BIOLOGICAL REMEDIATION OF LOW SULPHATE ACIDIC PIT LAKE WATERS WITH LIMESTONE PH NEUTRALISATION AND NUTRIENTS

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ABSTRACT

Pit lake water in Collie is typically acidic due to Acid Mine Drainage (AMD) caused by pyrite oxidation and ferrolysis coupled with a low natural buffering capacity in surrounding geologies. These pit waters have typically low sulphate, Fe and heavy metal concentrations. Nevertheless, Collie pit lakes have low biological productivity probably due to Al toxicity and low nutrient concentrations. Lake Kepwari (24 GL, max depth 65 m) is an acidic former coal open cut mine in Collie (Western Australia) that has been extensively revegetated and contoured for a water-ski park to facilitate its relinquishment back to the State. The main water treatment approach was rapid fill by river diversion but this has failed to prevent ingress of Fe^{2+} rich groundwater which has reduced pH to 4.8. In a manipulative mesocosm experiment using 1,200 L enclosures containing Lake Kepwari sediment and water, a control and three treatments were replicated three times. Treatment one, acidity was neutralised to pH 7 with powdered limestone, two had P concentrations maintained at eutrophic levels of approximately 20 µg L^{-1} (using K_2HPO_4), and three combined these same liming and P additions. Mesocosms were monitored for water quality (physico-chemical, nutrient and metal parameters) at 0, 77, 140, 191 and 255 days after establishment.

Rainfall dilution resulted in the pH of the control increasing slowly from 4.8 to 6.5. Neutralised treatments remained circum-neutral, whilst P addition alone produced a higher final pH of >7. Sulphate concentrations fell slightly in all mesocosms by about 10 mg L^{-1}, presumably due to SO_4^{2-} reduction or secondary mineralisation. In the treatments with P additions, stimulation of NO_3^{2-} reduction appeared to be the principal mechanism for increasing pH above those of the control. Addition of P had the additional benefit of reducing toxic mono-valent Al concentrations; probably by co-precipitation.

This study demonstrated that P additions alone might be a useful remediation approach for the Collie pit lakes, although remediation effectiveness is enhanced with concurrent limestone neutralisation. This combined approach, in addition to ongoing alkalinity production by nitrate reduction and primary production, may facilitate these lakes remaining circum-neutral over longer periods of time than single acidity neutralisation treatments alone.

1. INTRODUCTION

Water filled mining pits are a common legacy of open cut mining worldwide (Castro and Moore 1997). In Western Australia (WA) there are approximately 1,800 existing mine pits with more than 150 mines currently operating below the water table (Johnson and Wright 2003). Unless backfilled, many of these pits will eventually fill with ground and surface water to form pit lakes. These have the potential for a range of beneficial end uses including recreation, biodiversity conservation, stock and plant irrigation, aquaculture, extraction of industrial chemicals and as sources of potable and industrial water (McCullough and Lund 2006). The water quality in pit lakes; in particular acidity, salinity, hardness and metal composition, differ depending on the hydrology and geochemistry of the local and surrounding areas (Miller *et al.* 1996). As water quality in these lakes rarely meets end user water quality guidelines, remediation may be required for beneficial end uses to be realised (McCullough and Lund 2006).

Water acidification is a common problem of pit lakes and is mainly the result of oxidation of pyritic (FeS_2) geologies and subsequent oxidation of Fe (ferrolysis) (Castro and Moore 1997). Pit lake acidification can occur from oxidation of exposed overburden and pit wall geologies, AMD runoff into the lake and groundwater inputs. Acidification may cause toxicity to aquatic biota through its effects on the increased bioavailability of other toxicants, particularly Al and heavy metals (Lopes *et al.* 1999). Aluminium is generally thought to be responsible for pH buffering *ca.* pH 4.5–5.5 and toxicity (directly or indirectly) of moderately low pH lakes (pH 3–5) (Stephens and Ingram 2006). Aluminium toxicity derives from its replacement of divalent metal complexes, specifically Ca and Mg (Amonette *et al.* 2003). In acidified lakes it may also affect biota and nutrient cycling by reducing bioavailability of P (Kopacek *et al.* 2000). Phosphorus is removed from the water column by co-precipitation with Fe and Al oxyhydroxides (Lessmann *et al.* 2003), resulting in P limitation (Bittl *et al.* 2001). Therefore primary production in acidic lakes is typically limited by low ratios of P to N (Schindler 1980). Primary production of organic carbon by *in situ* biological communities is a weak process that can contribute to both alkalinity production and heavy metal removal (Davison *et al.* 1995; Tittel and Kamjunke 2004; McCullough 2007). Autotrophs may produce alkalinity *in situ* during carbon fixation when NO_3^{2-} (often high in pit lakes as a result of leached blasting residues) is biologically assimilated into organic matter, as in equation 1 after

Davison *et al.* (1995).

