Are microcosms tiny pit lakes?

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Abstract Microcosm experiments are frequent precursors to field trials for the treatment of acidic pit lakes using organic matter. We conducted field and microcosm experiments to test the effectiveness of hay to remediate two small, shallow acidic pit lakes. 'West' Lake was treated with 19 t of hay and 'East' Lake was untreated. Microcosms mimicked key lake trends in water quality, increasing pH and reducing metal concentrations to a greater extent and faster than the field trial. However, microcosms are not tiny pit lakes because they provide an overly optimistic picture of remediation efficacy.

Key words Mine pit lakes, remediation, organic matter, AMD

Introduction

Acidic pit lakes present challenges for successful closure due to water quality issues that impact on beneficial end uses. The only established technological solution to pit lake acidity is the use of chemical neutralisation (see Geller et al. 2013), although it is typically an expensive and temporary solution. Treating acid mine drainage (AMD) in mine discharges using organic materials has proven effective at metal removal and increasing pH (Skousen et al. 2017). Adding organic matter to pit lakes is potentially an economical way to stimulate sulphate reducing bacterial (SRB) reduction of acidity and metal contamination (Frömmichen et al. 2003). Therefore, when carbon inputs exceed loss in pit lakes, natural processes may improve water quality (Blanchette and Lund 2016).

The use of organic matter to improve pit lakes *in situ* has been rarely attempted at full scale and treatment effectiveness has varied (McCullough et al. 2008); iron cycling in the pit lakes can even work against effective treatment (Koschorreck et al. 2007). However, numerous small-scale laboratory experiments (microcosms) have demonstrated effective treatment of acidic pit lake waters with a wide variety of organic materials (e.g. Kumar et al. 2011a). We propose that there is still much to be learned from field-scale trials that cannot be anticipated or designed for in smaller experiments.

Previous microcosm experiments (MiWER, unpublished) tested the use of sewage for remediation of pit lakes in the Pilbara region of Western Australia. However, limited availability of bulk organic materials (Kumar et al. 2011b) and pit lakes have prevented *in situ* testing. Recently, the availability of spoilt hay and two small pit lakes provided an opportunity for a field test using organic matter for acidity remediation. A microcosm experiment (measuring water quality parameters) was run concurrently examining the effects of hay additions on water sourced from both the lakes. This paper focuses on how well microcosms represent processes observed in the field.

Methods

Study site – The climate in the Pilbara region of northern Western Australia is semi-arid to arid with hot summers and mild winters. Mean maximum temperatures range from 35.9-38.3 °C in summer (Dec.-Feb.) and 23-25.5 °C in winter (Jun.-Aug.). Rainfall is highly variable and characterised by periodic high intensity rainfall events occurring predominantly in summer months, followed by extended periods of drought. Mean annual rainfall is 399 mm and evaporation is generally >3000 mm annually. The field study occurred in two small temporary pit lakes less than 0.5 km apart (West Lake, 0.3 ha, max. depth 9.5 m; and East Lake, 1.5 ha, max. depth 8 m) that filled in 2010 with ground and rain water.

At the start of the microcosm experiment West Lake water was more acidic (pH 2.92 vs 4.69) and saline (11.8 mS cm^{-1} vs 9.9 mS cm^{-1}) than East Lake water (Hydrolab Quanta). Although many metal concentrations were similar between the lakes, Al, Co, Cr, Fe, K and Zn were higher in West Lake and Se and Cd were higher in East Lake (Table 1; ECU Analytical Chemistry Laboratory).

Table 1 *Select physico-chemical parameters measured in lake water used in the start of the microcosm experiment, where there were large differences between lakes.*

	pH	EC mS/cm	Al mg/L	Cd µg/L	Co mg/L	Cr µg/L	Fe mg/L	K mg/L	Se µg/L	Zn µg/L	SO_4 g/L
East	4.69	9.932	28.1	0.78	1.2	<0.1	0.7	26	29	539	9.0
West	2.92	11.83	55.9	0.48	1.7	1.4	5.4	43	9	942	11.1

