

CONTROLS OF ACID, SALT AND METAL DISTRIBUTION AT A COASTAL ACID SULFATE SOILS SITE

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INTRODUCTION

Acid sulfate soils are a major environmental problem in both coastal and inland areas of Australia. Oxidation of pyrite results in acidification, and an increased flux of salts and metals into solution. One strategy for remediation of acidic oxidized environments is to flood the area to induce anoxic conditions and limit further pyrite oxidation. However, this could also result in increased solubilization of sparingly soluble salts such as gypsum and jarosite, and an increase in the release of acid and ions to solution.

The field area for this study is Mayes Swamp, located within the Glycucca Creek subcatchment 25 kilometres north of Kempsey, NSW. The site chosen is significant because has been identified as an ASS Priority Area by the NSW Department of Natural Resources, illustrating areas where 'land management decisions in relation to ASS have contributed to, and can lead to further, severe soil and water acidification, poor water quality, reduction in agricultural productivity, loss of estuarine habitat and/or degraded vegetation and wildlife' (Tulau *et al.* 1999). The site has undergone remedial management through the installation of a weir in the main drain in 2001, with the goal to limit acidic discharge to surrounding waterways and to induce anoxic conditions to counteract the ASS problems. This site is one of the field areas visited by the SRES, ANU Water Resources Management class in the past several years, and has been the focus of several other pilot studies investigating the role of microbes on acidification and metal mobility (eg Kehoe *et al.*, 2004).

Previous work in 2003-2005 has shown severely degraded, scalded areas occurred over much of the site with large spatial variability in acidity, from approximately pH 3 to 7 over meter scale horizontal distances coincident with the change from scalded to vegetated area (Somerville *et al.*, 2004; Beavis *et al.*, 2005). The pH of the sediments was typically below 4 down to ~ 70 cm where acidity was buffered by a shell layer. Analysis of acid stores in the sediment showed acidity was largely controlled by jarosite and ion exchange reactions with clays. These extremely acidic conditions are associated with high salt content and elevated levels of trace metals (Somerville *et al.*, 2004 Beavis *et al.*, 2005, Kehoe *et al.*, 2004). The site has changed substantially since the original studies. The formerly scalded areas now have dense vegetation, and surface water pH is near neutral. This has resulted in the formation of reducing conditions and monosulfide black ooze from iron and sulfate reduction.

The purpose of this work is to conduct a detailed investigation of a sediment profile from a highly altered acid sulfate soil site to determine the physical, chemical and mineralogical controls on acidity, salinity and metal mobility and how this has changed as a result of flooding and revegetation.

METHODS

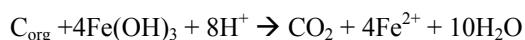
Sediment cores were collected with either a 1.5 m gouge auger or 6.5 cm ID PVC core tube along several transects that were roughly perpendicular to the drain. One intact core was chosen for extensive characterization based on its proximity to sites that had been previously sampled (near site 688) on numerous occasions. The core was cut length-wise and described using standard sedimentological nomenclature. The mineralogy of the core was determined from visual inspection and comparison with previous studies, X-ray diffraction and characterization with SEM and EDS. Pyrite content was estimated by a peroxide test, and also from analysis of sediment fractions by SEM.

Pore water chemistry was determined by several methods. Standard 1:5 sediment:water extracts were done on sediment samples from different horizons. The slurry was placed on an orbital shaker for several hours, and then allowed to react overnight. The slurries were centrifuged and the supernatant was removed and filtered using a 0.45 µm filter. Pore water was extracted from fresh sediment samples by centrifugation and filtration. Solution pH and EC were measured on aliquots of fresh solution. The remainder of the pore water or water extract were divided into two clean vials. One aliquot was acidified with nitric acid for analysis of major ions by ICP-AES. The second was analysed for major anions by ion chromatography.

RESULTS AND DISCUSSION

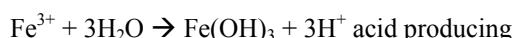
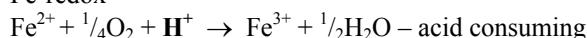
A description of the core is presented in Table 1. The section consists of a reduced organic rich A horizon that ranges from black at the surface to brown over ~ 20 cm. Pyrite and FeS were detected in the black layer from the peroxide test and from SEM analysis. The color of the B horizon ranges from tan at the top to a blue-grey at the base which is consistent with a change in the clay mineralogy from illite to Fe-rich glauconite. The B horizon is extensively mottled along former root channels, with mottles grading from yellow jarosite dominated at the top of the B horizon to brownish orange goethite towards the bottom. XRD analysis of the mottled minerals confirmed both jarosite and goethite. The mottles comprise up to several percent of the sediment. The transition between the B and C horizons (more oxidized compared to more reduced) is defined by a layers of shells. Gypsum crystals are abundant right above the shell layer which is consistent with sulfuric acid reacting with calcium carbonate. The C horizon is comprised of thick grey clay with sparse goethite-hematite mottles. The entire section is similar to others obtained at this site from this and previous sampling trips, except that as a result of flooding, the A horizon is reduced and contains pyrite.