Equation 1.

$106CO_2 + 16H^+ + 16NO_3^- + H_3PO_4 + 122H_2O \rightarrow (CH_2O)_{106}(NH_3)_{16} + 16OH^- + 138O_2 + PO_4^{3-}$

When organic matter is anaerobically decomposed further alkalinity is also produced through denitrification (Davison et al. 1995), as in equation 2.

Equation 2.

$NO_3^- + CH_3OH + H_2CO_3 \rightarrow N_2 + H_2O + HCO_3^-$

Biogenic assimilation of heavy metals also occurs within cells of planktonic biota; either deliberately as trace minerals through metabolic uptake, adsorption to cell walls, or incidentally through uptake of non-essential cations as analogue ions (Akber *et al.* 1992; Markich and Jeffree 1994). Metal removal by biota such as phytoplanktonic algae, requires conditions conducive to their growth and survival. Although low pH will modify algal community structure, actual phytoplankton biomass, through selection for smaller-celled species, may still be high provided there is sufficient nutrient availability (Lessmann *et al.* 2000; Woelfl 2000). Consequently, enhanced primary production and more natural ecosystem food-web functioning may occur when the low nutrient status of acidic pit lakes is addressed. However, the size of these primary producers may limit their availability to larger organisms (fish, waterfowl, etc.) higher up the food-chain. Furthermore bioaccumulation of metals in phytoplankton may pose a toxicity risk to organisms further up the food chain.

The potential impacts of, and remediation efficacy on acidification and metal contamination on aquatic environments, are often studied in mesocosms (Fyson *et al.* 1998; Bortnikova *et al.* 2001; Collins *et al.* 2005; Totsche *et al.* 2006). Mesocosms allow experiments to be undertaken at a more natural scale (compared to bench studies) and are easily replicated; an approach that is difficult to achieve in the field (McCullough 2009).

In Collie, the coal mining centre of Western Australia (WA), the WO5B open cut mine pit was filled with a mixture of ground and river water following the completion of coal mining and cessation of dewatering in 1999. As part of the rehabilitation of the new ‘Lake Kepwari’ prior to filling, acid-producing overburden dumps and un-mined coal seams along the lake margin were covered, battered and revegetated with native flora by direct seeding. In order to further reduce wall exposure and consequent acid production, Lake Kepwari was rapid-filled in 2005 by diversion of flow from the South Branch of the Collie River over the three preceding winters (Salmon *et al.* 2008). The current volume of Lake Kepwari is 24 GL, with a maximum depth of the lake of 65 m and surface area of 10 ha. Winter river diversions still occur when there is sufficient river flow and storage capacity within the lake. A source of Fe^{2+} entering via groundwater is believed to continue to reduce lake pH through ferrolysis, with the lake having seasonally low pH (~ 4.8) and elevated metal concentrations (Evans *et al.* 2007). Remediation of Collie pit lakes has seen limestone acidity neutralisations and organic matter and P additions (Lund *et al.* 2006; Evans *et al.* 2007). These treatments aim to remediate lake water toxicity through reducing metal solubility at increased pH and through increased algal growth. Limestone was used to increase pH to levels suitable for biotic growth and survival through reducing H^+ ions, dissolved metal and other contaminant concentrations (Lopes *et al.* 1999). However, the main limiting nutrient in freshwater pit lakes is typically P (Schindler 1980). The aim of this study was to evaluate the efficacy of treatments of limestone neutralisation and P enrichment for remediation of acidic yet poorly buffered and low SO_4^{2-} mine waters.

2. METHODS

In August 2005, sufficient water and sediment (dredged from 5 m depth) was transported from Lake Kepwari to Edith Cowan University (Perth, WA) to add to twelve fibreglass tubs (1.3 m diameter, 1.0 m depth and a working volume of 1,200 L). Three treatments and an untreated control were replicated three times and arranged in a randomised block design. The control (C) contained un-treated Lake Kepwari water and sediment while treatments consisted of L which was neutralised with ground limestone chip to pH neutral in two stages to prevent over-neutralisation; and PA which was amended with P (as K_2HPO_4) to increase the filterable reactive phosphorus (FRP) concentration to around 20 µg L^{-1}; and L&P which combined the L and PA treatments. In the PA experiment, P additions were conducted on days 2, 80, 161, 172, 189, 203, 219 to maintain the desired FRP concentration of around 20 µg L^{-1}.

