

Big Swamp acid sulfate soil study: Spatial extent of acid sulfate soils and potential for neutralisation of acidity upon re-flooding

Final report

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Executive Summary

Big Swamp located in the Otway Ranges has become acidified through reduced water levels, releasing acidic water into the lower reach of Boundary Creek and subsequently the Barwon River. This study was initiated with two key objectives. The first was to determine the extent and nature of acid generating material within the swamp. The second objective addresses the question as to what extent acid neutralising reactions including iron and sulfate reduction are likely to occur upon re-inundation of the swamp. It was found that the swamp contains localised net acidities in excess of 10000 mol/tonne H^+ heterogeneously deposited throughout the swamp. To date, only a small proportion of this material has been oxidised releasing 'actual acidity' in the surface 2 m of sediment. If the swamp undergoes further drying, there will be large and further long-term (many decades) releases of acidity upon re-wetting. It has been estimated that it will require up to ~100 000 tonnes of lime to neutralise this net acidity, but this will be technically difficult to apply given the heterogeneous nature of the sulfidic material.

It was found that the surface soils which have experienced oxidation and the generation of actual acidity had the potential to undertake iron reduction under anoxic conditions at rates sufficient to neutralise the local actual acidity in 1-2 years. This reaction, however, still produces mobile potential acidity in the form of dissolved iron (II), and any release of this from groundwater would regenerate acidity upon contact with oxygen. The timescale over which this occurs depends on the release rate of groundwater. Longer term immobilisation of acidity also requires sulfate reduction to take place and present indications suggest this process would not occur for several years and even then, there is unlikely to be enough sulfate present in the soil to lead to the complete immobilisation of dissolved iron.

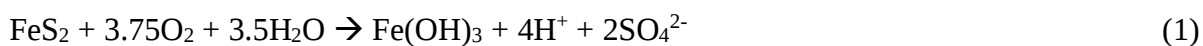
Based on these findings it is recommended that the swamp be maintained in a saturated state indefinitely, and that groundwater which will have both high actual and potential acidity (due to dissolved iron) be prevented from leaving the swamp. If the groundwater were to be released it would need to be neutralised either at the site of discharge (if localised) or the entire creek would be to be treated if the groundwater discharge zones are dispersed (most likely).

Background

Big Swamp is located to the North of the Otway ranges, just south of Colac. The swamp is fed by Boundary Creek, which has experienced reduced flows in recent years due to reduced rainfall and pumping of the Barwon Downs Borefield. This has led to a drying of the swamp and the, activation of acid sulfate soils, and the release of acidic water into the lower reach of Boundary Creek and subsequently the Barwon River.

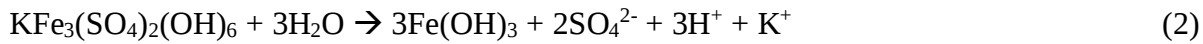
What causes acidity?

Reduced sulfidic material such as iron pyrite and iron monosulfides accumulate in anoxic water logged environments such as wetlands where no oxygen is present. The drying and reoxygenation of sulfidic soils and sediments leads to the release of acidity which can be summarised as the following reaction (Sullivan et al. 2018)



This reaction assumes the sulfidic material is present as pyrite (FeS_2) and it is complexly oxidised. The reaction produces 4 equivalents of acidity (H^+) per pyrite oxidised.

In reality, the oxidation of reduced sulfur compounds is often incomplete, resulting in the formation of minerals such as jarosite, which is also a store of acidity (referred to as retained acidity)



The net acidity of the soil can therefore be defined as:

Net acidity = Potential Sulfidic Acidity + Actual Acidity + Retained Acidity - Acid Neutralising Capacity

Potential Sulfidic Acidity is the potential for acid generation from reduced sulfur. This is represented by FeS_2 in equation 1.

Actual acidity is H^+ that has been released through oxidation of material. This is what leads to the low soil/water pH.

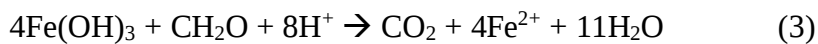
Retained acidity represents a store of acidity in minerals (equation 2) that can further release H^+

Acid neutralising capacity is not relevant in the context of this report because all the material being considered is less than pH 6.5 and is therefore zero and can be ignored.