The pH of the pore water ranged from ~ 4.5 at the top of the sediment profile, ~ 3.5 in the oxidized B horizon and near neutral below the shell layer in the C horizon (Figure 1). The slight increase in pH towards the surface was observed previously for vegetated regions of the site (Beavis et al., 2005) and can be attributed to biologically mediated iron and sulfate reduction reactions, both of which consume acidity.



The low pH values, ~ 3.5 are controlled by Fe redox and precipitation reactions, including dissolution and precipitation of jarosite

Fe-redox



Below ~ 40 cm, pH increases to near neutral due to buffering by dissolution of the $CaCO_3$ shell layer.

The pH of 1:5 extracts were similar to the pore water pH for the same intervals, in spite of the fact that these extracts should reflect at least a 10 fold dilution of acidity. This indicates that there is pool of rapidly released acidity stored in the sediment, either from the dissolution of jarosite or from ion exchange reactions with clays.

The concentrations of major cations and anions ions in pore waters show a generally increase with depth (Figure 2). This trend is almost exactly the opposite of what has been observed previously at the site when it was dry and scalped (Beavis et al., 2005). Previous analysis of 1:5 extracts of sediments show increasing salt concentrations towards the surface reflecting concentration from evaporation and evapo-transpiration. The major ions show no apparent relationship with pH, except that sulfate concentrations in pore water is lower in the surface sediments where there is active sulfate reduction.

High concentrations of trace metals, ppm levels of Zn, Co, Cu, Ni and REE, and 10's ppm levels of Fe and Mn were measured in pore water extracted from the sediments (Figure 3). Trace metal concentrations are inversely related to pH throughout most of the sediment profile. Concentrations are low at the surface, increase with increasing acidity, and then decrease with increasing pH with depth.

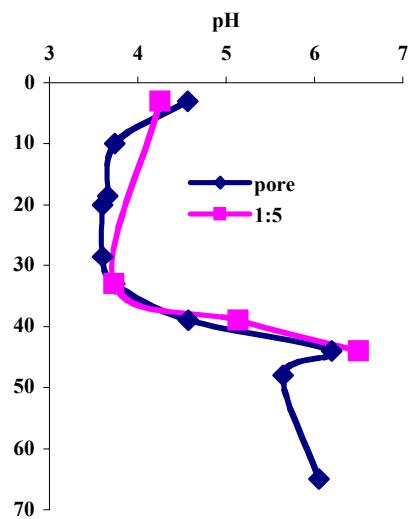


Figure 1 pH of pore water and sediment water extracts

Table 1: Vertical profile description for typical Mays Swamp stratigraphy

Horizon ID	Moisture Content %	Description
A ₁	A ₁ 42.48	Black, rich in organic matter, peat like sediment
A ₂	A ₂ 19.10	Lighter brown, alluvial like sediment, organic matter in the form of root cavities present.
B ₁	Oxidised B ₁ 21.55	Grey thick estuarine sediment interlaid with prevalent yellow crystalline mottles associated with root cavities.
B ₂	Oxidised B ₂ 22.92	Grey thick estuarine sediment interlaid with prevalent red/brown crystalline mottles associated with root cavities. Crystals up to 1cm prevalent.
B ₃	Transition B ₃ 18.49	Shell layer with thick grey estuarine sediment occurring between shell fragments
C ₁	Reduced C ₁ 24.58	Blue/Grey thick estuarine sediment, red/brown ochre mottles occurring around limited root cavities