Commencing in November 2005, water quality parameters of each mesocosm were measured on days 2, 24, 36, 77, 140, 172, 191, 242 and 255. Measurements included temperature, pH, dissolved oxygen (% saturation and mg L^{-1}), specific conductance, chlorophyll *a* concentrations and ORP (Pt reference electrode) and were collected *in situ* with a Hydrolab Datasonde 4a. Water samples were collected (days 77, 140, 191 and 255) from mesocosms and were divided into three aliquots; two were filtered through 0.5 µm glassfibre filter paper (Pall Metrigard) and frozen prior to analysis. One set of filtered samples was analysed for SO_4^{2-} and Cl^- on an ion chromatograph (Metrohm model 7961); ammonium, NO_x and FRP were analysed on a Skalar Autoanalyser after APHA (1998), and non-purgeable organic carbon (NPOC) on a Shimadzu Carbon Analyser. The second filtered sample was acidified to 1% with reagent grade HCl and selected metals analysed by Inductively Coupled Plasma Atomic Emission Spectrophotometry for Al, As, B, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, K, Mg, Mo, Mn, Na, Ni, Sb, Se, Sn, V and Zn.

The third unfiltered aliquot was frozen prior to later digestion with persulphate and then analysed as per FRP and NO_x on a Skalar Autoanalyser to determine total P and total N respectively according to APHA (1998).

3. RESULTS

pH increased in all mesocosms from 4.8±0.1 to 6.4±0.1 (C), 7.3±0.1 (L), 7±0.1 (L&P) and 6.7±0.0 (PA) by day 55 (Figure 1). pH increased markedly following the initial neutralisation with limestone to >7.5 before returning to circum-neutral after Day 100 (Figure 1). In the PA treatments, P alone produced a consistently higher pH after Day 100 than the control in the order of 0.2–0.5 pH units. This increased pH was not replicated in the L&P treatment when compared to L.

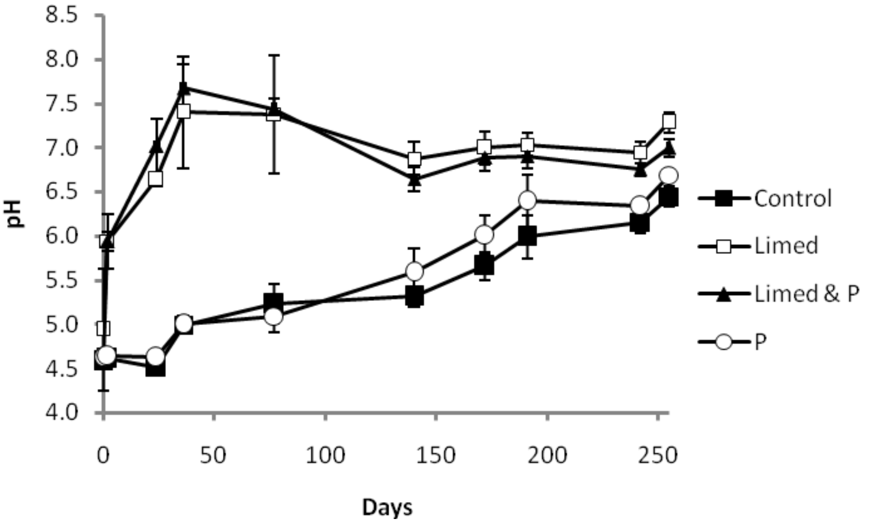

Figure 1. Mesocosm pH over time in response to limestone neutralisation and P amendment.
Error bars are single standard errors of the mean.

Specific conductance changed little over the course of the experiment or between treatments, and ranged between 2.4 and 2.6 mS cm^{-1}. ORP of the water remained positive at between 80–110 mV which is a range suitable for denitrification and reduction of Mn and Fe (120 mV). The water was generally saturated with dissolved oxygen which ranged from 70–118 %. Chlorophyll *a* was detected on occasion in individual mesocosms, but overall concentrations remained low at <5 $\mu g\ L^{-1}$.