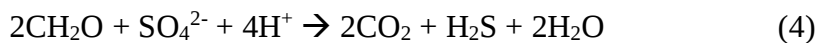
Can acidification be neutralised?

Once produced, acidity can be neutralised by the addition of lime, and the amount required can be calculated based on the net acidity. Acidity can also be neutralised by the reverse reactions that led to the accumulation of reduced sulfidic materials initially. This process is driven by the oxidation of organic carbon by bacteria coupled to the reduction of iron oxide and sulfate. Effectively, these reactions are the reverse reactions that have driven the initial acidification:

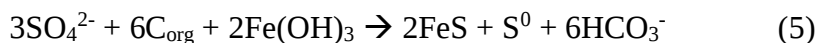
Iron oxide reduction



Sulfate reduction



In plain English, these reactions are saying that bacteria burn organic matter (CH_2O) by 'breathing in' iron oxide ($\text{Fe}(\text{OH})_3$) and sulfate (SO_4^{2-}). In this process, they consume acidity (H^+) and produce carbon dioxide (CO_2), reduced iron and sulfur (Fe^{2+} , H_2S) and water (H_2O). These two reactions occur sequentially, with iron reduction taking place first and sulfate reduction then taking place once all the iron oxide is consumed. Once sulfate reduction commences, the H_2S produced will react with Fe^{2+} produced from iron reduction to form reduced inorganic sulfur compounds such as iron monosulfide, which then converts to pyrite over time. It should be noted that both Fe^{2+} and H_2S are soluble and highly mobile and have a high potential acidity, so if exposed to oxygen (for example after release in ground water), acidity will be generated again. Insoluble iron monosulfide and pyrite are not mobile and therefore easier to contain. The overall reaction can be summarised as follows (Whitworth et al. 2014).



The production of CO_2 (referred to here as dissolved inorganic carbon, DIC) is therefore a key measure of the rates of the above reactions and can give us some indicative timescales for the neutralisation reactions to take place. The key factors controlling the rate and extent of reactions (3-5) are the availability of degradable organic matter, sulfate (SO_4^{2-}) and iron oxide ($\text{Fe}(\text{OH})_3$).

Objectives

1. Map the extent of acidity within Big swamp
2. Classify the soils into key groups for further study in objective 3

3. Determine the rates of acid neutralising reactions occurring within the different soil types and the timeframes and likelihood of this occurring

Study Site

Soil samples were collected at depth intervals of 0.5m (higher resolution in the surface meter where possible) from a grid of boreholes shown in Figure 1. Samples were kept on ice until return to the lab where they were frozen before later analysis and incubation.

