Potential of sewage and green waste for acidic pit lake bioremediation

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Abstract Bacterial sulfate reduction-based bioremediation was trialled in an acidic pit lake, divided into two sections by an earth wall. Sewage and green waste was added to the smallest section, while the other was kept untreated as a control. Bioremediation initially increased the pH of the hypolimnion of the treatment lake but after 12 months the pH suddenly returned to pre-treatment levels. This proved to be only temporary and pH bounced quickly back to previous highs. The pH decreases appeared to be associated with heavy rainfall events. These rainfall events affected the bioremediation by mixing the lake and increasing acidity inputs from the catchment.

Key Words Acidic pit lake, bioremediation, acidity, SRB, sulfate reduction

Introduction

Pit lakes are increasingly becoming common following open cut mining. The most problematic pit lakes are often those that are influenced by either moderately or severely by acid and metalliferous drainage (AMD) due to biogeochemical oxidation of sulfidic minerals (McCullough 2008). AMD affected pit lakes are typically characterised by high acidity, sulfate and metal concentrations. Past practices of failing to remediate acidic pit lakes during mine closure are no longer seen as sustainable practice by the mining industry and regulators. Efforts are increasing to remediate pit lakes with poor water quality to avoid environmental and social liabilities (McCullough and Lund 2006; Schultze *et al.* 2009). Internationally, there is increasing research into viable technologies for acidic pit lake treatment.

The primary issue with acidic pit lakes is that there is often a continuous acidity generating cycle occurring both in and around the lake (Peine *et al.* 2000). Therefore, treatment technologies for acidic pit lakes must deliver either a partially or fully self-sustainable solution. Bioremediation processes are based on enhancing naturally-occurring in-lake alkalinity generation capacity which in turn may lead towards the establishment of a functioning aquatic ecosystem (McCullough and Lund 2006; Nixdorf *et al.* 2010). The major bioremediation processes are based on stimulating two important biological functions that are generally limited in pit lakes: phytoremediation and sulfate reduction. Phytoremediation requires amendments of inorganic nutrients to enhance the pit lake's algal primary productivity (Lessmann *et al.*. 2003) which can produce alkalinity. Sulfate reduction by sulfate reducing bacteria (SRB) requires organic matter amendments to provide appropriate substrate and create anoxic conditions for alkalinity generation (Wendt-Potthoff *et al.* 2002; Fyson *et al.* 2006). Phytoremediation may be more suited to moderately AMD affected lakes or when there is not sufficient iron and sulfate available to negate the total acidity generated (Davison *et al.* 1995; Lund *et al.* 2006; Lund and McCullough 2008). Bacterial sulfate reduction appears to be more suitable for moderately to highly AMD affected pit lakes (Koschorreck 2008; Nixdorf *et al.* 2010; McCullough and Lund in press).

SRB have the potential to remediate acidic pit lakes by reversing the acid generation processes through sulfate reduction to sulfide in low redox environments using labile organic carbon as electron donors (Totsche *et al.* 2006). Sulfides generated by SRB activity can also form amorphous FeS when reduced iron is present, resulting in an accumulation of Fe and S in and on sediments, thereby breaking the acidity generating cycles (Castro and Moore 2000; Nixdorf *et al.* 2010). Sulfides can also form insoluble metals precipitates such as CuS, PbS and ZnS, thereby removing acidity and metals from the water in a single process.

Since SRB activity is often limited in pit lakes by low concentrations of labile organic carbon, bioremediation hence can be stimulated by organic matter amendments (Blodau 2006; Kumar *et al.* 2011). The majority of studies that have trialled SRB based bioremediation for pit lake treatment have been conducted mainly under laboratory conditions using microcosms and field studies are rather scarce. Further, field studies have largely only realised limited success due to a various issues such as high ferrous iron inputs from groundwater (Geller *et al.* 2009), low hydraulic lake retention time (Brugam and Stahl 2000) and shallow lake depth making the it unable to hold organic material over the large surface area of the lake bed (Davison *et al.* 1989).

In order to evaluate the efficiency of SRB based bioremediation for treating acidic pit lakes using municipal sewage and green waste a phased study was undertaken in Australia where initially laboratory microcosm experiments were conducted followed by a field experiment. The field experiment was based on the results of successful laboratory study (McCullough and Lund in press). Bioremediation in field was conducted by bulk organic carbon amendments to an acidic pit lake along with an untreated control pit lake. The present paper highlights the field scale potential of municipal sewage and green waste for treating a highly acidic pit lake in tropical North Queensland, Australia.

