



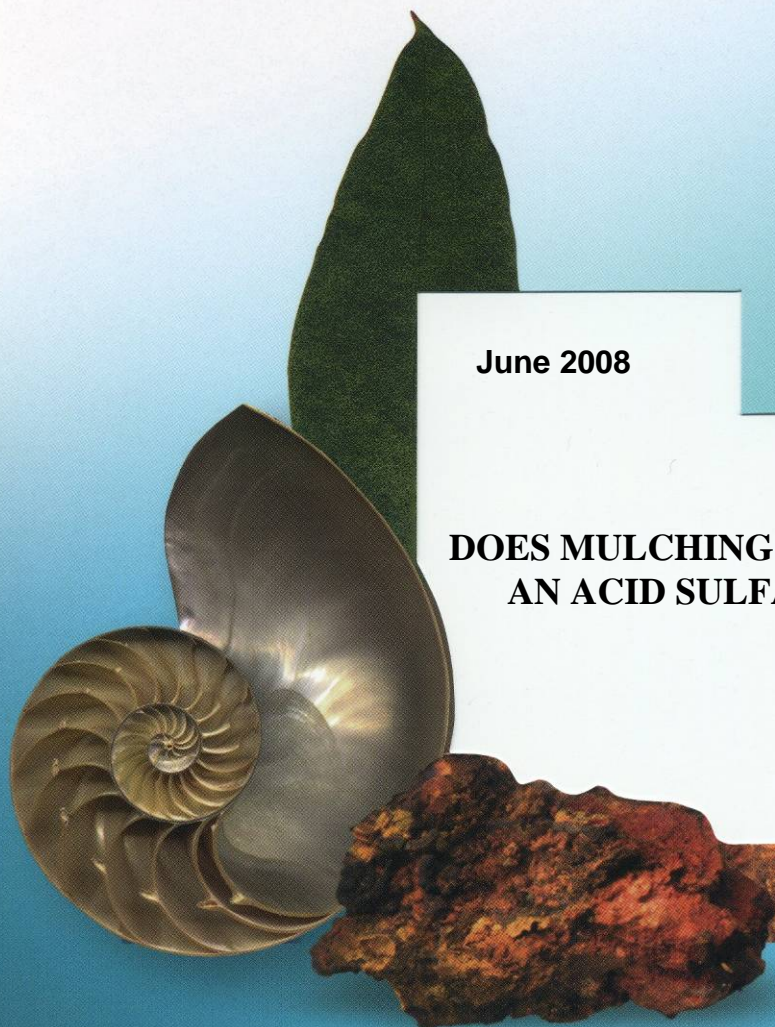
EDITH COWAN  
UNIVERSITY  
PERTH WESTERN AUSTRALIA

Centre for ecosystem management

June 2008

**DOES MULCHING IMPROVE WATER QUALITY IN  
AN ACID SULFATE SOIL AFFECTED LAKE?**

By, Miss Kimberly Harmsworth  
Dr. Clint McCullough  
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Centre for Ecosystem Management Report No. 2008-7

*Prepared for,*

**City of Stirling**

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***Frontispiece***



**Figure 1.** Kimberley Harmsworth physico-chemical sampling the north end of South Lake, Spoonbill-Shearwater Reserve, City of Stirling.

This document should be referenced as follows.

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## **1 Contents**

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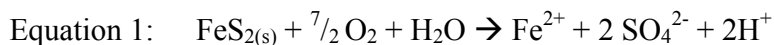
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## **2 Background**

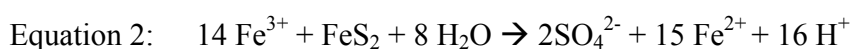
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Acid Sulfate Soils (ASS) are sediments containing sulfide minerals such as pyrite ( $\text{FeS}_2$ ) which were deposited under estuarine conditions in the Holocene (<10 000 y ago). They are a common global problem (White et al, 1997). ASS are common in Australia and are well documented on the eastern seaboard (Tulau & Naylor, 1999) where conditions over the past 10 000 years have favoured the formation of sulphides in sediments underlying coastal floodplains and wetlands. The most favourable conditions for sulfide formation include a steady supply of sulphur and organic matter in Fe rich sediments, under anaerobic conditions where reducing microbes are present (White et al, 1997). These conditions are typical of mangrove environs which occur in protected sites along the east coast of Australia. The situation is different on the west coast where the sandy soils of the Swan Coastal Plain have little or no acid generating potential (Appleyard et al, 2004) and, whilst ASS of marine origin do occur, they are not as widespread as those on the east coast. Instead, more common on the west coast of Australia are sulfidic peaty sediments that occur in groundwater fed wetlands. Teakle and Southern (cited in Appleyard et al, 2004, p. 579; Appleyard et al, 2006, p 85) first recognised the acidity of these sediments in 1937. They concluded that the acidity was due to the oxidation of iron sulfide minerals within the peat. These sediments contain 15% by weight of oxidisable sulfur (Appleyard et al, 2004) which can cause groundwater acidification and heavy metal contamination when disturbed.

Acid sulphate soils are considered as Potential Acid Sulfate Soils (PASS) if left undisturbed and inundated, as in this state the sediments are only potentially harmful. Actual Acid Sulfate Soils (AASS) occur when the sediments are exposed to oxygen through physical disturbances such as excavation or by a combination of other factors including dewatering and climatic decreases in groundwater levels and rainfall. As a result of the disturbance and exposure to oxygen, pyrite is oxidised to iron II and sulfate (Equation 1).



Iron II can then be oxidised further to iron III producing more acidity. Where pH is greater than 4, iron III can form a precipitate of ferric hydroxide. If pH is less than four iron III can remain in solution. Iron III in solution can oxidise pyrite (Equation 2) producing ferrihydrite ( $\text{FeOOH}$ ), a red-brown precipitate (White et al, 1997).

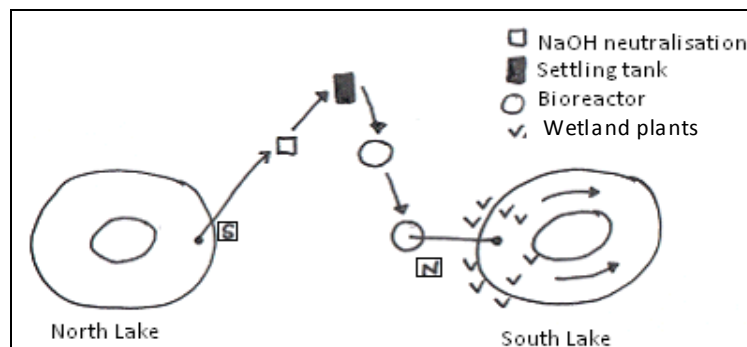


The sulphuric acid formed is a strong acid capable of mobilising Fe, Al, heavy metals and metalloids including As, present in host sediments (Hinwood et al, 2006). Groundwater acidification caused by sulfuric acid is elevated by an increase in  $\text{Fe}^{3+}$  (ferric iron),  $\text{Fe}^{2+}$  (ferrous iron) and  $\text{Al}^{3+}$ . Acidified groundwater contaminated with heavy metals (e.g. As) are a threat to public health (Appleyard et al, 2004). ASS negatively impact surrounding vegetation and infrastructure (White et al, 1997). In stream impacts may include fish kills and destruction of native macrophytes followed by invasion of acid tolerant species (Sammut et al, 1996).