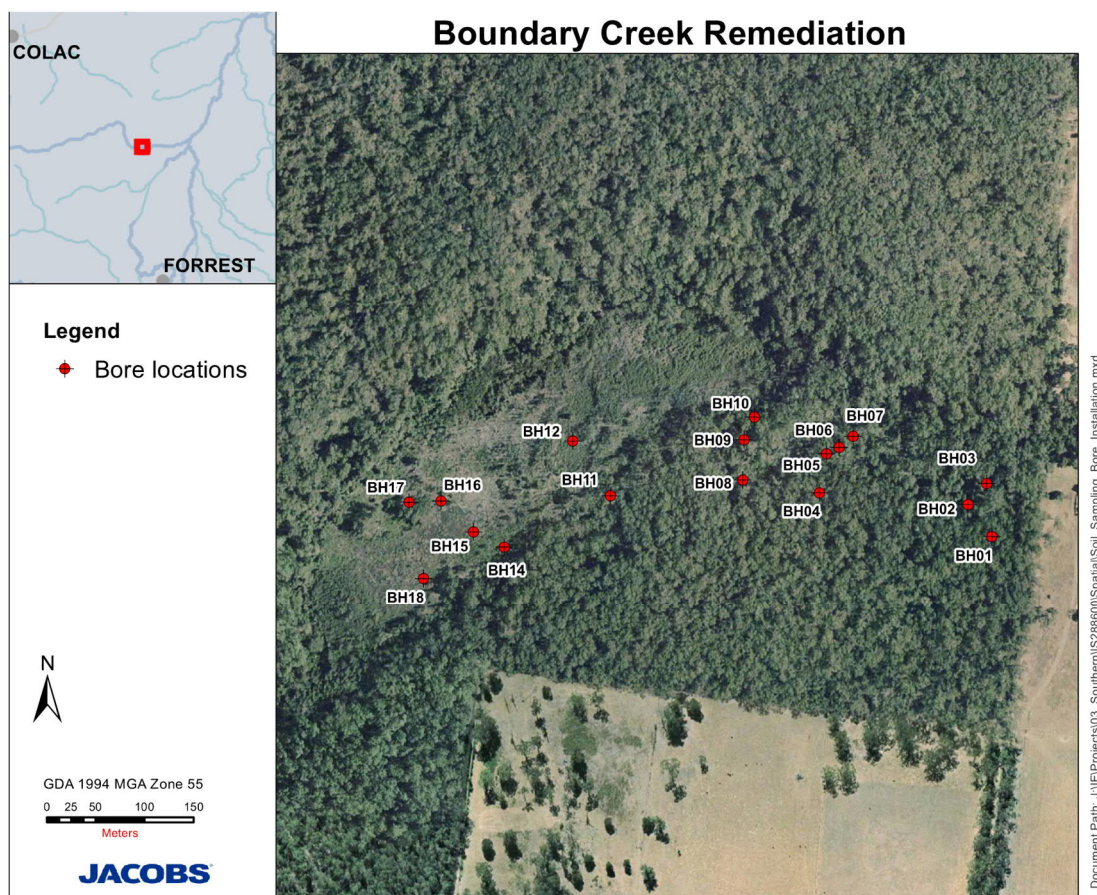


Figure 1. The location of the sampling boreholes

Analysis

Static testing (objective 1)

Samples were analysed for colour, texture, moisture content, density, particles size, loss on ignition, acid sulfate net acidity (sent to Southern Cross University), magnetic susceptibility and water extractable SO_4^{2-} . A selection of soil types representing, burned, unburned, wet and dry sediment were chosen for further analysis of NO_3^- , NH_4^+ and oxalate extractable Fe and Mn (Kostka and Luther III 1994). Samples were analysed using standard methods according to national acid sulfate soils identification and laboratory methods manual (Sullivan et al. 2018).

Kinetic testing (objective 3)

The soil incubations were carried out as follows

5 soil types were selected for incubation. For each soil type, the following treatments were run: Control (no additions), +alkalinity as lime (added at a rate calculated to neutralise measured net acidity), + 10 mM acetate, + 10mM acetate + lime, + SO_4^{2-} . Where possible, each treatment was run with three replicates of the same soil type run from 3 locations within the wetland (soil types 1 and 2). For soil types 3, 4 and 5 the availability of sample meant that incubations were conducted in duplicate on a blend of the material.

Table 1 summarises the treatments and their purpose.

Treatment	Purpose
Control	What rate of metabolism takes place in unamended sediments (a proxy for in-situ rates and pathways)?
+acetate	Does the addition of acetate (labile carbon) stimulate sulfate reduction?
+lime	Is microbial activity limited by low pH?
+acetate + lime	Is microbial activity co-limited by pH and organic matter?
+SO ₄ ²⁻	Is sulfate reduction limited by the availability of SO ₄ ²⁻ ?

The incubations were carried out in 160 mL serum vials with a 1:5 soil water (water taken from Boundary Creek) ratio (Figure 2). The vials were purged with Ar for a period of time shown to be sufficient to remove all oxygen (~1 minute) and sacrificed in a times series of 9 points over 6 months (1,2,4,8,16,32,64, 128 and 200 days). At each time point, a water sample was taken of overlying water (100 ml) for analysis of pH, alkalinity, acidity, dissolved organic carbon, SO₄²⁻, H₂S, Fe²⁺, Mn²⁺, NO₃⁻ and NH₄⁺. The headspace was sampled for CH₄ and CO₂.



Figure 2. Images of the soil types 1-5 in serum vials undergoing kinetic incubation tests

At the commencement and end of each incubation, the water was also sampled for dissolved As, Cd, Cr, Cu, Pb, Ni and Zn. Similarly, sediments were analysed for KCl extractable pH, acid neutralising capacity (depending on pH), acid volatile sulfur and chromium reducible sulfur (determined sequentially), oxalate extractable iron, and oxalate extractable manganese at the beginning and end of the experiment.

Rates were calculated using linear regression of metabolite concentrations over time and reported per mass of sediment.