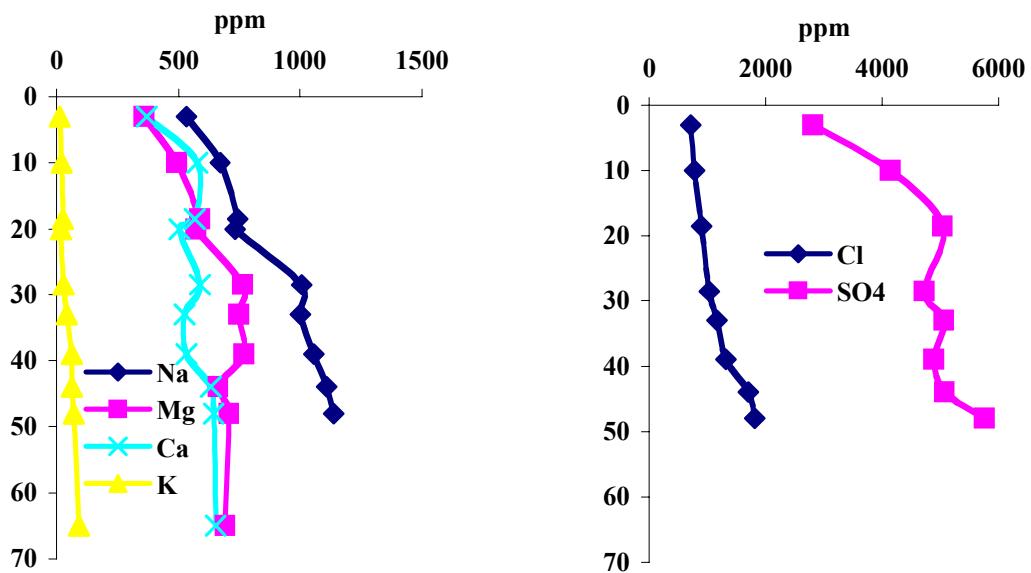


Figure 2 Concentrations of a) major cations and b) major anions in pore water extracts from core MS2C2

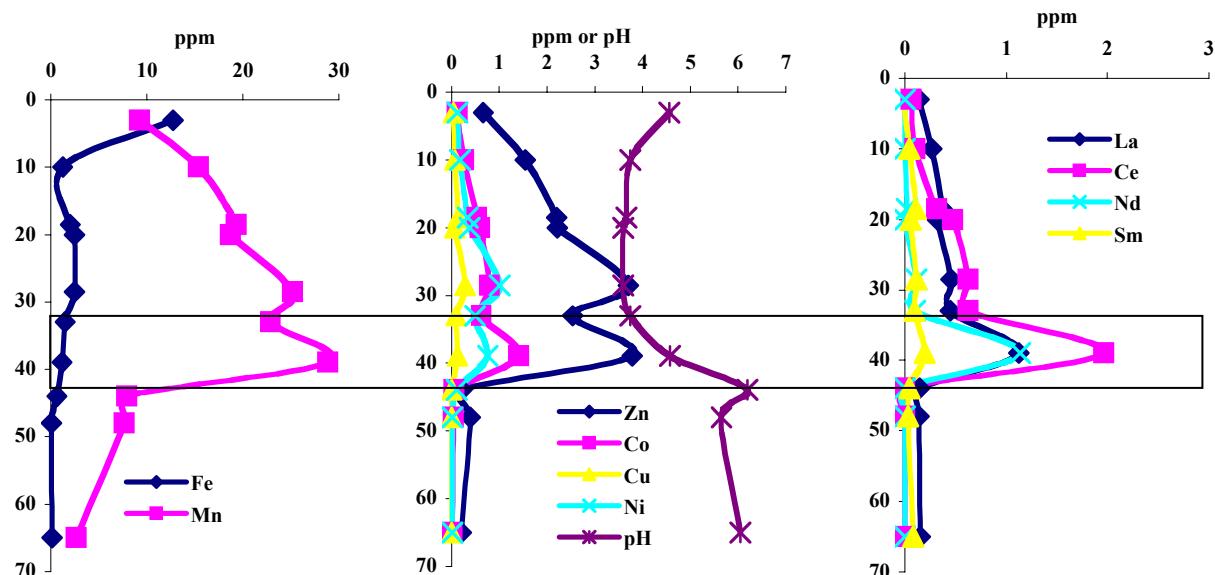


Figure 3 concentrations of trace metals and pH as a function of depth. Trace metals are inversely correlated with depth except for the spike in trace metal concentrations at ~ 40 cm that occurs as pH starts to increase

The concentration of dissolved Fe is controlled by both acidity and redox state. The elevated Fe concentration at the surface reflect reductive dissolution of Fe mineral phases under mildly acidic conditions. The subsurface bulge in Fe concentration from ~ 10 to 30 cm reflects jarosite dissolution and the solubility of Fe oxyhydroxide phases.

One notable exception to the above trend is a secondary spike in trace metal concentration in the 36-42 cm interval just above the shell layer. This zone is coincident with the transformation of jarosite to goethite mottles and an increase in solution pH.

There are 4 possible explanations for this secondary spike in metal concentration-

- 1- Metals could have come from leaching of sediments under acidic conditions from higher in the sediment profile, and are mobilized down profile as the acidic water percolates down from flooding.
- 2- The spike in metal concentrations coincides with the transformation of jarosite to goethite- jarosite will incorporate many elements into its crystal structure, therefore dissolution of jarosite and precipitation of goethite could release the metals to solution.
- 3- Alternatively- since jarosite will incorporate many other elements into its structure, the relatively low concentrations of trace metals in the upper part of the profile may reflect the solubility of trace metal substituted jarosite.
- 4- The high metal concentrations could have come from the dissolution of other phases, such as associated carbonates or other minerals. This layer also contains abundant gypsum crystals formed as a result of dissolution of shells by sulfuric acid.

CONCLUSION

The site has changed dramatically from the original investigations. Continued flooding has resulted in anoxic condition and acid consumption at the surface. However, below the surface the sediments are still extremely acidic, with elevated salt and trace metal concentrations.

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