A localised example of ASS exists in the City of Stirling, WA (Appleyard et al, 2004; Appleyard et al, 2006). In the past, peaty soils of the area were not well-suited for house foundations and so such land was not used for residential housing. However, the ever growing population of Perth has resulted in a high demand for land and consequently extensive urban in-fill development has now occurred in the area. As a result of disturbing PASS, the local groundwater has become acidified and contaminated with heavy metals and metalloids (Appleyard et al, 2004; Appleyard et al, 2006). Of major concern to local residents, specifically those who use bore water for watering their gardens was the contamination of groundwater with arsenic (Hinwood et al, 2006).

Various studies on the area (Appleyard et al, 2004; Appleyard et al, 2006; Hinwood et al, 2006; McCullough et al, nd) have pointed to several contributing factors to ASS in Stirling. These include dewatering in two development areas to lower the watertable for development and stockpiling of acidic sulfidic peat for a prolonged period of time. A decreasing trend in regional rainfall (global warming), increased groundwater abstraction (due to increasing population density); both caused lowering of the watertable and excavation of two lakes in the Spoonbill-Shearwater Reserve for public amenity and aesthetic appeal.

The situation in Spoonbill-Shearwater Reserve created an opportunity for further research into the problem of urban ASS. In 2005 a collaborative between the City of Stirling and Edith Cowan University's Centre of Ecosystem Management explored research opportunities into the remediation of ASS in Spoonbill-Shearwater Reserve (McCullough et al, nd, Lund et al, nd). An experimental treatment system was established (Figure 1) and began operating in November 2006 to treat acidic water from the northern lake and remediate the effects of ASS in the area (see Lund et al, 2007 for details).



*Figure 1.* Schematic representation showing water taken from southern edge of North Lake, acidity being neutralised, treated and returned to northern edge of South Lake. The aerobic wetland was made by planting wetland plants and mulching.

Problems arose when mulching of the northern edge of the receiving wetland saw a decline in water quality. It was suggested that the decline in water quality following mulching was due to accumulated oxidised Fe, Al and other ASS derived ochre being reduced and mobilised back into the lake (Lund et al, nd). However, littoral soils have benefited from mulching as seen by the successful establishment of planted wetland plants (*Schoenoplectus validus* and *Baumea articulata*) around the lakes (McCullough et al, nd; Lund et al, nd). It appears that mulching was beneficial to wetland plants but detrimental to water quality and at the onset of this current study the City of Stirling were considering mulching the whole lake without any concern for the latter.

This current study aims to investigate the effect of adding mulch to the lake system in a series of microcosm experiments. The effect of adding lime chip will also be investigated as a means of improving water quality. Lime ( $\text{CaCO}_3$ ) is used to increase pH. Acid mine drainage (AMD) is a problem similar to ASS and addition of lime to systems affected by AMD has been a way of increasing pH (McCullough, 2007). Bioremediation of AMD has had various rates of success, particularly with sulfate reducing bacteria (SRB), a group of bacteria that use sulfate as an oxidising agent, reducing it to sulfide and essentially converting sulfate to pyrite. If pyrite is reduced this then reduces the acidity of the system, however SRB may be sensitive to pH (Kolmert & Johnson, 2001). A resulting increase in pH by adding lime creates an environment suitable for SRB. Physico-chemical data and concentrations of metal cations, including Al and Fe were measured to determine if mulching improved water quality and the presence of sulphate reducing bacteria (SRB) were analysed to determine if mulching and or lime-chipping stimulated SRB activity.

Three hypotheses were tested in this study:

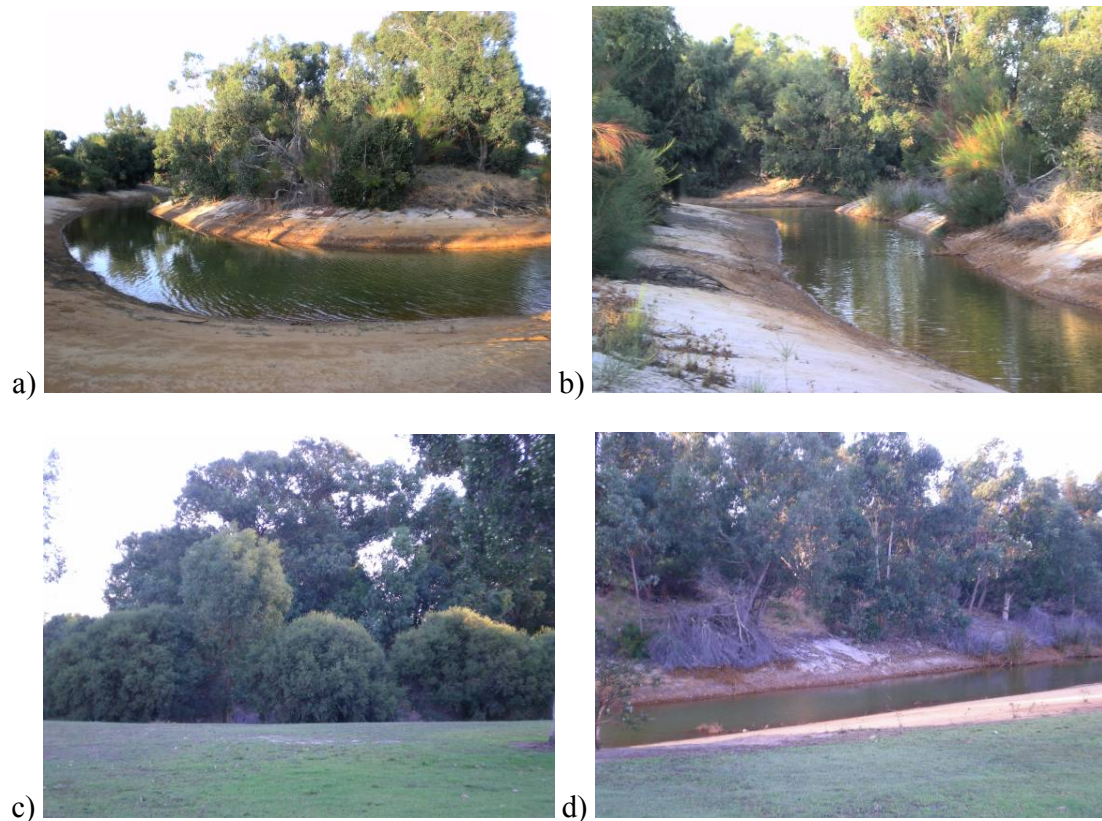
1. Mulching mobilises iron ( $\text{Fe}_{(s)} \rightarrow \text{Fe}^{2+}_{(aq)}$ ) and aluminium ( $\text{Al}_{(s)} \rightarrow \text{Al}^{2+}_{(aq)}$ ) from ochre.
2. Mulching stimulates sulfate reducing bacteria.
3. Lime-chipping enhances the activity of sulfate reducing bacteria.