Analyses were carried out using standard procedures in the Water Studies laboratory which is NATA accredited for NO_3^- , NH_4^+ and DOC. Acid sulfate soil parameters were outsourced to Southern Cross University which is NATA accredited. Metals were analysed using ICP OES. DIC was analysed using an Apollo SciTech AS-C6 DIC analyser. Gases in the headspace of the vials including CO_2 and CH_4 were analysed using an Agilent greenhouse gas analyser.

Results

All raw data from this study are available as an electronic appendix supplied with this report. For brevity and clarity, this report focuses on the data of key relevance to the management of the swamp.

Static tests

The soils sampled from Big Swamp were classified into the following 5 categories on the basis of their acidity, organic matter content and burned status.

SOIL 1 - Deep reduced, medium organic carbon (OC, most common) - medium pH (~4), high net acidity, ~20% OC

SOIL 2 - Deep reduced, low OC - medium pH, %OC <5%, low net acidity

SOIL 3 - Burned surface - Red soil, %OC variable (<10%), low net acidity

SOIL 4 - Surface oxidised medium OC - Very low pH (~2), 20%OC

SOIL 5 - Surface oxidised high OC - Very low pH (~2), 40-50% OC

Soil type 1 is the most common, has a high potential to generate acidity, but has not yet done so as it has not been exposed to oxygen. Soil type 2, has a low organic matter content and is a clayey soil, with a much lower potential to generate acidity. Soil 3 represents the burned soil type, which has a relatively low potential acidity. Soil types 4 and 5 have undergone oxidation and have a very low pH (high actual acidity) but still have significant further potential to oxidise as indicated by their high potential acidity.

Table 2. Summary of key geochemical characteristics of the different soil types

Soil ID	% OC	St dev	pH	St dev	Potential acidity mol/tonne	St dev	Net actual acidity mol/tonne	St dev	Sulfate mol/tonne	St dev	Oxalate extractable Fe mol/tonne	St dev
Soil 1	22	6.0	4.1	0.2	3300	2700	220	100	19	27	140	160
Soil 2	2	1.5	4.1	0.3	61	100	100	70	25	12	70	70
Soil 3	4	2.5	4.3	0.5	34	36	160	80	10	4	3300	5000
Soil 4	22	5.1	2.8	0.1	1300	1800	830	360	290	230	2500	1700
Soil 5	44	7.4	2.8	0.4	3500	3800	490	230	31	27	160	15

The distributions of key soil parameters are shown in Figure 3. The distributions are quite heterogeneous, but conform to the generally expected distribution of acidity, with the highest actual acidity (that released through the oxidation of sulfides) occurring in the surface sediments (low pH areas, soil types 4 and 5). Deeper within the sediment, there is a large store of net acidity in the form of reduced sulfides (dominated by soil type 1).

The highest organic carbon content soils are present in surface soils at the top (western) end of the swamp. The lowest pH was observed in the surface soils in the middle of the swamp on the southern side, and also in the soils around 2 m depth at the top (western) end of the swamp. These pockets of low pH coincided with high concentrations of sulfate indicating they were caused by oxidation of reduced sulfides as would be expected. In addition to the actual acidity, there are pockets with a very high potential for further acidification at depths between 1~5 meters throughout the swamp as indicated by the high net acidity and liming rate required to neutralise this.

