SPATIAL AND TEMPORAL VARIABILITY OF ACIDITY AT A COASTAL ACID SULFATE SOIL SITE

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INTRODUCTION

Acid sulfate soils are a major environmental problem in coastal areas of Australia. Changes in land use, including clearing and the construction of drains, have resulted in the oxidation of previously reduced sediments. This results in the oxidation of metal sulfides, primarily pyrite, and generation of acidity. The overall reaction can be described as (White *et al*. 1997):

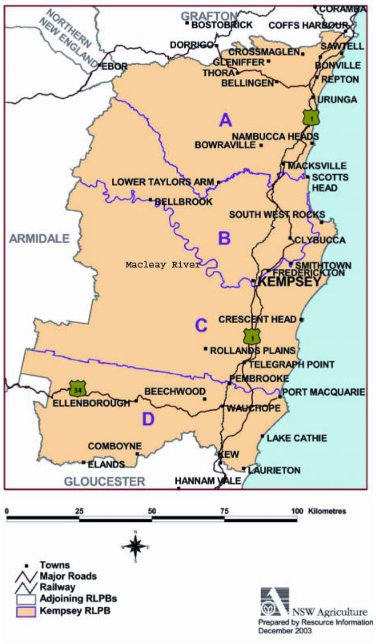
$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

Since oxidation of sulfidic sediment has caused the problem of acidity, land managers have considered that re-flooding and inducing anoxic conditions will mitigate the effects. However, even in the absence of dissolved O_2, pyrite oxidation can occur if there is available ferric iron via the reaction (White *et al*. 1997):

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

Formation of intermediate pyrite oxidation products, such as jarosite, can store acidity in the sediments, releasing it long after the initial disturbance occurs, generating a flux of acidity out of the system in response to subsequent wetting and drying events. In addition to these acid generating reactions, the dissolution of carbonates and silicates, ion exchange reactions with clays and microbially mediated sulfate reduction will all consume acidity.

In order to understand the variability of acidity in sediments, groundwater and surface water we have been focusing on a study site at Mayes Swamp near Kempsey, NSW (Figure 1), which has experienced seasonal inundation of floodwater.



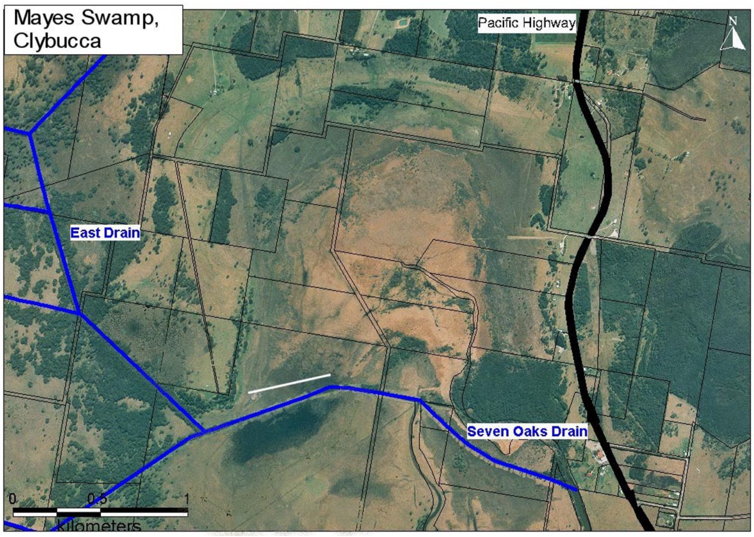


Figure 1: A map of Kempsey area (left), and aerial photograph of the Mayes Swamp field site (above). The original transect is along the white line just north of the Seven Oaks Drain.

