes, or even ex situ in bioreactors.

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