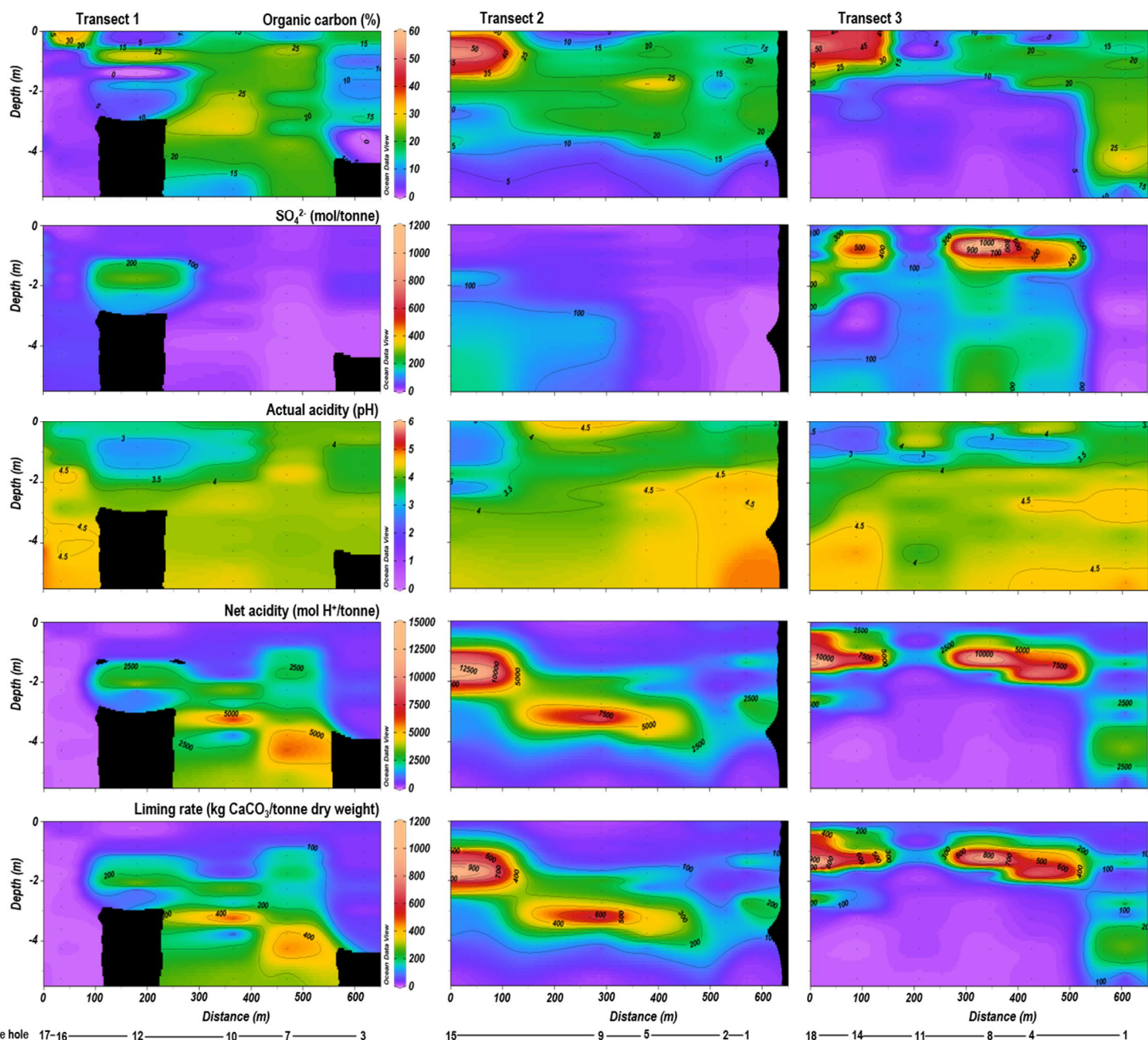


Figure 3. The two-dimensional distribution of key soil parameters along 3 transects of key soil parameters. The borehole numbers are shown in Figure 1.

Kinetic tests

Soil pH

Soils 1 and 2 did not show any clear trend in pH over time (Figure 4). This is consistent with their already reduced nature and one would not expect a further increase in pH under anoxic conditions. Soils 3-5 which are oxidised with varying degrees of actual acidity showed an increase in pH of 0.5-1 pH unit after 127 days, however there was a more limited change after this. The addition of sulfate and acetate did not appreciably change the rates of pH change. The lack of stimulation by acetate is surprising as one would expect this to stimulate carbon neutralising reactions. The lack of any reactions was confirmed by the soil metabolism measurements (see below). The limed treatments showed a jump in pH to 8-10 for soils 1 and 2, and a pH of 6-7 for soils 3-5 (data not shown).