### **3 Methods**

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#### **3.1 Study Site**

Spoonbill-Shearwater reserve is located in the City of Stirling (31°52'S; 115°48'E), accessible off Cedric Street from the Mitchell Freeway, approximately 9 km from the centre of Perth. The population in Stirling exceeds 180,000 (ABS, 2006). Local land-uses include urban, light industrial, commercial and market gardening. Two excavated lakes sit in the middle of the reserve ( $\approx 1.4$  ha). Each lake, North and South is 2–4 m deep and has its own island. The reserve is mostly grass with a few trees scattered around. The islands are covered in dense native and exotic vegetation (Figure 2). Groundwater flows in a west to south-westerly direction (Appleyard et al, 2004).



*Figure 2.* Spoonbill-Shearwater Reserve, a) view from southern edge of North Lake, scalded shoreline is thought to be due to ASS, b) view from western side of North Lake, the island sits to the right, c) view from northern edge of South Lake, vegetation in background is on the island, d) view from western side on South Lake, vegetation in background is typical of both islands.

Microcosm experiments were designed to mimic the natural lake system at Spoonbill-Shearwater Reserve. Fifteen, clean 120 mm diameter and 600 mm long acrylic tubes were set up in a 50 L tub filled with water to even the temperature as microcosms with 150 mm of sediment and 450 mm of lake water (Figure 3). Sampling occurred on March 25, 2008 (Day -1) at Spoonbill-Shearwater Reserve, Stirling, WA. Cores were pushed into the littoral sediments to a depth of 150 mm and sealed with rubber bungs at the bottom and loose fitting caps at the top. Nine cores were taken from the wet edge where ochre covered the sand for the following treatments; sand and ochre (SO), sand, ochre and mulch (SOM) and sand, ochre, mulch and lime (SOML). Six cores were taken from

the dry edge where ochre was not present for the following treatments; sand (S) and sand and mulch (SM). Dry mulch was collected from the top of Bioreactor 2 of the treatment system (Figure 1). Lake water was collected in clean 20 L carboys at a depth of 300 mm in the south of South lake. Care was taken not to collect benthic algae. Four, 30 mL 0.5 µm (PAL Metrigard) filtered water samples were taken from four sites around the lakes (Figure 4), acidified with 10% concentrated HNO<sub>3</sub> and analysed for metal and metalloid cations (Al, As, B, Ca, Cd, Co, Cu, F, Hg, Mg, Mn, Na, Ni, Pb, S, Se and Zn) using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Physico-chemical variables; temperature, pH, specific conductance, oxidation-reduction potential and dissolved oxygen (% saturation and mg/L) were measured using a Hydrolab Quanta probe at the same sites where water samples were taken around the lakes.



*Figure 3.* Microcosm cores, a) Day 19 S1 (left) with sediment and lake water, SM1 (right) with sediment, mulch and lake water, b) microcosm cores sitting in tub filled with water (Day 5). Microcosm treatments were allocated randomly, in this view from left to right are S1, SO1, SOM1, SOML2 and SM1. Sediment is concealed by black tub.

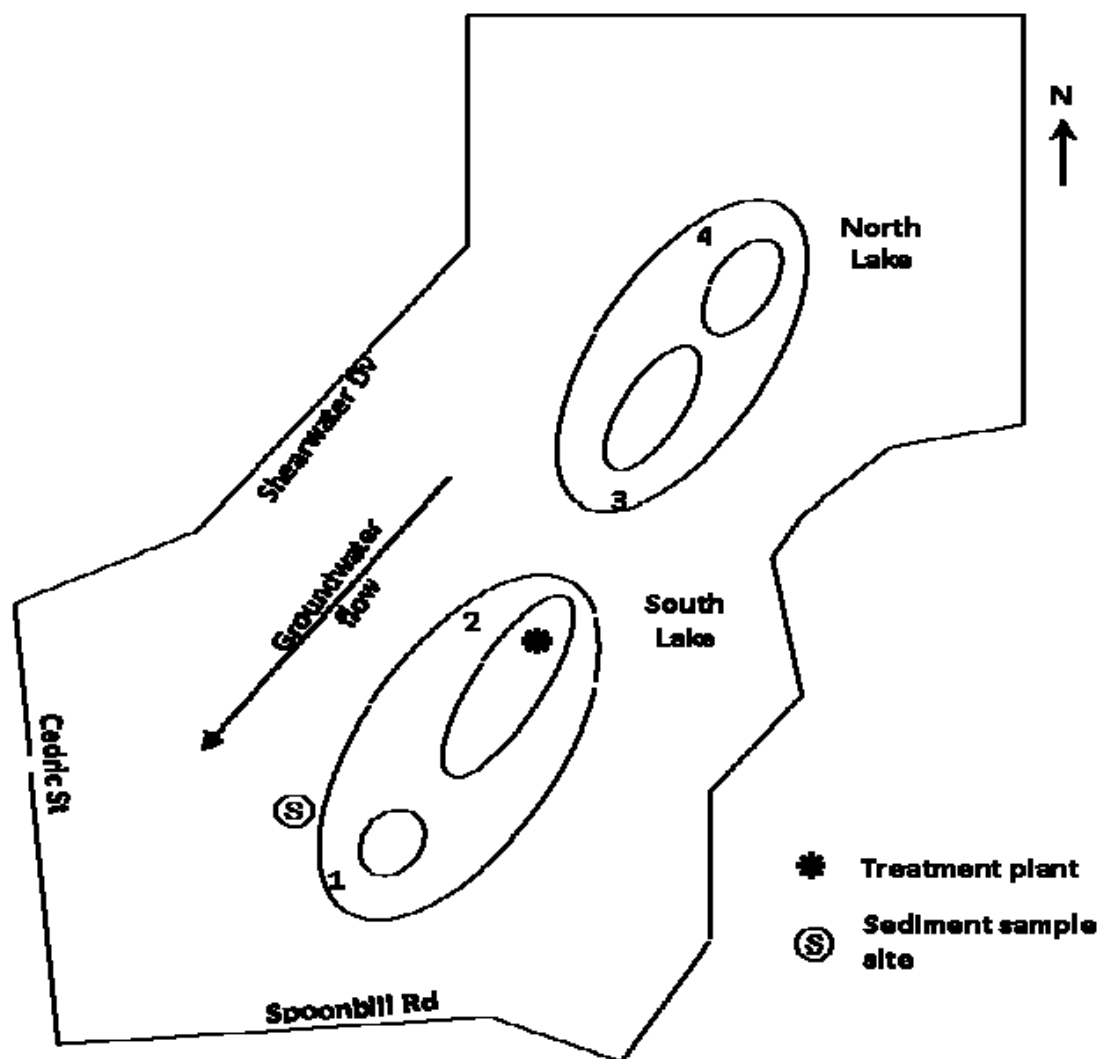


Figure 4. Schematic map of Spoonbill-Shearwater reserve showing field sample sites (1–4) and site where sediment was taken for microcosm cores.