A bund and pipe culverts were constructed along the Seven Oaks Drain wall to retain water in Mayes Swamp in 1993. In 2001, a weir was constructed on Seven Oaks Drain with a crest height of -0.20 m AHD. The optimal depth of water for pasture productivity (water couch/soft rush) within Mayes Swamp is ca. 12 cm. To

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achieve this, the landholder has placed drop boards on the culverts that link the Swamp to Seven Oaks Drain, in order to capture rain during dry conditions. This promotes inundation of the Swamp and growth of pasture. Under prolonged wet conditions, the boards are removed to allow drainage back into Seven Oaks Drain down to the weir height of -0.20 m AHD. Over the last few years, during prolonged drought, the Swamp has been inundated for approximately 4 months (March-June). In 2004, the period of inundation was limited to approximately 6 weeks. Under 'normal' conditions, the Swamp would remain wet for 6 months. A preliminary study at the site in April 2002 focused on determining actual (pore water pH) and potential (pyrite and jarosite content) acidity along a transect in a flooded site. Subsequent surveys in April 2004, during flooding, and July 2004, during dry conditions, focused on comparing a scalded area with the adjacent vegetated pasture.

METHODS

Sediment samples were collected with a hand auger, bagged, and sealed tightly to limit evaporation and oxidation of sulfides. The sediment profile was split into 3 to 6 different horizons based on differences in colour, mineralogy, moisture and texture. Moisture content was determined after allowing sediment samples to dry overnight at 80°C. The pH and electrical conductivity was determined on 1:5 sediment-water extracts (5 gram sediment and 25 ml deionized water) on both wet and dried samples. For sediments collected in April 2004, an aliquot of these extracts was filtered with a 0.2 µm filter and then analysed for major cations. Pyrite content was estimated on dried samples using a standard peroxide test. Mineralogy was determined on selected samples by X-Ray Diffraction (XRD) analysis of bulk samples and clay separates. Several sediment samples were analysed by Cambridge Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectrometer (EDS) detection. Several samples of surface and groundwater were collected in 500 ml HDPE bottles. Aliquots were filtered using 0.2 µm filters and acidified for metal analysis on water samples and water extracts of the sediments by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using standard methods

RESULTS AND DISCUSSION

The preliminary study at the site focused on determining the variability in acidity in the different soil horizons over a transect of almost 700 m across a partially flooded paddock. Results show that pore water within the top ca. 50 cm of the sediments is generally very acidic with pH ca. 2.5-5 and increased with depth (Figure 2). The change in acidity corresponds to a change in mineralogy and geochemistry of the sediments. Jarosite mottles are abundant below ca. 20 cm in all the depth profiles indicating pyrite oxidation has occurred. Although jarosite is abundant in the sediments at this location, comprising ca, 1-10 % of the total weight, pyrite content was substantially lower, comprising less than ca. 0.03 wt. % of the total sediment. Below ca. 60 cm, dissolution of $CaCO_3$ shells, which occur as a distinct layer across Mayes Swamp at a depth of ca. 70 to 90 cm, buffers the acidity generated from pyrite oxidation and dissolution of jarosite.

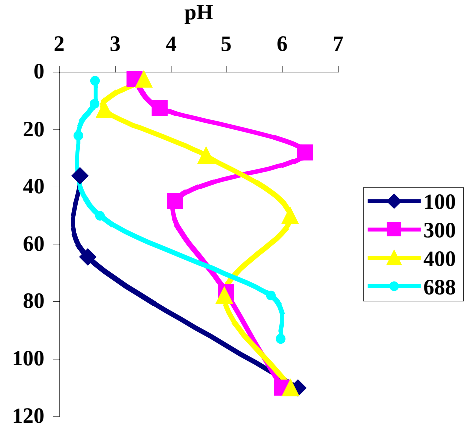
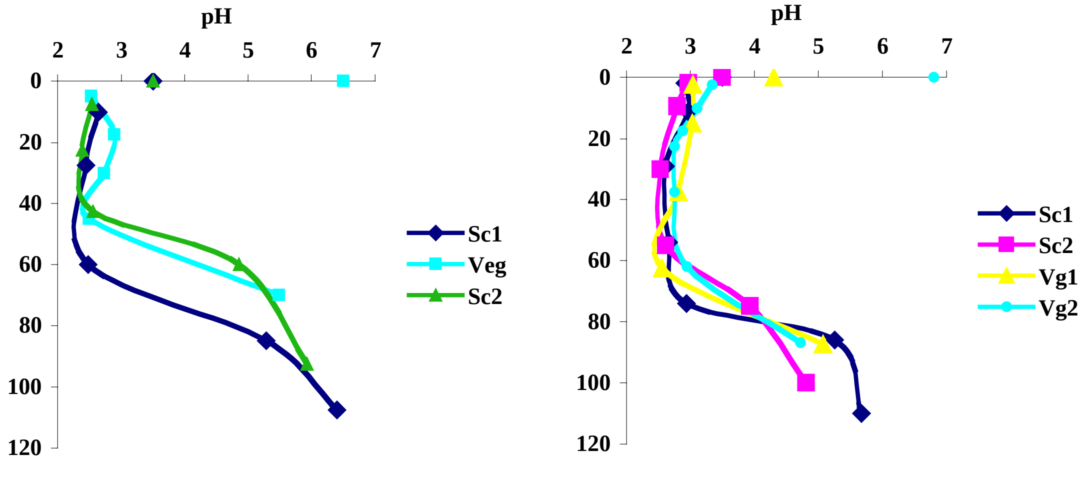