In situ *full-scale trial* – In September 2015, 27 bales of water-spoiled locally-grown hay (~19 t fresh weight) was added to West Lake using a telescopic handler. Floating hay naturally dispersed across the lake, with the majority sinking by October and final traces disappearing from the surface in January 2016. The aim was to create a benthic layer approximately 0.3 m deep (~6 kg m^{-2}). Hay was analysed for select chemical concentrations (such as Cl). Both lakes were monitored (at 30 min intervals) for stratification using thermistor chains, with dissolved oxygen (DO; bottom only) and conductivity (EC; bottom and surface) loggers (Hobo, Onset). An autonomous logging probe (Hanna HI9829) was used to measure pH and oxidation reduction potential (ORP) in West Lake at hourly intervals (located at the surface until 11/11/2015 and then 4 m). Water was collected on 10 occasions (Nov. 2014-March 2016), 12 samples from West Lake (n surface = 10, n bottom = 2), 10 surface samples from East Lake. Bottom samples were collected using a low-flow bladder pump QED MP50, after 15 min of purging the line. Samples were analysed for pH, EC, select metals and metalloids, sulfate, chloride, acidity and dissolved organic carbon (DOC). The field trial finished in March 2016 due to backfill of the void.

Microcosm trial – Twelve tubular acrylic microcosms (0.6 m long, 0.12 m dia.) were sealed at the bottom using a rubber bung and left open to allow ambient gas exchange (Fig. 1). Sediment (50 mm depth) followed by water (220 mm height, ~1.5 L), was added to each microcosm sourced from East and West Lakes. Three microcosms from each lake were left untreated (controls) and another three were treated with 10 g hay from the field site (~2 kg m^{-2} – based on results from a pilot study). Microcosms were randomised in a block design across holding aquaria and held at 25°C (± 2°C). A tube of fibreglass flyscreen mesh was installed prior to adding the hay, allowing measurements at the sediment/water interface (see Fig. 1).

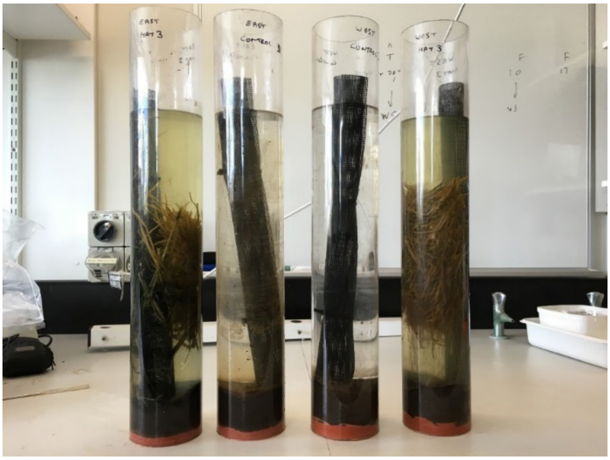

Figure 1 *Examples of microcosms, L to R: East Lake + hay, East Lake control, West Lake control and West Lake + hay, 14 days after hay was added (hay was later pushed down closer to the sediment).*

On each sampling occasion, water physico-chemical properties were measured twice in the microcosm: near the surface (pH, EC, ORP, DO using a Hydrolab Quanta (Hach Ltd)) and at the water-sediment interface (DO, EC and pH using single parameter probes (Orion, Thermo)). Care was taken to minimise disturbance to the water column and sediment. Sampling occurred daily for 6 days prior to the addition of hay, then at intervals ranging from 1 to 3 days up to day 113 with a final measurement (surface only) on day 145.

At weekly intervals, a 60 ml water sample was collected 30 mm below the water surface of the microcosm using a 60 ml syringe and filtered (0.2 μm Millipore). An aliquot of the filtrate was separated and acidified to pH<2 with conc. HNO_3 acid for later metal analysis by ICP-MS, with the remaining aliquot frozen for analysis of Cl, SO_4, DOC and nutrients. To maintain water volumes in the microcosms, 60 ml of MilliQ Ultrapure water was added to replace the removed sample. Concentrations of ions were corrected for dilution and evapo-concentration effects using Cl concentrations in the controls as a reference.