Sediment cores were re-wetted in the laboratory using a sprinkler filter system that minimised sediment disturbance and were then allowed to settle for one day. Filtered water samples were taken from each core on Day 0, acidified and analysed using ICP-OES as per the lake samples. Baseline physico-chemical variables; temperature, pH, specific conductance, oxidation-reduction potential and dissolved oxygen (% saturation and mg/L) were measured in each core using a YSI 600XLM multiprobe. The following treatments were applied (three replicates each); 100 g mulch added to SM, SOM and SOML and 5 g of lime chips added to SOML (before mulch), S and SO were control groups and not treated. Mulch was stirred to encourage it to sink.

Physico-chemical variables were measured weekly (Day 7, 14, 21 & 28). Acidified filtered water samples from Day 7, 14 and 21 were analysed using Atomic Absorption Spectroscopy (AAS) to detect the level of Fe in the water column. Acidified filtered water samples from Day 28 were analysed using ICP-OES to measure the suite of metals as per samples taken on Day 0.

The amount of H<sub>2</sub>S was measured using Draeger Tubes on Day 35. Gas was pumped from each replicate (1.5 L) for the treatments SM, SOM and SOML. The presence of sulfate reducing bacteria and iron related bacteria were tested using Droycon BART™ tests. BART-IRB tests were carried out on each treatment and BART-SRB tests were carried out on SOM and SOML on Day 35. A 20 mL water sample was required for each test; 7 mL was taken from each replicate microcosm and mixed. BARTs were observed for 8 days with the type and amount of bacteria were determined by colour changes as per BART guidelines.

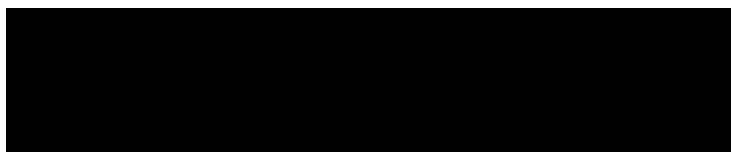
## 4 Results

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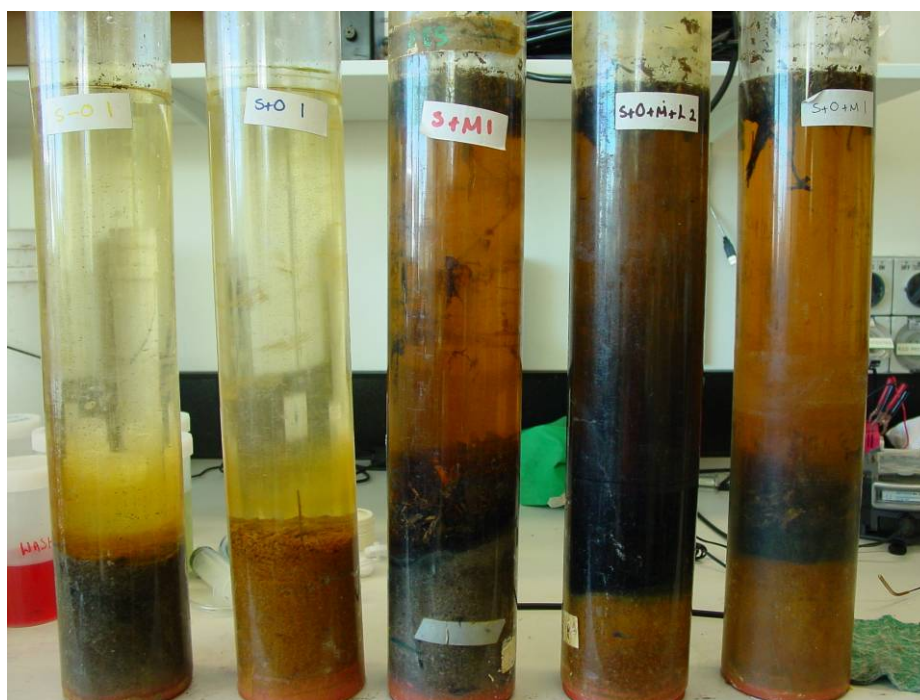
### Physico-chemical

Initial physico-chemical variables taken on Day 0 in the laboratory were similar across all microcosms. However, Day 0 physico-chemical variables were very different to measurements taken in the field (Day -1), except for pH and temperature. Field pH was 3.4 and average microcosm pH was 3.2, specific conductance decreased from 1.67 mS/cm (field) to 0.40 mS/cm (microcosm) (Table 1).

Table 1. *Comparison of field and laboratory physico-chemical variables. Field values are from Site 1 which was closest to where sediment samples were collected. Microcosm values are averaged from all 15 microcosms.*

A large black rectangular box redacting the content of Table 1.

Physico-chemical results clearly separate the five treatments into two groups; mulched (SM, SOM & SOML) and non-mulched (S & SO). This separation was also seen visually by colour changes in the microcosms over the course of the experiment (Figure 5).



*Figure 5.* Microcosm cores on Day 19, from left to right; S, SO, SM, SOML and SOM. The water colour has changed distinctly in all mulched treatments. Note the colour of the sediment is consistent for each treatment; treatments without ochre (S, SM) appear black while treatments with ochre (SO, SOM, SOML) appear red.

There was a slight drop in ORP across all treatments from Day 0–7, after which ORP for non-mulched treatments decreased rapidly and stabilised at an average -84 mV. Non-mulched treatments steadily dropped to +187 mV. (Figure 6a). The separation between mulched and non-mulched treatments is clear from pH results; mulched treatments doubled from strongly acidic pH 3.2 to circum-neutral pH 6.3, non-mulched treatments remained unchanged; strongly acidic through to Day 28 (Figure 6b). There is an inverse relationship between ORP and pH, where pH increased as seen in all mulched treatments, ORP decreased. Specific conductance fluctuated across all treatments in a similar pattern over 28 days. Mulched treatments increased from 0.404 mS/cm to 0.557 mS/cm from Day 0–7; non-mulched treatments increased from 0.405 mS/cm to 0.439 mS/cm. By Day 28, mulched groups showed an average higher specific conductance than non-mulched groups; 0.535 mV compared to 0.428 mV (Figure 6c).