Figure 2: pH of pore water in 4 sites along a 688 m transect across the paddock. Acidity of the pore water is estimated from the moisture content and the measured pH in the 1:5 sediment water extract. The transect ends at 688 m in the middle of a scald site.

The site was revisited twice in 2004 during flooded (April) and dry (July) conditions. The more recent study focussed on a much smaller area, comparing the physical, chemical and mineralogical properties of the scald site, at the end of the original transect at 688 m, with the adjacent vegetated area and smaller scald area over a distance of approximately 50 metres. Results of the survey of acidity in the pore water were similar to what had been determined previously (Figures 2 and 3). The pH of the pore water is extremely acidic, measuring ca. 2.5 to 3.5 down to ca. 40 to 80 cm depth and then increasing significantly due to buffering from the shell layer (Figure 3). In April, the zone of extreme acidity (pH < 3) in the pore water in the centre of the scald site persisted ca. 20 cm deeper than the adjacent vegetated and smaller scald sites (Figure 3a). The acidity of the pore water at this site is in striking contrast to the acidity of the overlying surface water (Figure 4). The pH of the ca. 15 cm deep surface water was ca. 3.5, or ca. 1 pH unit higher than the pore water over both scald areas. The pH in the overlying water in the vegetated area however, was ca. 6.5 (Figure 4). The transition from pH 3.5 to 6.5 occurred laterally over ca. 30 cm in a continuous water body. The cause for the extreme pH difference between the pore water and overlying surface water is not entirely clear. One possibility is that the overlying water is relatively 'fresh', with limited interaction across the sediment-water interface in the vegetated area, and slightly larger flux of pore water across the sediment water interface in the scald areas. This seems unlikely, since the water is shallow and should mix and equilibrate rapidly and the last major influx of freshwater had occurred many weeks previously.

The other possibility is that acidity is rapidly consumed in the vegetated zone, presumably by sulfate reduction, and that the rate of sulfate reduction is greater than the mixing-diffusion of surface water into the vegetated zone. This seems likely since there is abundant organic material associated with the vegetation available for consumption by heterotrophic sulfate-reducing bacteria. SEM and EDS analysis of sediment collected from the vegetated area in July showed evidence of iron monosulfide mineral phases (black ooze) in the top few centimetres of the sediment. This was not observed in the scald areas or in the vegetated area months earlier, suggesting very active sulfate reduction during that time. Although the pH in the pore water at the surface of the vegetated site was still extremely acidic in July, at ca. 3.5, it was higher than in the scald areas where pH was <3. Pore water pH in the vegetated area decreased with depth from the surface to approximately 40 cm, suggesting an acid consuming reaction such as sulfate reduction.