Statistical Analysis – Water quality data from the microcosms was analysed in Primer v6 (E-Primer), following removal of parameters with missing values (turbidity, total N and P), or were irrelevant (temperature), or where >50% of the values were below detection (Mo and Cd) – other values below detection were given a value equal to half the detection limit. Data was tested with a draftsman plot to identify any correlations >±0.95 (where one parameter would have been removed, none needed to be removed). Metal and nutrient data were $\log_{10}$ transformed and then all data were normalised. A repeated measures PERMANOVA tested the hypothesis of differences among variables, with lake, treatment and time as fixed factors and replicates random factors nested under treatment and lake. To determine the cause of interactions, one-way PERMANOVA of measured variables from each lake and time were undertaken separately to compare treatments.

Results and Discussion

In the microcosms containing East Lake water (hereafter referred to as 'East Lake microcosms'), the addition of hay increased surface pH from 4.13±0.06 (mean ± sd) at day -1 (prior to addition of hay) to circumneutral by day 44. However in treated West Lake microcosms, surface pH increased from 3.73±0.10 to just over 6.2 by day 106. East Lake controls maintained their low surface pH, while in West Lake they increased to 5.48±0.30 at the end of the experiment. In contrast, in the West Lake field trial, *in situ* pH remained between 3 and 3.5 at the surface waters for the duration of the experiment. Over the same period in East Lake, pH at the surface was between 4.5 and 5.5 and declined to ~4.5.

In East Lake treated microcosms, pH at the bottom increased from 4.75±0.09 (day -1) to 6.49±0.07 (day 40) before crashing to 4.5, then recovering to >6.5 from day 72 onwards (although never exceeding 6.9). East Lake controls reached a pH of 6.18±0.08 by day 90 before declining back to 4.63±0.52 at the end of the experiment. In West Lake microcosms, pH at the bottom was 4.11±0.24 (control) and 4.07±0.12 (treatment) at day -1, which increased to 5.53±0.13 (control) and 6.52±0.05 (treatment) by day 113. In the field, West Lake *in situ* pH at the bottom of the lake (4.5 m) ranged between 3 and 3.5 until four months after addition where it increased to 4.45. Acidity within the microcosms and lakes was occasionally highly variable (by up to 2 pH units), with algal blooms, evaporation and water inputs (ground and surface) likely responsible in the lakes, although in the microcosms the cause remains unclear (Fig. 2).

In line with pH changes observed in the microcosms, there was a statistically significant effect of treatment ($P<0.05$), difference between 'lakes' (i.e., lake water) and over time, with all interactions being significant ($P<0.05$). Lakes and treatments behaved differently over time, which resulted in the significant interaction effects.

There were no changes in *in situ* EC for both lakes and related parameters other than what could be explained by rainfall and evaporation. Similarly, EC and related parameters were not affected by straw and grass treatments of acidic mine water in mesocosms (Lund and McCullough 2015). Parameters associated with EC, including Ca, K, Mg, and Na, were not impacted by the hay addition, other than minor increases due to leachate (presumably out of the hay). There were also no changes in the microcosms in B, Ba, Mn and Sr.