Methods

Study site description

Collinsville coal mine is located approximately 70 km inland from the coast of North Queensland, Australia. Regional geology mainly comprises of highly weathered geologies and soils with very low organic matter content. In the mid 1950s Collinsville mining switched from underground to open cut mining. Collinsville has a semi-arid tropical climate with a rainfall pattern that falls into a transition between sub-humid and semi-arid. The monsoonal tropical climate is dominated by moderately low and sporadic summer rainfall with very high annual evaporation rate (annual mean of 1,860 mm). The majority of Collinsville rainfall occurs during the wet season (December to March) with very sparse rainfall events during the dry season (June to September).

There are 20 pit lakes in the Collinsville Coal Project (CCP) area and all have very low pH (ca. pH 2), high concentrations of dissolved solutes (electrical conductivity = 9–19 mS/cm), high ORP (560–640 mV) and also very high metals/metalloid concentrations (McCullough and Lund in press). Garrick East pit lake was selected for the bioremediation study due to its proximity to the Collinsville wastewater treatment plant and green waste dump (<500m away) and good sampling accessibility. Garrick East has a maximum depth of 13.8 m, surface area of 5.9×10^4 m^2 and a volume of 4.7×10^5 m^3.

Organic matter amendments for bioremediation

Garrick East was partitioned into two sections by an earth wall, a treatment section Garrick East West (GEW) with a volume of 7×10^4 m^3 and a control, Garrick East East (GEE) with a volume of 4×10^5 m^3. The bioremediation trial followed a Before-After-Control-Impact (BACI) design where GEW and GEE were monitored for water physico-chemical changes both before and after organic dosing. Bioremediation was initiated in GEW in mid-2006 by amending with municipal sewage (wastewater 3,200 t, solid sludge 60 t) and green waste (980 t). The pit lakes were monitored for physico-chemical changes by vertical profiling of water columns every month from April 2005 to March 2008 for temperature, pH, electrical conductivity, redox potential, and dissolved oxygen at 1 m intervals using a Hydrolab Quanta multi-parameter probe (McCullough *et al.* 2008).

The results of the bioremediation’s potential remained inconclusive following sudden decreases in treatment response following initial rapid increases in GEW hypolimnion pH (McCullough *et al.* 2008). The present paper reports on studies undertaken to better understand the field potential of SRB bioremediation and factors affecting the process. The pit lakes were monitored for vertical profile variations for another 18 months (March 2008 to September 2009), rainfall data was also collected and acidity contributions from the treatment lake’s catchment were also estimated. To estimate the amount of acidity present in the catchment around the treatment lake, representative rock and soil samples were collected for Net Acid Generation (NAG) and Neutralisation Potential (NP) tests. For this, the collected rock and soil samples were initially crushed in a ball mill to fine fractions (<75 µm) and used for acid-base measurements following the procedure described by Sobek *et al.* (1978).

Results and Discussion

In this paper, combined results both from McCullough *et al.* (2008) and the current study are presented (April 2005 to September 2009). The yearly temperature data in the absence of cyclonic rainfall events in GEE and GEW indicate that both remained stratified during summer (thermocline at 4 m depth) and in autumn the thermal stratification starts to breakdown (Fig. 1a, b), with mixing occurring during winter. Epilimnion temperature was usually much higher (≈ 4–7 °C) than the hypolimnion during the summer.

The control GEE epilimnion maintained high ORP between 600–700 mV throughout the monitoring period whereas the hypolimnion ORP was slightly lower at around 500 mV (Fig. 1c). The treatment GEW’s epilimnion also showed a similar trend for ORP to that observed in the control lake albeit with slightly lower values at around 600 mV (Fig. 1 d). GEW exhibited declines in ORP from 4 m deep. The hypolimnion of GEW showed very low ORP (50–100 mV) throughout the study; as has been consistently recorded in GEW hypolimnion following the organic materials amendment (McCullough *et al.* 2008). The most likely reason for ORP reduction in the GEW hypolimnion could be attributed to organic matter degradation consuming oxygen and reducing oxidants such as NOx and Fe(III) in the pit lake water and sediment. On the other hand consistently high ORP recorded in the control lake highlighted the fact that in the absence of organic materials the pit lake would not support any remediation. Further high ORP indicates the prevalence of favourable conditions for the acidity generating processes of biogeochemical iron and sulfide oxidation.