It is clear from the surface and pore water pH measurements that there is a considerable acidity problem at this site, however, this is only a small fraction of the total potential acidity. Several possible sources of acidity in the system can be identified. We have estimated acidity for this system based on a column of sediment 10 cm square and 1 m deep with 10 cm of standing water (11 L total volume). Assuming a pH of 3, the total moles of protons per 100 cm^2 of surface area in the standing water would be 10^{-3} moles H^+, or 100,000 moles of H^+ per km^2 of pasture. Draining of the surface water from this pasture could result in a large acid flux to the local drains and creeks. However, this is only a small fraction of the acidity in the sediment pore water, which contains on average 25 times higher proton content per 100 cm^2, or 0.025 moles H^+. Two other major sources of acidity within the sediments are oxidation of pyrite and dissolution of jarosite with subsequent precipitation of iron oxyhydroxide mineral phases. The pyrite concentration in the sediments was estimated based on the acid generated by the peroxide test, and was << 0.1 % throughout the sediment. SEM observation and EDS analysis of the sediments confirmed that pyrite was scarce. If all the remaining pyrite was oxidized, this would only produce an additional 0.08 moles H^+ within the top metre of the sediment column, or roughly three times more acidity than is present in the pore water.



April **July**

Figure 3a (left): pH of pore water from the middle of two scalds and vegetated sites along a ca. 50 m transect; **b (right)** pH of pore water from the middle of the scald site (Sc1), ca.1 m from the edge of the scald site (Sc2), ca. 1 m into the vegetated area (Vg1) and middle of the vegetated area (Vg2).

The major source of potential acidity at this site is from the dissolution of jarosite. Jarosite is an intermediate oxidation product of pyrite that forms under acidic conditions (White *et al.* 1997). The dissolution of jarosite can be described by:

$$KFe_3(SO_4)_2(OH)_6 + 3H_2O \rightarrow 3Fe(OH)_3\downarrow + 2SO_4^{2-} + 3H^+ + K^+$$

Jarosite mottles are abundant throughout the top metre of the sediment column, comprising at least 2% of the total volume. The estimate of potential acidity in an average sediment column at this site is ca. 1.5 moles H^+, or roughly 10 fold higher than all the other sources of acidity.

Major sinks of acidity at the site are anaerobic respiration of ferric iron and sulfate, dissolution and ion exchange reactions of silicate minerals and dissolution of the $CaCO_3$ shell layer. We saw evidence of sulfate reduction and formation of iron monosulfides in the top few centimetres of the vegetated site, which resulted in an increase in pore water pH of ca. 0.5, and an increase in surface water pH of ca. 3 pH units. If this effect is localized to the surface water and upper few centimetre of the pore water, this would account for ca. 0.002 moles H^+ per 100 cm^2 surface area. It is possible that the proton consumption by anaerobic microorganisms could be considerably greater than this, since removal of dissolved ferric iron and sulfate will shift solution equilibrium and jarosite will dissolve. However, since the zone of abundant jarosite is below the organic rich zone where anaerobic microorganisms would be most active, it is unlikely that this process is important over short time scales. Dissolution of silicate minerals and ion exchange reactions could also buffer acidity. Thermodynamic calculations of mineral solubility on the pore water extracts showed that pore solutions are generally supersaturated with respect to the expected silicate mineral phases in these sediments. The major potential sink for acidity at this field site is from dissolution of the carbonate rich shell layer that is found at ca. 80-100 cm below the surface. The estimate of buffering capacity from the dissolution of shells is ca. 2.5 moles H^+ per 100 cm^2, comparable to the estimated acidity at the site.

Although there is the potential for a typical sediment column to be pH neutral, the acidity and the buffering capacity are physically separated from each other. Acid neutralization within the sediments will depend on the dissolution rates of jarosite and calcium carbonate, the moisture content of the sediments, the residence time of the pore water, and the flux of water through the sediment column. In July, when the surface of the pasture was dry, the depth of the extreme acidity correlated with the depth of water table (Figure 5), suggesting that pore water with its associated acidity was percolating down through the sediments.