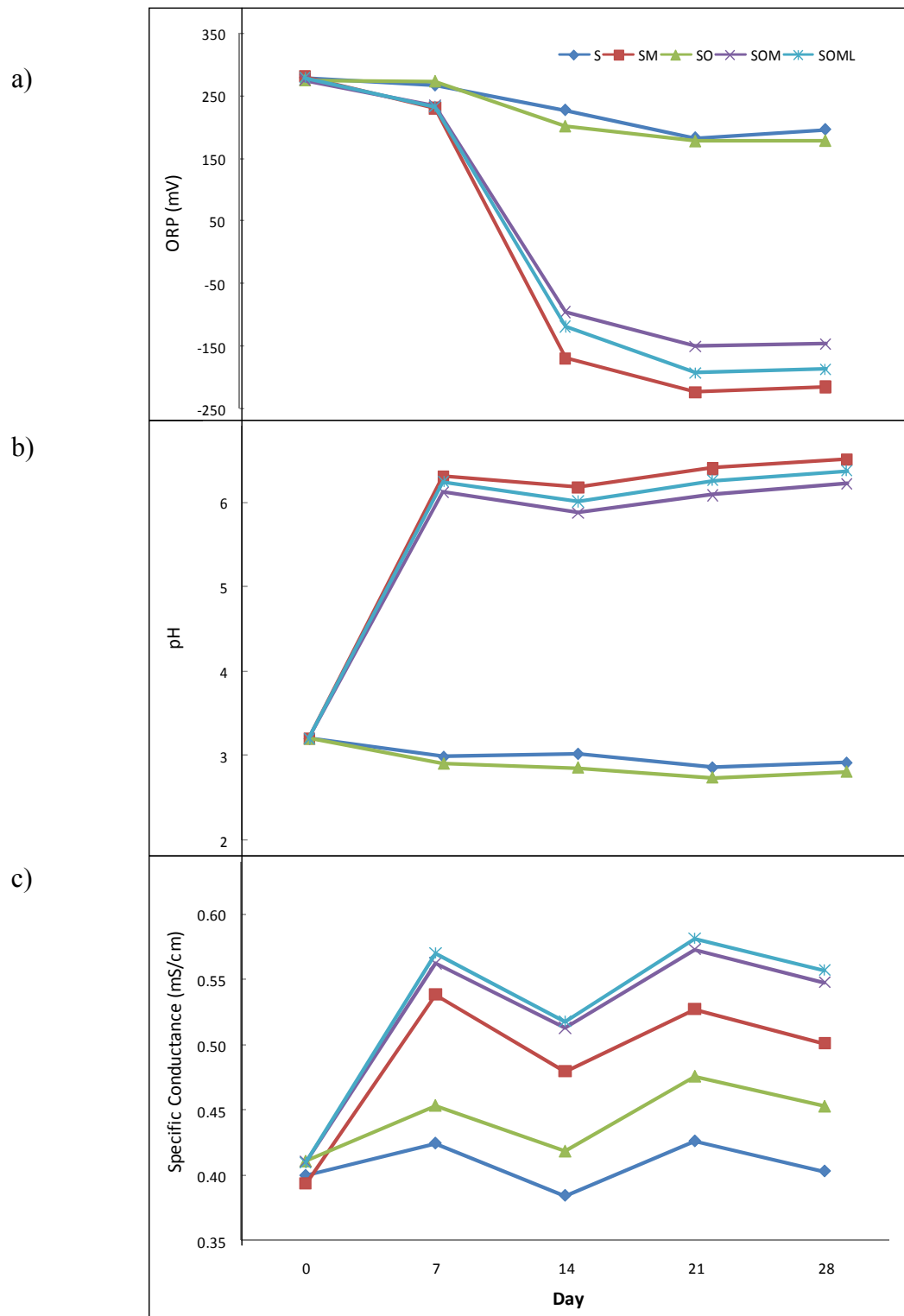


Figure 6. Mean a) oxidation-reduction potential, b) pH, c) specific conductance of microcosms over 28 days.

## **Chemistry**

Water samples collected in the field on Day -1 and from microcosms on Day 0 and Day 28 were analysed using ICP-OES. A suite of 19 metals and metalloids were analysed, ten of which fell below detection levels (DL): As, B, Ni, (DL<0.05 mg/L), Cd, Co, Cr, Hg, Pb, Se (DL<0.01 mg/L) and Cu (DL<0.02 mg/L). The only exception being Br which was detected at Field Site 4 (0.09 mg/L) and in all microcosms on Day 28; 0.08 mg/L (S), 0.08 mg/L (SO), 0.10 mg/L (SM), 0.10 mg/L (SOM) and 0.12 mg/L (SOML). Mn, S, Ca, K and Mg increased in concentration across all mulched treatments (Figure 7a & 7b), most noticeably S increased by 50% in SM (Figure 7b). In non-mulched treatments concentrations of S remained constant. Sodium increased across all treatments, more so for mulched treatments SM, SOM and SOML; 93 mg/L to 139 mg/L compared to non-mulched treatments S and SO; 94 mg/L to 110 mg/L. Zinc also increased in concentration across all treatments but more so for non-mulched treatments, especially Sand (S) where Zn increased by 0.49 mg/L, compared to mulched treatments where Zn increased by an average 0.03 mg/L. Aluminium decreased in all mulched treatments from 0.67 mg/L to 0.055 mg/L, this was slightly above the detection limit, Al slightly increased in mulched treatments from 0.69 mg/L to 0.82 mg/L. Iron was the only metal to decrease across all treatments from an initial average concentration of 27 mg/L to a final average concentration of 0.05 mg/L, in SOM and SOML Fe was below the detection level (<0.05 mg/L). Results from AAS revealed that Fe slowly decreased across all treatments from Day 7 to Day 21 (Figure 8). There was a rapid decrease in concentration of Fe between Day 0 and Day 7. Final Fe concentrations in mulched treatments were lower than for non-mulched treatments.