This study did not sample metals and nutrients in Lake Kepwari when the water was initially collected, but data on the lake are available for the 2/5/05 (Department of Environment, WA) and 27/7/05 (U. Salmon, University of Western Australia *pers. comm.*). Nutrient and metal concentrations within the lake vary little seasonally (except during periods of river inflow) (Evans *et al.* 2007) therefore these dates are considered to be representative of the day 0 mesocosm data. Concentrations of ammonia dropped from 195 μgL^{-1} in the lake to 16±2 (C), 11±4 (L) and <3 μgL^{-1} in the PA experiment with P added after day 255. NOx dropped from 1,000 μgL^{-1} in the Lake to 61±34 to 6±1 to <3 μgL^{-1} in the PA test. The lake had only 0.04% of its N in a form other than NOx and ammonia, however in test C this increased to 20%, 5.4% in test L and 2.2% in tests PA and L&P. FRP was marginally higher in the mesocosms than the lake (2 μgL^{-1}), reaching 19±4 μgL^{-1} in the PA treatment. NPOC increased over the experiment from 0.5 mgL^{-1} in the lake to 71±34 mgL^{-1}in the control to >136 mgL^{-1} in the L&P treatments. Sulphate concentrations declined by about 20% in all the treatments by day 255 compared to the lake (100 mgL^{-1}) suggesting sulphate reduction or secondary mineralisation had occurred. A similar trend was seen for S.

Metals and metalloid concentrations on Day 255 are compared to initial Lake Kepwari (day 0) water and ANZECC/ARMCANZ Water Quality Guidelines for Protection of Aquatic Ecosystems (95% of species) (ANZECC/ARMCANZ 2000) in Table 1. Lake Kepwari water had metal concentrations that exceed the guidelines for Al, Co, and Zn. By day 255, Zn, Ni and Cu all decreased by about 50% in the control and PA treatment, and by 80% in the limestone neutralised treatments (L). Aluminium decreased by over 95% in all treatments and the control but concentrations were approximately twice as high in the limestone neutralised treatments (L) compared to the control and PA treatment. Iron concentrations declined by 95% in the control but only around 90% in the treatments. Manganese and Co dropped around 50% in the control and over 95% in the treatments. After 255 days concentrations of Al (control only), Co, and Zn although greatly reduced still exceeded the guidelines. Phosphorus addition had minimal effect on most metal levels but did substantially reduce Mn and Co compared to the control. Limestone neutralisation appeared to marginally increase concentrations of Al, although due to the higher pH, concentrations fell below the guideline.

Limestone neutralisation also successfully reduced concentrations of Zn compared to the control and PA but not below the guideline level. Calcium concentrations for un-neutralised treatments were around 30 mg L^{-1}, and for limestone neutralised treatments were around 35 mg L^{-1}. Sodium, K and Mg concentrations remained largely unchanged throughout the experiment, across all treatments. Boron concentrations increased from <15 μgL^{-1} to >80 μgL^{-1} by day 255 across the control and all treatments, presumably this indicates release from the sediments.

Table 1. Mean (±SE) of water quality parameters taken from Day 0 (or Lake Kepwari) or Day 255 from treatments. ANZECC/ARMCANZ (2000) metal and metalloid concentration guideline values for the protection of 95% of species in aquatic ecosystems are shown.