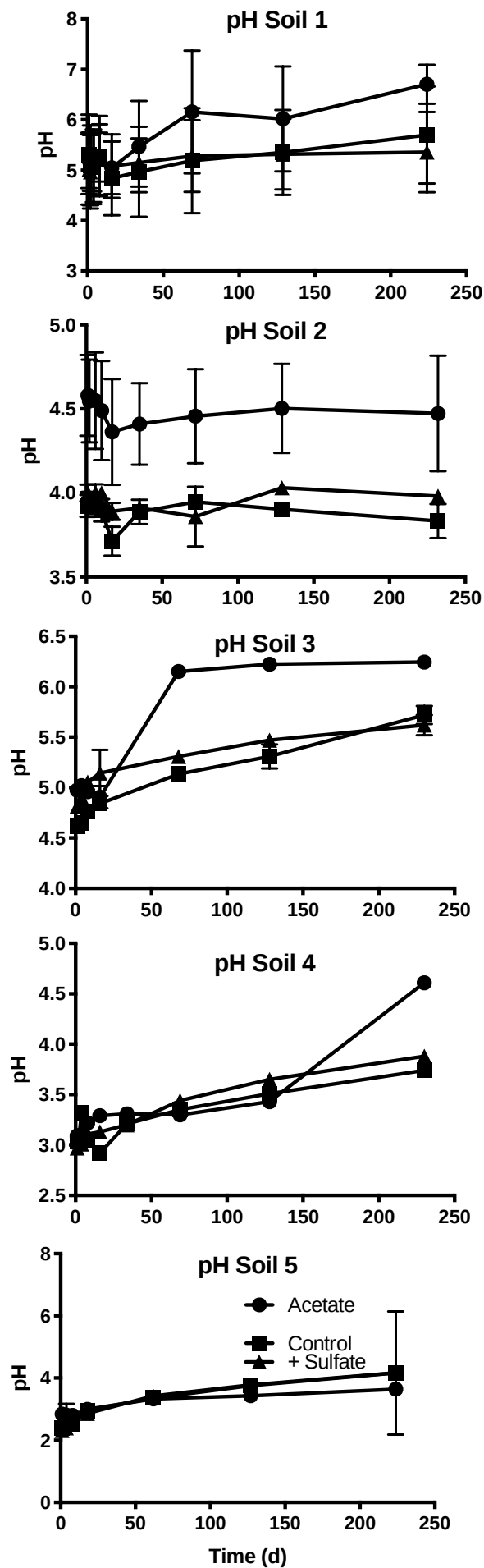


Figure 4. Shows the pH time series for each of soil types 1-5 (top to bottom panels), for the acetate, control and sulfate treatments.

Soil metabolism

Total metabolism (DIC production)

Soils 1 and 2 showed no clear trends in DIC production consistent with the lack of trends in the pH measurements (Figure 5). Soils 3-5 showed clear trends in DIC production for the first 100 days which allowed us to calculate rates of metabolism for this initial period. This was equivalent to 0.05, 0.2 and 0.2 mol DIC/tonne soil/day for soils 3, 4 and 5 respectively. Methane production was generally negligible except for in the acetate treatments (data not shown).

Iron and sulfate reduction

No sulfide accumulation was observed, indicating sulfate reduction is not taking place to any significant extent. For soils 1 and 2 there was generally no clear increase in dissolved Fe over time, suggesting little iron reduction was taking place, consistent with the soil metabolism measurements (Figure 6). For soils, 3-5, there was a clear increase in the dissolved iron concentrations for the first 100 days. After this dissolved iron production generally tapered off. These observations are also consistent with the metabolic measurements, where the fastest rates were observed in the control and +sulfate treatments.