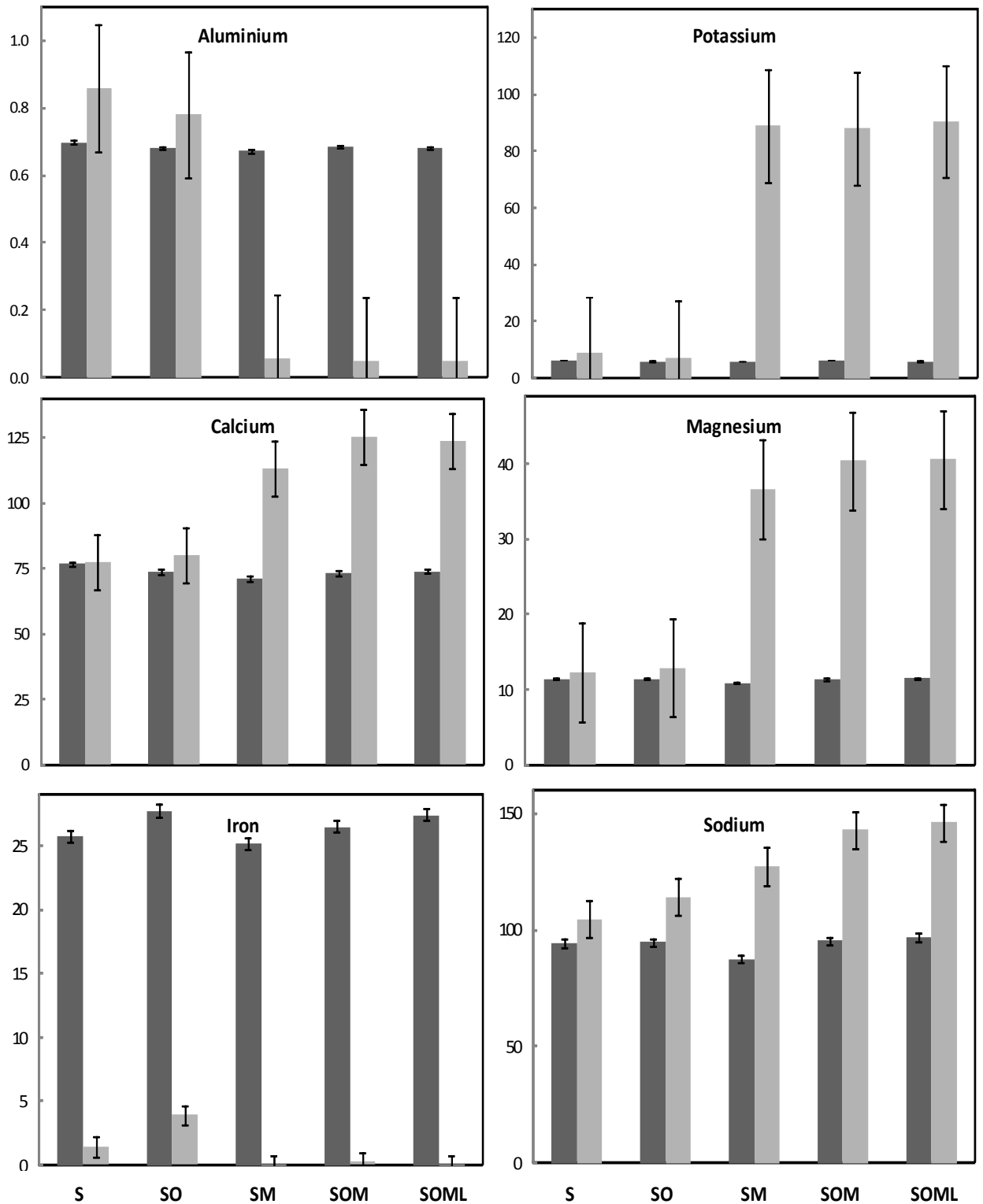


Figure 7a. Mean concentrations of metals measured by ICP-OES on Day 0 (dark bars) and Day 28 (light bars), all values are in mg/L, error bars show mean  $\pm$  standard error.

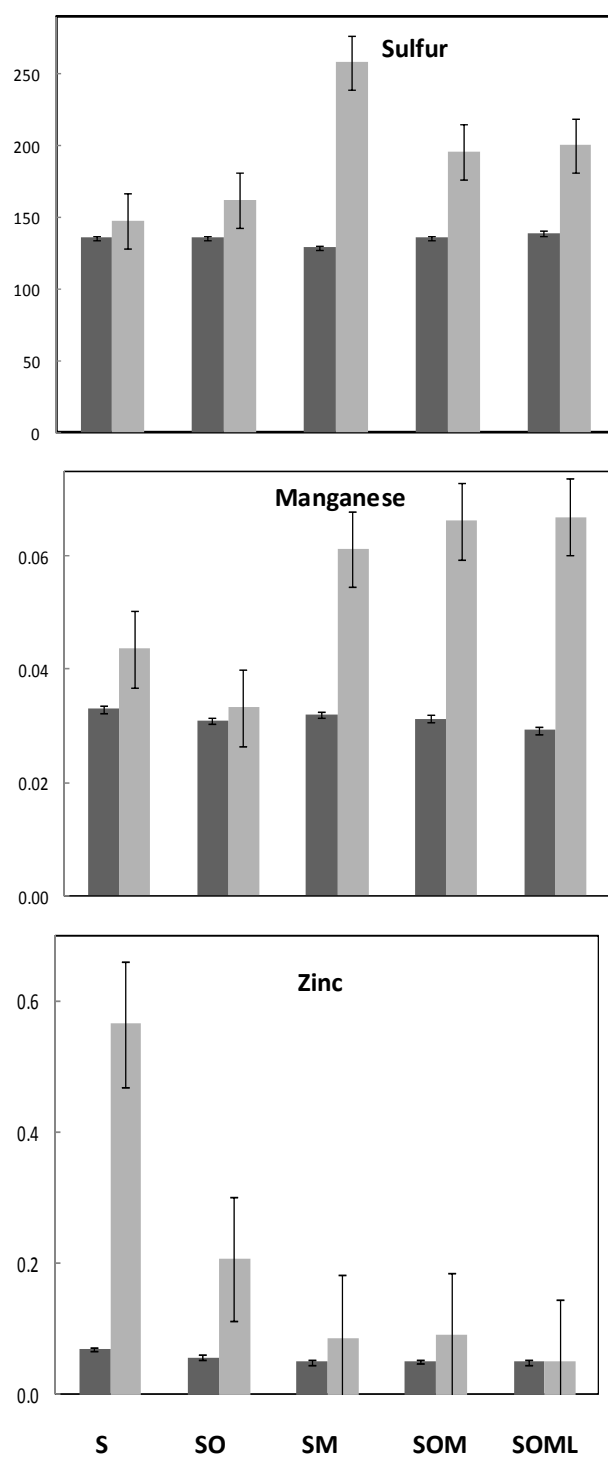


Figure 7b. Mean concentrations of metals measured by ICP-OES on Day 0 (dark bars) and Day 28 (light bars), all values are in mg/L, error bars show mean  $\pm$  standard error.