The control's pH was very low (2.0–2.5) throughout the water column and remained unchanged during the study (Fig 1e). The epilimnion of the treatment lake GEW also showed similar pH to that recorded in the control lake (Fig 1f). How-

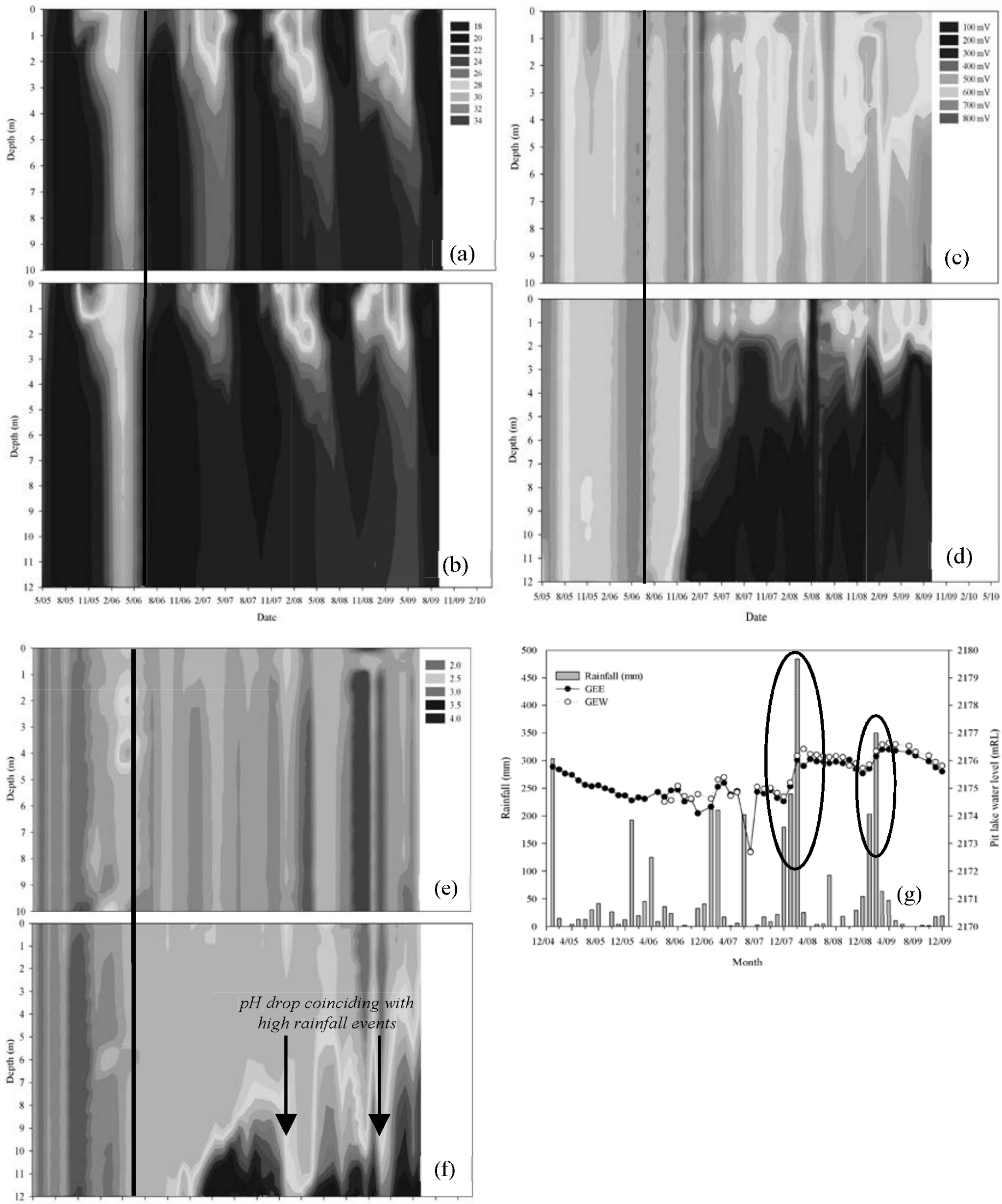

__Figure 1__ (a) Temperature profile of GEE with time, (b) Temperature profile of GEW with time, (c) ORP profile of GEE with time, (d) ORP profile of GEW with time (e) pH profile of GEE with time (f) pH profile of GEW with time (g) Monthly rainfall level data for Collinsville during the study period and pit lake water levels (Secondary axis). The dark vertical line in figures (a–f) indicates amendments of organic matter and the ovals in figure (g) highlights the intense rainfall events.

ever, the GEW hypolimnion showed considerably higher pH (≈ 4.0). High hypolimnetic pH in GEW could be chiefly due to bacterial sulfate reduction and this was further substantiated by the strong sulfidic smell that emanated from hypolimnetic water samples (McCullough *et al.* 2008). Amended organic materials sank down to the lake bottom and their breakdown appears responsible for the favourable reducing conditions for SRB activity (see Fig 1d). Higher pH recorded in the GEW hypolimnion than in the epilimnion is in agreement with literature emphasising that sulfate reduction-based bioremediation initially starts at the sediment-water interface and later extends upwards in the water column (Fyson *et al.* 1998; Frömmichen *et al.* 2003; Geller *et al.* 2009). Conversely, the main reasons for low pH prevalent in the treatment epilimnion could be attributed to the oxygen diffusion from the surface during thermal stratification and, in particular, acidity inputs from the catchment following rainfall events (Fig. 1g and Table 1).