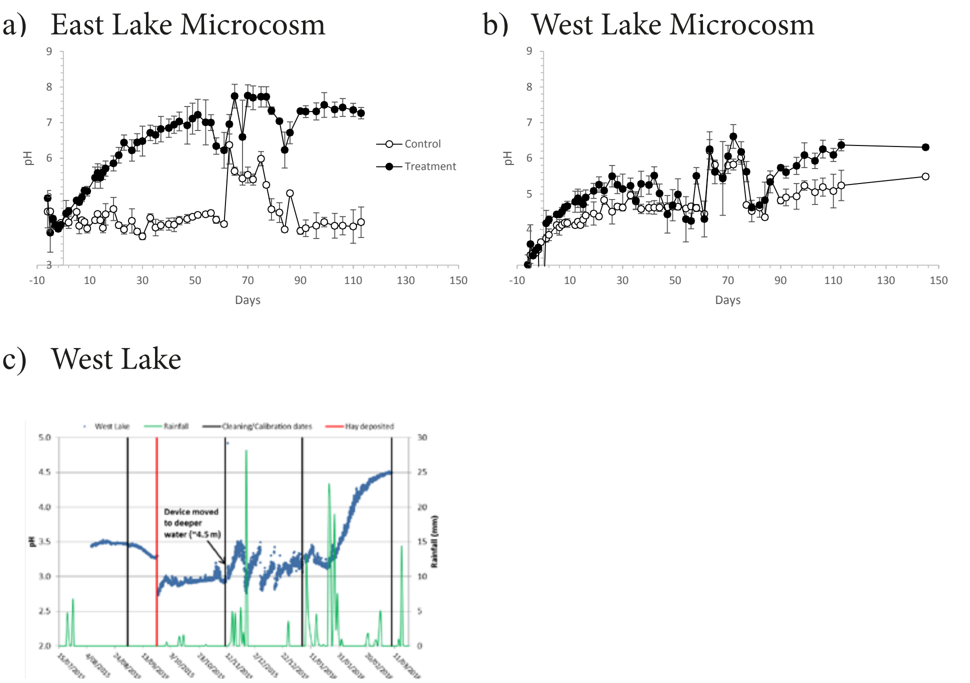

Figure 2 *pH changes in surface waters of a) East Lake microcosm, b) West Lake microcosm and c) West Lake (note probe moved from surface to ~4.5 m during experiment).*

In both lake microcosms, hay reliably drove DO to hypoxia (often anoxia) at the bottom, compared to only occasionally hypoxic conditions in the controls. ORP was consistently lower at the surface of the microcosms in the treatments compared to the controls, dropping frequently below -200 mV in the East Lake replicates, but only after day 90 nearly reaching -200 mV in the West Lake replicates. There was a significant ($P<0.05$) inverse correlation ($r>0.68$) between ORP and pH within treatments for each lake.

In the field, both lakes were thermally stratified with differences of 3-4 °C over 5 m, and a hypoliminion formed at 5 m in West Lake and 7 m in East Lake. However, temperature stratification disappeared in both lakes within 24 h of rainfall events of >20mm. Mixing in West Lake did not increase dissolved oxygen in the hypoliminion – in East Lake high rainfall in January 2016 appeared to trigger a decline in DO from ~8 mg L^{-1} to ~2 mg L^{-1} before recovering back to ~8 mg L^{-1} two months after the rain event. Logger data did not indicate salinity stratification, however the January rain event may have created a freshwater lens over the lakes resulting in a halocline, which when combined with groundwater inflows may account for the decline in benthic oxygen observed in East Lake following the mixing event. Lake turnover can re-oxidize reduced sulphides by effectively reversing positive improvements made by the treatment (Koschorreck et al. 2007). As apparent in West Lake and in a previous field trial at Collinsville (Qld), turnover failed to sufficiently alter conditions in the hypoliminion to prevent a rapid return to improving water quality. The microcosms were not thermally stratified, but after day 44, the bottom waters (regardless of treatment or 'lake') became salinity stratified with a 1000 to 1500 mS cm^{-1} difference in the controls and ~2000 mS cm^{-1} in the treatments. These differences were likely due to the replacement of sampled water with low EC MilliQ water. The salinity stratification had virtually disappeared in the controls by day 106, and was decreasing in the treatments as evapoconcentration countered the dilution following the patterns seen for Cl. The addition of replacement sample water in the microcosms appeared to mimic the effects of rainfall observed in the field trial.

Sulphate concentrations over the microcosm experiment suggest that there was no significant SRB activity due to similarities between treatment and controls. However, visual inspection indicated the likely presence of iron monosulfide under the hay. It was expected that SRB activity would be the main mechanism for increasing the pH – water quality samples of bottom waters might have been useful to determine whether sulphate reduction was occurring beneath the hay. In the field trial, sulphate (adjusted for Cl) remained unchanged in East Lake but decreased by approximately 2000 mg L^{-1} in West Lake at the benthos but not at the surface (changes in Cl at the surface and bottom suggest that there was a halocline present at the time). The reduction in sulphate is indicative of sulphate reduction although there is only very limited benthic data.