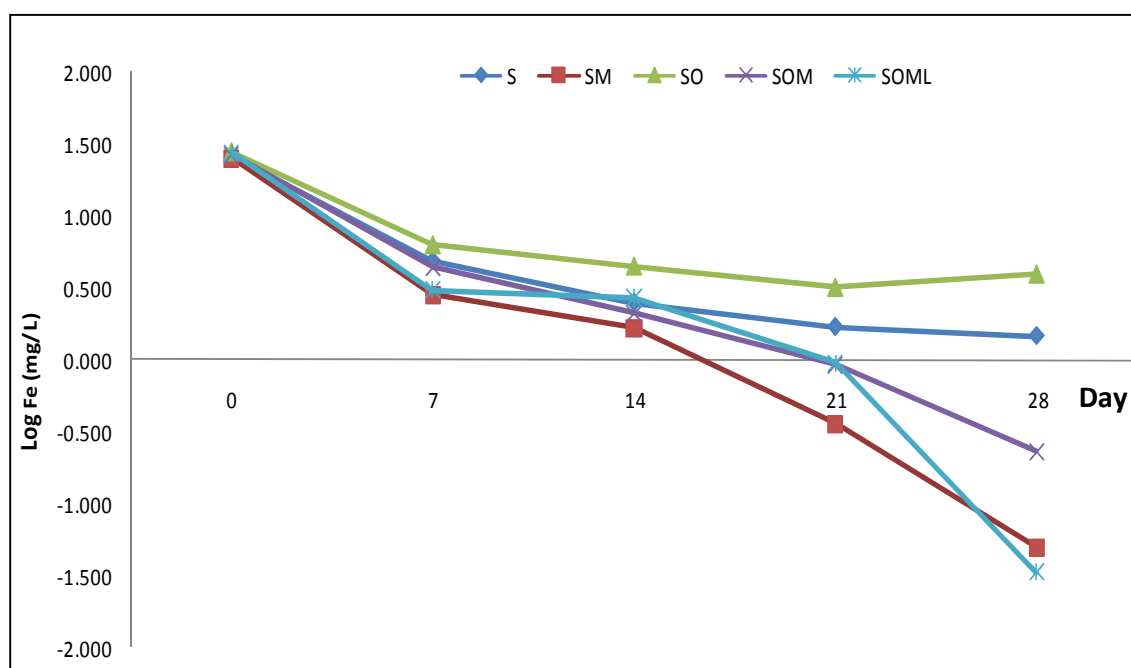
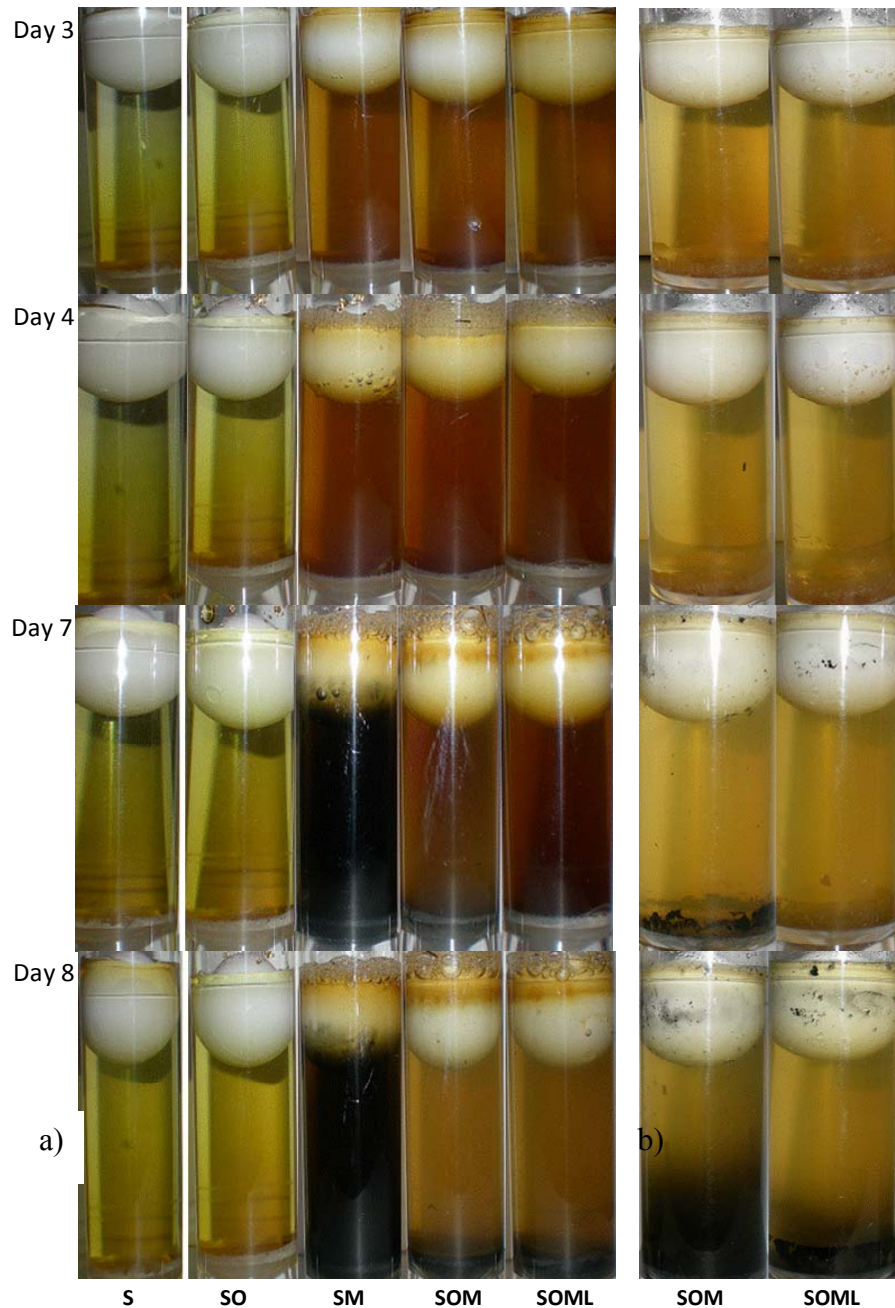


Figure 8. Mean concentration of Fe, Day 7 to Day 21 measured using AAS, Day 0 and Day 28 measured using ICP-OES. Both techniques were correlated by passing the same sample through to check for consistency.

## Microbiology

All mulched treatments (SM, SOM & SOML) were positive for IRB (Figure 9a). There was an obvious difference after 7 days when SM turned completely black indicating the presence of Pseudomonads at an approximate concentration of 100 cfu/mL. SOM and SOML turned dark brown with black deposits at the bottom, this indicated the presence of IRB (exact type unknown) at a concentration of approximately 100 cfu/mL. All non-mulched treatments tested negative for IRB. Only SOM and SOML treatments were tested for SRB activity and both returned a positive result, indicating the presence of SRB at an approximate concentration of 200 cfu/mL (Figure 9b). Treatments SM, SOM and SOML tested negative for  $H_2S$ , S and SO treatments were not tested.



*Figure 9.* BART-tests for bacteria a) BART-IRB tests, no reaction in any treatment until Day 4, bubbles appear on all mulched treatments (SM, SOM and SOML), SM turns black on Day 7 and black deposits appear in SOM and SOML on Day 8. No reaction in any mulched treatments. b) BART-SRB tests, no reaction in either treatment until Day 7 when black deposits appear in SOM.

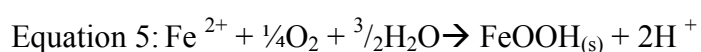
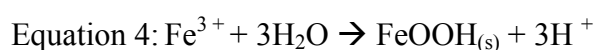
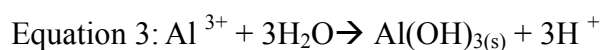
## **5 Discussion**

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Results clearly separate the five treatments into two distinct groups; those that were mulched (SM, SOM and SOML) and those that were not (S and SO). Mulching affects the system in a positive way by reducing acidity. Mulching appears to have created a reducing environment shown by negative oxidation-reduction potentials where metals such as K, Ca, Mg, Na, Zn and Mn were reduced, also shown by higher conductivity in mulched treatments. However some metal species were oxidised as shown by a reduction in their concentrations over time.