		Guideline	Day 0	Day 255			
Parameter	Units	value	Lake	Control	Limed	Limed & P	P Addition
pH			4.69 ± 0.1*	6.45 ± 0.06	7.28 ± 0.07	6.99 ± 0.06	6.69 ± 0.04
Dissolved O_2	%		102.2 ± 0.3*	84.7 ± 0.7	88.0 ± 0.6	81.3 ± 1.1	87.4 ± 2.7
Dissolved O_3	mgL^{-1}		10.1 ± 0.0*	8.3 ± 0.1	8.5 ± 0.1	7.8 ± 0.1	8.4 ± 0.1
Specific Conductance	$mScm^{-1}$		2.50 ± 0.01*	2.47 ± 0.03	2.49 ± 0.04	2.50 ± 0.04	2.45 ± 0.07
ORP	mV		190 ± 3*	143 ± 10	120 ± 7	126 ± 4	125 ± 3
Chlorophyll *a*	μgL^{-1}		0.15 ± 0.07*	0.70 ± 0.67	0.00 ± 0.00	0.72 ± 0.38	0.00 ± 0.00
Ammonia	μgL^{-1}		195#	16 ± 2	11 ± 3	3 ± 1	3 ± 0
NOx	μgL^{-1}		1000#	61 ± 34	6 ± 1	2 ± 1	3 ± 0
Total N	μgL^{-1}		1200#	383 ± 18	303 ± 37	251 ± 30	243 ± 26
FRP	μgL^{-1}		2#	4 ± 2	1 ± 1	6 ± 4	19 ± 4
Total P	μgL^{-1}		<5#				
Sulfate	mgL^{-1}		100#	81 ± 3	82 ± 3	82 ± 4	61 ± 29
NPOC	mgL^{-1}		0.5#	71 ± 34	145 ± 25	137 ± 15	136 ± 54
Al	μgL^{-1}	0.8-55+	1213&	17 ± 3	43 ± 23	43 ± 18	20 ± 10
As	μgL^{-1}	13-23	<0.8^				
B	μgL^{-1}	370	<15^	83 ± 1	81 ± 4	82 ± 4	84 ± 3
Ca	mgL^{-1}		30#	29 ± 1	35 ± 0	35 ± 1	30 ± 1
Cd	μgL^{-1}	2.2++	0.5&				
Co	μgL^{-1}	1.4	61&	20 ± 6	2 ± 0	2 ± 0	2 ± 0
Cr	μgL^{-1}		<10^	1 ± 0	2 ± 1	1 ± 0	2 ± 0
Cu	μgL^{-1}	14++	<10^	8 ± 1	4 ± 1	5 ± 1	7 ± 2
Fe	μgL^{-1}	300**	150#	8 ± 2	13 ± 5	18 ± 4	15 ± 1
Hg	μgL^{-1}	0.6	<0.6^				
K	mgL^{-1}		4.8#	6 ± 0	6 ± 0	7 ± 0	7 ± 0
Mg	mgL^{-1}	300ψ	79#	72 ± 1	71 ± 1	72 ± 2	72 ± 2
Mn	mgL^{-1}	1700	242.5&	133 ± 30	2 ± 1	2 ± 0	6 ± 1
Na	mgL^{-1}		340#	343 ± 3	343 ± 9	343 ± 7	340 ± 10
Ni	μgL^{-1}	108++	60^	24 ± 3	4 ± 0	4 ± 0	27 ± 9
Pb	μgL^{-1}	103++	6^				
S	mgL^{-1}		35#	28 ± 1	27 ± 0	28 ± 1	28 ± 1
Se	mgL^{-1}	11	<0.005^				
Zn	μgL^{-1}	78.4++	440&	257 ± 47	81 ± 28	100 ± 40	227 ± 23

+ ANZECC/ARMCANZ (2000) Al guideline pH <6.5 = 0.8 $\mu g\ L^{-1}$, pH >6.5 = 55 $\mu g\ L^{-1}$.

++ This figure has been adjusted to a water hardness of 440 mg L^{-1} as $CaCO_3$.

ψ This figure applies to a Mg:Ca ratio of <10:1 after McCullough (2007).

** There are currently insufficient data to derive a reliable trigger value for Fe. The current Canadian guideline level is 300 $\mu g\ L^{-1}$ (CCREM 1987), which is used as an interim indicative working level.

* Data from this study taken on Day 0, averaged across all mesocosms

Data from Lake Kepwari on 27/7/05 (U. Salmon, University of Western Australia *pers. comm.*)

^ Data from Lake Kepwari on 2/5/05 (Department of Environment, WA)

& Average of Lake Kepwari data taken on 2/5/05 and 27/7/05

4. DISCUSSION

Isolating Lake Kepwari water from surface and groundwater inputs (as in the control) resulted in a sustained and significant improvement in pH and reduced metal concentrations (except B). However, concentrations of Al, Co, Zn and possibly Se remained above ANZECC/ARMCANZ Water Quality Guidelines (ANZECC/ARMCANZ 2000) for Protection of Aquatic Ecosystems (95% of species) by Day 255. This clearly indicates that if the sources of acidity into Lake Kepwari can be controlled, then there is potential for improvement in the lake's water quality.

However Salmon *et al* (Salmon *et al.* 2008) believed that Fe^{2+} entering the lake in groundwater resulting in acidification through ferrolysis was the main cause of declining lake pH once river diversion had stopped. Groundwater inflows will be difficult to control, especially if they are deep, although the technologies used to recharge aquifers potentially could be used to inject neutralising compounds/carbon sources directly into the problem aquifer. Apart from isolation from sources of acidity, the loss of N from the waters suggest that denitrification was the primary alkalinity generating process responsible for increasing mesocosm pH (Davison 1987). It appears that small P additions encourage biological activity which enhances this process producing slightly higher pH than the control. Furthermore a small amount of SO_4^{2-} reduction was suggested by the 20% reduction in SO_4^{2-}concentrations. Lund *et al.* (2006) found that targeting SO_4^{2-}reduction for alkalinity generation in historic Collie pit lakes was not successful in remediating pH, primarily due to the very low SO_4^{2-} concentrations. Formation of secondary minerals utilising the S compounds might account for the decrease seen, but these processes also typically generate acidity.