The degree of success recorded for remediation of Garrick East pit lake water and sediment in the laboratory microcosm study with sewage and green waste (McCullough and Lund in press) could not be replicated in the field experiment. Under field conditions bioremediation, appeared to be strongly affected by acidity inputs following heavy rainfall events as indicated by the bioremediation slowing down or even reversing previous pH increases (Fig. 1f). These pH decreases in the treatment hypolimnion correlated well with rainfall recorded for the same period (highlighted areas in Fig. 1g). The intensity of the two significant rainfall events in early 2008 (484 mm) and 2009 (350 mm) are also shown by corresponding increases in both the pit lakes water levels (Fig. 1g). Heavy rainfall events seemed to affect bioremediation in two main ways, degrading lake stratification thereby increasing diffusion of oxidants to the hypolimnion which could lead to the re-oxidation of sulfides and monosulfides generated following bacterial sulfate reduction (Geller *et al.* 2009). The other main effect of heavy rainfall is likely mobilisation of the acidity present in waste rock and pit walls geologies in the pit lake catchment. For instance, out of the eight rock and soil samples collected around the GEW catchment, three were found to be Potentially Acid Forming (PAF) based on the NAGpH (Table 1) (Sobek *et al.* 1978). Among these three sites with PAF materials, two were highly acid generating with $NAG_{4.5}$ of 220 and 30 kg/t H_2SO_4, respectively and no neutralisation potential. Samples from other locations showed moderate neutralisation potential ranging from 6.5 to 18 kg/t H_2SO_4. These results indicate that there can be significantly high acidity contributions from the lake catchment during rainfall events. Acidity inputs from the pit lake catchment may have significant implications in determining the net success of SRB-based bioremediation. The SRB based bioremediation processes occurring in the pit lake have to neutralise this ex situ acidity as well as in situ acidity reducing the overall rate of remediation. For an effective SRB based bioremediation to occur, the pit lake needs to be largely permanently stratified i.e., meromictic, have adequate labile organic carbon (Castro and Moore 2000), minimal acidity inputs from the catchment and minimal oxidants diffusion into the reactive sediment zone (Geller *et al.* 2009).

The field results indicated that while ORP proved relatively resilient (≈ 100 mV) to temporary mixing events, pH reduced immediately following mixing and then recovered slowly. Overall pH improvements did slowly appear to be extending throughout the hypolimnion upon the absence of heavy rainfall events, although the highest pH achieved did not change significantly. Along with catchment acidity inputs into the treatment lake few other important factors may also have affected the bioremediation in the field.

Table 1 *Acidity contributions from the catchment of treatment (GEW) pit lake. NAG – Net Acid Generation, NP – Neutralisation Potential.*

Sample	NAGpH	NAG 4.5 (kg H_2SO_4/t)	NAG 7.0 (kg H_2SO_4/t)	NP (kg $CaCO_3$/t)
Sample 1	2.0	220	260	0
Sample 2	7.4	–	–	7
Sample 3	4.0	0.6	3	4
Sample 4	7.2	–	–	18
Sample 5	7.0	–	–	14
Sample 6	7.0	–	–	15
Sample 7	3.0	30	60	0
Sample 8	8.0	–	–	18
	Total	**251**	**323**	**76**

For instance, the total amount of organic material that was added into the treatment pit lake was less than half of that used in the successful laboratory study. Furthermore, organic carbon forms (solid sewage, liquid sewage), organic materials age (e.g., old sewage) and organic materials dosing regime (pulsed dosing compared to dosing all the organic material at once) also seems to restrict the amount of labile organic carbon available for SRB activity (Kumar *et al.* 2011).

Conclusions

The present study demonstrated that SRB bioremediation has significant potential for acidic pit lake treatment. The bioremediation processes started well following organic matter amendments but remediation rates were impacted by heavy rainfall events leading to lake over turn and acidity inputs. Bioremediation rates increased again once lake mixing and acidity inputs had ceased indicating SRB bioremediation's robustness under field conditions can be very good. When conditions are favourable for bioremediation i.e., anoxic environment, adequate labile organic carbon and an active SRB population, remediation rates can be very high. Control pit lake water quality (pH 2.4 and ORP 530 mV) remained largely unchanged indicating that AMD affected pit lakes will not simply evolve into self-sustaining ecosystems in the absence of any intervention treatment. Although the bioremediation process requires careful planning and design to achieve a lake environment conducive to treatment by SRB, many acidic pit lakes might be able to be remediated by bacterial sulfate reduction based bioremediation (Kumar *et al.* in press).

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