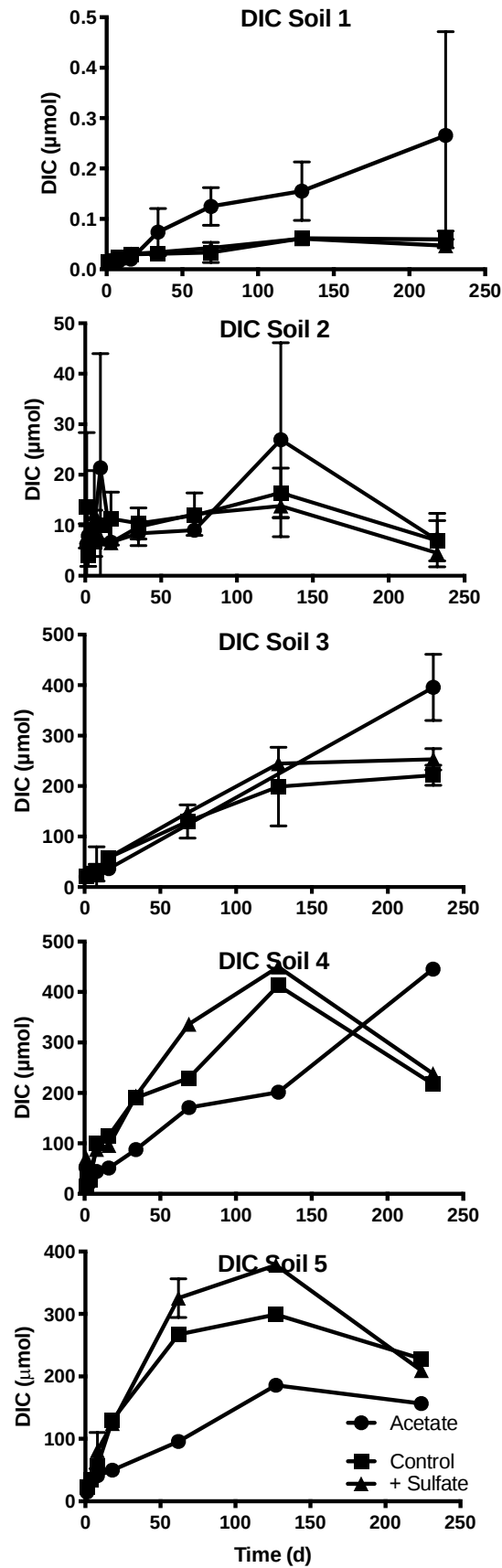


Figure 5. Time series of dissolved inorganic carbon (DIC) production over time in each of the treatments. Note: limed is not shown as this has added a massive excess of DIC, making meaningful changes impossible to measure.

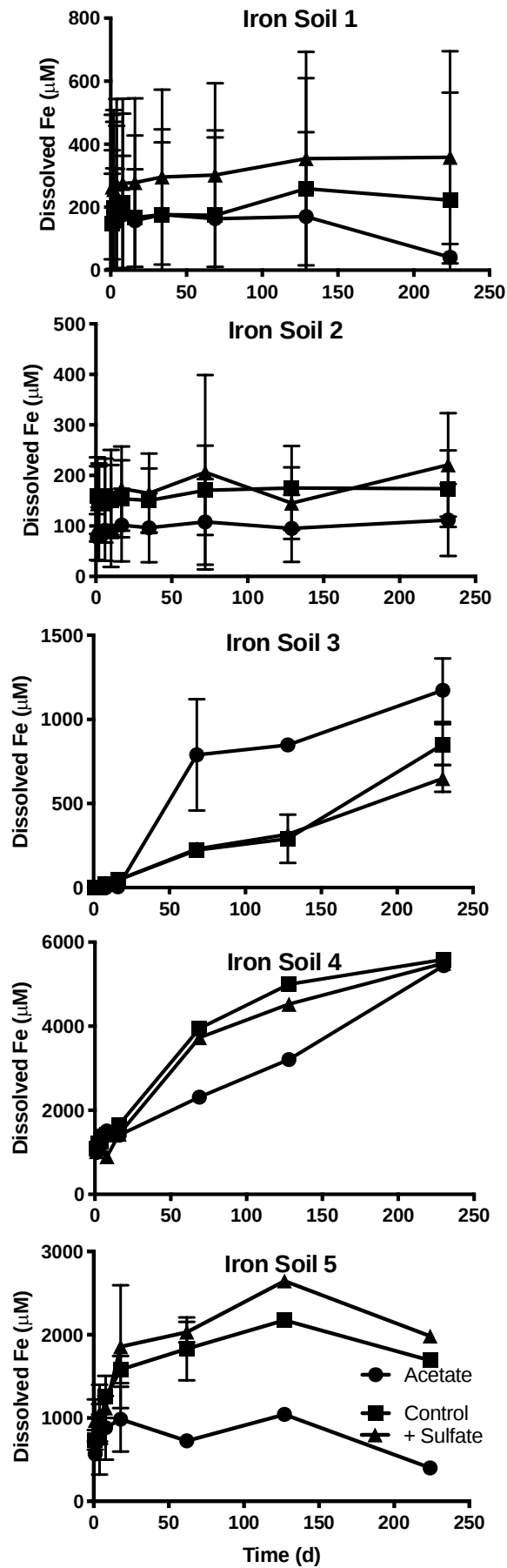


Figure 6. Dissolved Fe accumulation in the control, acetate and sulfate treatments for the 5 soil types. Note limed data is not shown because there was little iron accumulation observed in these treatments, most likely as a consequence of the precipitation of FeCO_3 .