Limestone neutralisation of Lake Kepwari water successfully increased pH and substantially reduced most metal concentrations to below ANZECC/ARMCANZ Water Quality Guidelines (ANZECC/ARMCANZ 2000) for Protection of Aquatic Ecosystems (95% of species) by Day 255, with the exception of Zn (still substantially above its guideline), Co and possibly Se. Consequently, limestone neutralisation of lake water alone would remediate most metals to environmental guidelines. Limestone neutralisation and P amendment of Lake Kepwari, equivalent to that necessary to raise mesocosm water from mean pH 4.6 to circum-neutral, would require 800 t of limestone (limestone chip of ca. 80% $CaCO_3$, CSBP Fertilisers Limited, unpublished data). Successful application of this quantity of limestone might be a practical challenge but is possible. Furthermore there are other (potentially more expensive) neutralising compounds around that might be more practical to use e.g., CaOH.

Phosphorus additions alone resulted in slight increases in pH, probably through assimilation and dissimilation of NOx into organic matter generating alkalinity. Although these improvements are minor, they were accompanied by substantial decreases in Mn and Co to levels close to that of liming. Furthermore only a small change in Lake Kepwari pH is required to keep the pH at a level suitable for human recreation (pH>5). Phosphorus in combination with limestone appeared to offer little additional benefit than either used alone. Phosphorus amendment of Lake Kepwari equivalent to the mesocosms would require only 640 kg of P, or 6.4 t superphosphate per dose (CSBP Fertilisers Limited, unpublished data), with a total annual dosing equivalent to the mesocosm experiment for around 10 doses of only around 64 t. We believe that large doses might be more effective than a series of small doses, as a large dose is more likely to induce an algal bloom, which will generate further alkalinity and provide a valuable source of carbon for other biota. In our opinion, there is little risk in P additions to the Lake resulting in eutrophication due to the high quantities of Fe and Al in the water and sediment that can bind excess P. The need to continually add P to mesocosms to maintain FRP concentrations illustrates this. Algae are photosynthetic and do not need organic carbon, but can become a source of organic carbon and may become the base of a trophic system (Bocioaga and Mitman 2002). As a result, stimulation of primary production can also significantly improve environmental values of the pit lake through provision of a carbon sources for herbivores and increasingly complex food webs (Kalin *et al.* 2001). However, the potential for eutrophication and bioaccumulation of metals need to be managed. Presently, aquatic community colonisation in the aluminium-buffered lake is complex and mostly believed to be controlled by the sensitivity of the organisms towards both protons and also to inorganic reactive aluminium species (Nixdorf *et al.* 2003). There is currently a consideration for the Collie River to be permanently connected through Lake Kepwari which would necessitate discharge of pit lake water back into the river. However, releasing low pH water with metals at toxic environmental levels is unlikely to be permissible, without careful use of dilution by river water or treatment of the discharge water.

In conclusion, despite the work undertaken with rehabilitation of the Lake Kepwari catchment to control acidic surface inflows, the continued inputs of Fe^{2+} from groundwater will result in low pH pit lake water. Furthermore, pit lake water pH is likely to continue dropping as further exposed reactive geologies leach acid, and Al and heavy metal concentrations will also increase. The increased acidity will require more limestone chip to neutralise, and concentrations of these toxicants will make it more difficult to implement successful bioremediation strategies. This study has demonstrated that bioremediation of Lake Kepwari water is possible and there are several promising lines of enquiry that could be pursued to test these approaches at more realistic scales.

5. ACKNOWLEDGEMENTS

Our grateful thanks to Joseph Steenbergen and Carlieke te Beest of the School of Aquatic Ecotechnology, Hogeschool Zeeland, Netherlands, and Gary Ogden of Edith Cowan University for their assistance in the field and laboratory. Thanks also to Wesfarmers Premier Coal for facilitating sediment and water collection from their project lease. This project was jointly funded by the Centre of Excellence for Sustainable Mine Lakes and Edith Cowan University.

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