In the microcosms, Al decreased from 28 mg L^{-1} (East) and 56 mg L^{-1} (West) to <5 mg L^{-1} in both treatments (although more rapidly in East; day 28 vs day 54 for West, and this decrease was observed in the controls between 10-20 mg L^{-1} and by day 68). Removal of Al in the hypoxic microcosms was most likely due to binding to the organic matter. Cobalt, Be and Zn also declined similarly to Al, with large decreases (10 to 100 times) in the hay treatments by day 28 (although for Co and Be in the West treatments, this did not occur until day 68) and smaller declines (<5 times) in the controls. Removal of Co and Zn typically occurs through formation of metal sulphides. Despite the lack of obvious sulphate reduction, the relatively small quantities of sulphide required to form precipitates would not noticeably alter the overall sulphate concentrations. Selenium remained unchanged in the controls but declined to <3 μg L^{-1} (from 28 μg L^{-1} in the East microcosms and 9.2 μg L^{-1} in the West microcosms) by day 28 in the East and day 68 in the West. In the field trial, Zn declined soon after hay addition from 2 mg L^{-1} to 0.05 mg L^{-1} in the bottom waters and dropped by ~0.5 mg L^{-1} at the surface and remained unchanged in East Lake. Cobalt and Ni concentrations were not impacted by the treatment, and increased slightly in both lakes (surface) and at the bottom of West Lake. Copper followed the trend observed for Zn (although concentrations were typically low (<0.5 mg L^{-1})). Large reductions in Al, Co and Zn, with both straw and grass treatments were also noted by Lund and McCullough (2015), highlighting a commonality of removal processes regardless of initial water qualities.

Manganese did not appear to be impacted by the hay treatment in the field or microcosms. In the microcosms, regardless of the treatment, there was an increase (~50% in East and

~100% in the West) in concentrations of Mn at day 1, likely released from the sediments. Manganese is removed from waters primarily by bacterially-catalysed oxidation in circumneutral waters, which may explain the lack of removal in the acidic microcosms (Skousen et al. 2017). Iron concentrations were largely unchanged in the surface waters of both lakes in the field, but increased by 10 fold in bottom waters of the treated West Lake. In the surface of the microcosms, Fe concentrations were generally low but on occasion increased up to 10 fold compared to the start of the experiment – these increases were often short lived and only seen in some of the replicates. There was no apparent relationships between ORP, DO (% sat) and Fe concentrations in the microcosms. As suggested for sulphate, there might be an oxidation/reduction cycle for Fe occurring within the lakes and microcosms that maintains the status quo in terms of concentrations where small changes in DO and ORP result in the short-term peaks of ferrous iron.

In the microcosms, NH_3 increased in the East Lake control at day 1 (~10 fold; presumably released from the sediments), which did not occur in West Lake microcosms. Ammonia concentrations after day 1 remained largely unchanged in the controls until the end of the experiment. Adding hay increased NH_3 concentrations in the water of both 'lakes,' although there was a high degree of variability among replicates. Concentrations of NH_3 in the treated microcosms returned to baseline levels after day 40 for East Lake and day 68 for the West Lake. The low pH inhibits nitrification (Jeschke et al. 2013) and NOx concentrations declined to <20 µg L^{-1} by day 40 in all treatments and lakes presumably due to denitrification. The addition of hay caused release of FRP in both 'lake' microcosms which peaked on day 1, although by day 9 had returned to low levels. Hay maintained FRP concentrations 4-5 times higher than measured in the controls, which may be due to maintenance of low DO and ORP conditions preventing binding to Al or Fe (Kafper 1998). Hay increased DOC concentrations by about 100 mg L^{-1} initially and then maintained them at concentrations about 5 times higher than the controls.

Conclusions

Microcosms containing hay had higher pH levels which was reflected in the field trial, contrasting with the findings of Lund and McCullough (2015) where straw failed to increase pH but grass did (in mesocosm trials only). This suggests that the hay used in this experiment had more labile carbon than the straw and was likely a better material for pit lake remediation. West Lake microcosms responded more slowly and less dramatically to hay treatment than East Lake microcosms, which may explain the limited responses observed in the field trial. The lower initial pH and higher levels of many metals would probably have made it more difficult for SRB activity to activate, slowing down remediation. Our microcosms reproduced many of the major trends measured in the field trial. Unfortunately, the field trial was too short and sampling (replication) too limited by operational constraints to demonstrate the long-term effectiveness of the hay addition. However, there were positive signs of water quality improvement that suggest further trials are warranted. More detailed sampling of the microcosm waters at the sediment/water interface would have aided interpretation of potential Fe and sulphate cycles. We have microbial community (16S RNA) data for the microcosms and lakes that will be evaluated in subsequent publications. This research suggests that microcosms paint an overly optimistic picture of remediation efficacy. Therefore we contend that field trials are the ultimate scale for experimentation and therefore all opportunities to conduct experiments at field level enhance our understanding of these approaches to remediation.

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