Discussion

High net and potential acidity within Big Swamp

As previously noted in a memo by Baldwin, there is a substantial amount of acidity stored in Big Swamp. Based on the average net acidity of the Swamp, Baldwin estimated that 65 000 to 100 000 tonnes of lime would be required to neutralise this acidity. The highly heterogeneous nature of the acidity means that targeting the hot spot would probably be expensive and technically difficult. The most cost effective and environmentally acceptable solution to prevent the release of this net acidity is probably the maintenance of the saturated soil conditions.

Potential of anaerobic reactions to neutralise actual acidity

One of the key questions addressed in this study is the extent to which anaerobic reactions such as sulfate and iron reduction can neutralise the actual acidity present in the oxidised regions of Big Swamp represented by soil types 4 and 5. Both the kinetic and static test data from this study allow us to estimate the rate and extent of neutralisation of actual acidity. The initial rates of DIC production for sites 3, 4 and 5 were ~ 0.05 , 0.2 and 0.2 mol DIC/tonne soil/day, respectively. Given the accumulation of dissolved iron, and the absence of sulfate reduction, it is most likely this metabolism is taking place via iron reduction as shown in equation 3 which neutralises 8 equivalents of H^+ for each mole of carbon oxidised. Therefore, the net actual acidities of 162, 833 and 493 mol/tonne (Table 1) for soils 3, 4 and 5 respectively could be neutralised within ~ 1 -2 years assuming bioavailable iron and carbon do not become limiting. The incubations do however suggest that organic matter or some other factor did become limiting after about ~ 100 d as indicated by the tapering of the production rate of DIC after this time. If organic matter was limiting, one would expect the acetate treatment to have led to significantly higher rates than the controls, which was not the case. Macronutrients such as nitrogen can also potentially limit microbial growth, however, this is unlikely to be the case here given that ammonium concentrations in the slurries were at least several mg/L after 100 days. Phosphorus is another possible limiting factor, however, we did not measure this in the slurries. Irrespective of the cause of the limitation of the microbial communities, the slurry incubations suggest that there is limited capacity to drive neutralising processes for much more than 100 days. Therefore the actual capacity of Big Swamp to neutralise the acidity generated is negligible.

Microbial limiting factors notwithstanding, we can make an estimate of the maximum size of bioavailable iron pool (which is a geochemical control on the extent of neutralisation) based on the oxalate iron extractions shown in Table 1. Based on these pools and the neutralisation stoichiometry of $4H^+$ per mole of iron reduced, then we get neutralisation capacities of ~ 13000 , 10000 and 640 mol H^+ /tonne for soil types 3, 4 and 5, respectively which is well in excess of their actual acidity. It should be noted that oxalate will extract bioavailable iron fractions such as ferrihydrite as well as more refractory forms such as magnetite (Kostka and Luther III 1994), and this neutralisation capacity should be considered an absolute maximum. It is suggested that further iron extractions be carried out using ascorbate, which is known to be a better proxy for bioavailable iron (Hyacinthe et al. 2006).

At this point it should be noted that although iron reduction will neutralise acidity through the production of dissolved Fe^{2+} (albeit to a limited extent), this species is mobile, and if it is released from the swamp via groundwater, acidity will be generated again at the point of release. As such, potential acidity will only be immobilised once sulfate reduction takes place leading to the precipitation of FeS (equation 5). Given the large pools of iron oxide and the limited microbial capacity to undertake organic carbon oxidation, it seems likely that it will take several years (if at all) for these to become exhausted before sulfate reduction commences. Once sulfate reduction does commence, its extent will be limited in the short term by the relatively small pool size of sulfate compared to iron which means that there will be an excess of dissolved Fe^{2+} (and mobile potential acidity). As such, any remediation option should be aimed at preventing groundwater leaving the swamp indefinitely. If this is not possible, then treatment of the emerging groundwater or the stream water (e.g., through liming) will be required.

Recommendations

1. The swamp should be maintained in a saturated state to prevent further release of stored net acidity
2. The release of groundwater from the swamp should be minimised indefinitely (or treated upon emergence) to prevent further release of actual and potential acidity.

References cited

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