Lund et al (nd) suggested that mulching creates an environment where previous accumulations of oxidised Fe and Al are reduced and released back into the water column; then re-oxidised (further downstream) and precipitated out contributing to acidity. Lund et al suggested that, as a result, the constructed aerobic, polishing wetland caused water quality to decline while those materials were being reduced. Lund et al also noted that due to the limited supply of reducible Fe and Al, acidity should gradually decrease over time.

This current study suggests that Al and Fe are not reduced by mulching; rather they are likely oxidised and precipitated out of solution, most likely as aluminium hydroxide and or ferrihydrite (Equation 3 – 5).



Iron concentrations decreased considerably across all treatments, regardless of pH, ORP or conductivity indicating that iron oxidation was not affected by mulch in this system. Presence of mulch or ochre were not contributing factors to the concentration of iron. The presence of mulch does, however, affect Al concentrations. Al was oxidised in mulched treatments, while in non-mulched treatments it was reduced. Again, the presence of ochre is not a contributing factor because there was no difference between ochre and non-ochre treatments.

It appears that ochre has no effect on water quality, except for contributing to conductivity. Out of the non-mulched treatments; S and SO, conductivity was higher for SO suggesting that ions are released from the ochre over time. pH was also slightly lower for SO (more acidic) which could affect the mobilisation of some ions, although results from ICP didn't show this, concentrations for most metals were very similar in both S and SO except for sulfur, Ca and Na.

The difference between what was observed by Lund et al (nd) and what was observed in this study suggests that factors outside the microcosm environment could affect Fe and Al, possibly groundwater/surface water flow and level or rainfall and evaporation. Or that the supply of reducible Fe and Al has diminished with time. It is also possible that the type (freshness) and amount of mulch added to the microcosms is a critical factor when evaluating the response of the system.

As indicated by results from the BART-tests, mulching does appear to stimulate sulfate reducing bacteria. Mulched treatments, SOM and SOML tested positive for SRB. It should be noted that non-mulched treatments were not tested so it is difficult to say if it actually was due to the mulch. However only mulched treatments tested positive for IRB. If sulfate reducing bacteria are present, sulfate is reduced to  $\text{H}_2\text{S}$ , which reacts with ferrous iron to form black iron sulphide - the equivalent of pyrite reduction (Equation 6). This is in line with the formation of black rings in the sediment of the microcosms (Figure 10). With sulphate reduction occurring we could expect to see a corresponding decrease in concentrations of S species, this was not the case and S increased in concentration across all treatments. Further analysis would

determine the exact nature of this S, be it sulphate or otherwise. Also hydrogen sulfide is an intermediate product of sulphate reduction but no gas was detected in the microcosms suggesting that it was consumed in the further reactions.

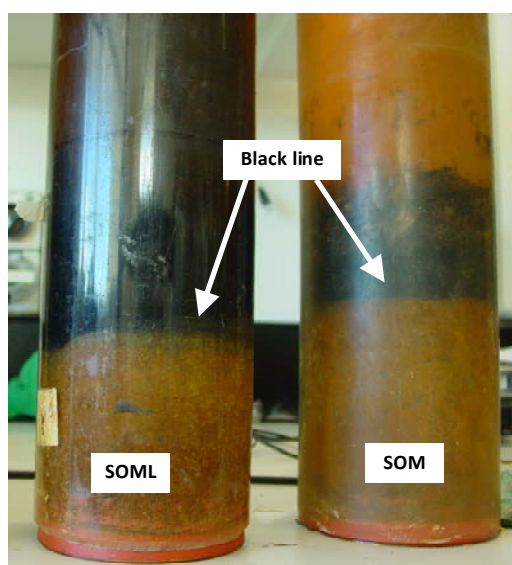
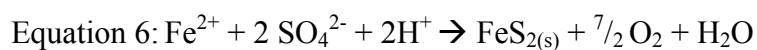


Figure 10. Microcosms on Day 19, black line indicates formation of iron monosulphide.

The optimum pH for SRB activity is not clearly defined, this study favours SRB activity at high pH; average for mulched treatments was pH 6. The rapid oxidation of Fe (Equation 6) can be explained by the presence SRB which catalyse the process. However since Fe concentrations also decreased in non-mulched treatments it is possible that SRB were present there too, but if pH does affect SRB activity, the pH of non-mulched treatments may have been too low. Mulching effects pH which could in turn could affect SRB activity.

From this study, lime chipping does not have a great effect on SRB activity; there was no overwhelming difference between SOML and SOM in relation to SRB activity except for SOM recording slightly higher activity. We would expect pH to respond to lime-chipping, but it did not. It is likely that the amount of lime added to the microcosms was not proportional to the amount of mulch, sediment and water.

Recent studies concerned with the acid sulphate soil problem in Stirling have been focused on the concentrations of heavy metals in the local groundwater and the potential health effects as a result of exposure (Hinwood et al, 2006; Appleyard et al, 2006). Of main concern is arsenic which had been detected in local bores at levels exceeding NHMRC drinking water guidelines and ARMCANZ recreational quality guidelines (Table 2). In this study arsenic was below DL (<0.05 mg/L) but could potentially be above NHMRC drinking water guidelines. This only has implications if bore water is used for drinking, which in some households it is (Appleyard et al, 2006).

Table 2. Comparison of this study with Hinwood et al (2006) of heavy metal concentrations, all values are in mg/L.

Parameter	2004		2008			Drinking water guidelines <sup>d</sup>	Recreational water quality guidelines <sup>e</sup>
	a	Detection Limit	b	b	Detection Limit		
Al	1.4	<0.005	3.30	0.05	<0.05	0.20	0.20
As	0.1	<0.050	<0.05	<0.05	<0.05	0.01	0.05
Fe	31.5		59.4	0.11	<0.05	0.30	0.30
Se	<0.05	<0.050	<0.1	<0.10	<0.10	0.01	0.01

<sup>a</sup> Concentrations detected in residential bores in Stirling (Hinwood et al, 2006).

<sup>b</sup> Concentrations detected in the lakes of Spoonbill-Shearwater reserve.

<sup>c</sup> Concentrations detected in mulched treatments after 28 days (average).

<sup>d</sup> NHMRC (2004).

<sup>e</sup> ARMCANZ (2000) .

Appleyard et al (2004) cites deficiencies in the environmental approvals process and a lack of planning policies that address acid sulphate soils for acidification problems in WA. From a management perspective, ASS needs to be assessed at the local scale. Detailed site specific information and data is required to combat the problem, especially in Western Australia where ASS are very different to the coastal ASS found on the east coast. This study should contribute to the current knowledge of ASS in the City of Stirling and assist in developing remediation programmes.

## **6 Acknowledgements**

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Thanks to Mark Bannister, Senior Laboratory Technician at Edith Cowan University for assistance with chemical analysis.

## 7 References

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