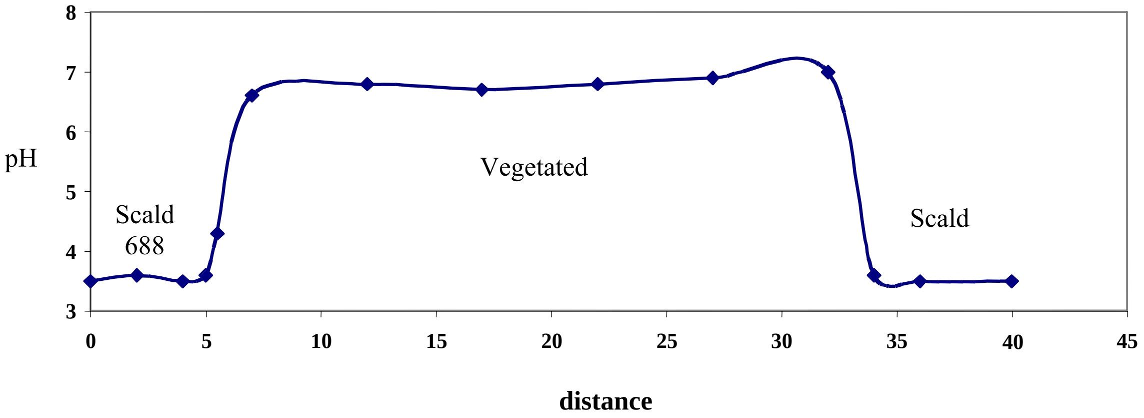


Figure 4: pH of the standing water along the transect.

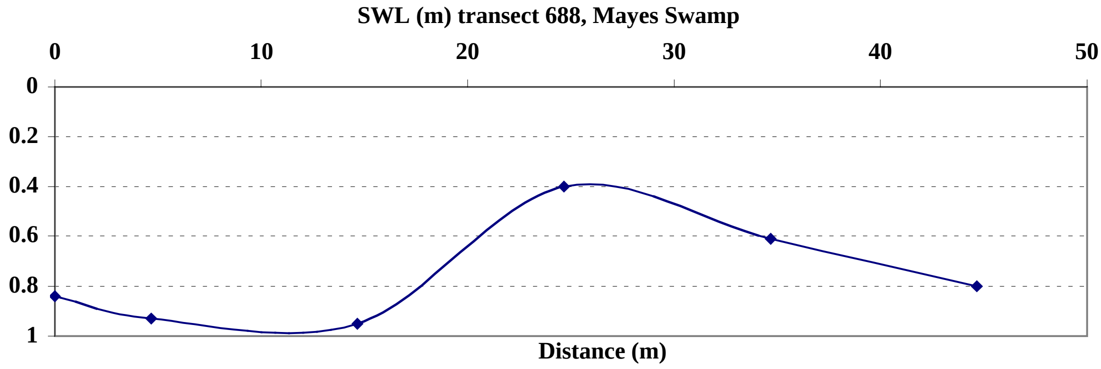


Figure 5: Height of water table along transect below scalded and vegetated sites.

CONCLUSIONS

Differential pore water acidity in the vegetated and scalded sites is a function of very rapid sulfate reduction by heterotrophic sulfate reducing bacteria in organic material associated with vegetation. Differential pore water acidity in a vertical direction is a function of:

- Acid consuming reactions by heterotrophic sulfate reducing bacteria at the surface where organic material is available;
- Chemical reactions associated with soil mineralogy, including oxidation of pyrite (which is supply-limited), dissolution of jarosite in the upper profile, and dissolution of $CaCO_3$ in the shelly layer; and,
- Spatial and temporal variability of groundwater levels.

Current work involves:

- Identification of the organic matter to quantify the proportion of organic content of sediments in pasture and scald sites down-profile;
- Groundwater fluxes and chemistry; and,
- Hydraulic properties of the soil mass.

REFERENCES

WHITE I., MELVILLE M., WILSON B.P. & SAMMUT J. 1997. *Wetlands Ecology and Management* **5**, 55-72.