SPATIAL AND TEMPORAL VARIABILITY OF ACIDITY AT A COASTAL ACID SULFATE SOIL SITE II: A TIME FOR CHANGE

Sara Beavis[1], Fern Beavis[2], Peter Somerville[1] & S.A. Welch[2,3]

[1]CRC LEME, Center for Resource and Environmental Studies, Australian National University, Canberra, ACT, 0200
[2]CRC LEME, Department of Earth and Marine Sciences, Australian National University, Canberra, ACT, 0200
[3]CRC LEME, Research School of Earth Sciences, Australian National University, Canberra, ACT, 0200

INTRODUCTION

Acid sulfate soils are a major environmental problem in both coastal and inland areas of Australia. The oxidation of pyrite, and subsequent acidification, results in an increased flux of salt, metals and acid from the impacted areas into the surrounding waterways. The lower Macleay River catchment, on the mid north coast of NSW, was the first area in Australia where these soils were identified (Walker 1972) and where acid sulfate soil hotspots have been targeted for management. Within this general area, the Mayes Swamp field site is located within the Clybucca Creek subcatchment, 25 kilometres north of Kempsey (Figure 1).
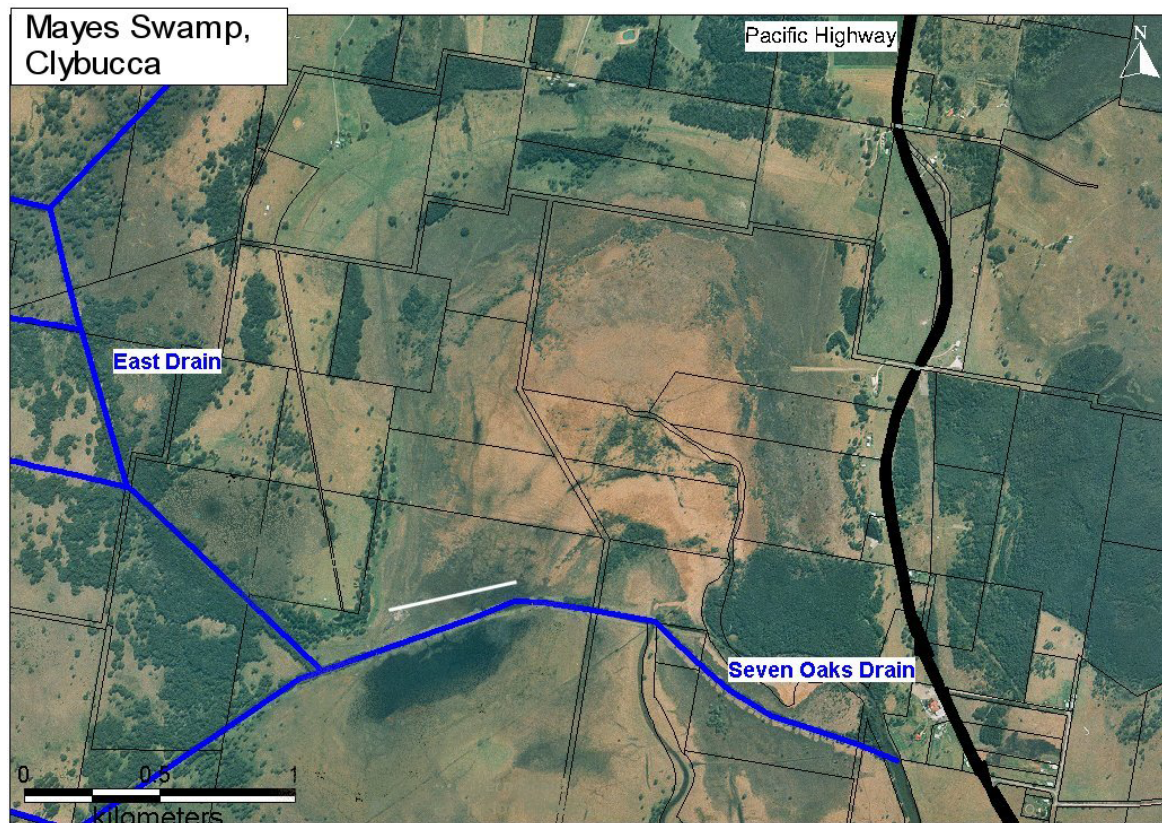

Figure 1: Map of Mayes Swamp near Kempsey.

This site is one of the field areas visited by the School of Resources, Environment and Society (SRES), ANU, Water Resources Management class in the past several years. The site has been a focus of study due to a number of unique attributes relating to management and to trends and responses to rainfall events. Here, acid discharge events are highly responsive to rainfall in terms of response times and severity of water quality degradation. This sensitivity is demonstrated by acidic discharge occasionally occurring *prior* to major rainfall events, in response to changes in air pressure and associated mobilisation of soil porewater. However, there can be a lag between the onset of rainfall and acidic discharge, as a function of antecendant moisture conditions—the drier the conditions, the longer the lag period. In the case of prolonged drought, acid discharge may only occur after the second, rather than the first 'drought-breaking,' rainfall event. Once acidic discharge is initiated, poor water quality in terms of pH can persist for extended periods of time, from weeks to months. This study originated from an effort to understand the drivers of the responsiveness and

persistence of this system.

Previous work at this site focused on the spatial variability of acidity between adjacent scalded and vegetated areas and surface and pore water (Somerville *et al.* 2004). We found that the pH of the surface water varied from pH 3 (scald) to 7 (vegetated) within about 1 m horizontal distance. However, the pH of the pore water in this area ranged from ca. 2.5 to 3 in about the upper 50 cm of the profile, showing an acidity gradient of 4 pH units over a few cm scale from pore water to overlying surface water in the scalded areas.

The purpose of this work is to determine the physical and chemical controls on the flux of acidity and salts from the sediments. Although there could be a large amount of acidity stored in the sediments and water, as evident from the mineralogy and sediment water leaches, it is not clear how rapidly the acidity could be released and flushed from the system. The previous work at the site indicated that either acid exchange between surface and pore water was limited, or else acid consumption in the standing water was rapid compared to mixing or diffusion. Acid discharge into the drain near the site generally lags behind rainfall events, suggesting that the kinetics of acid release are slow compared to infiltration and surface runoff.

METHODS

The pH and electrical conductivity were determined on 1:5 sediment-water extracts (5 grams of sediment and 25 ml of deionized water) on both wet and dried samples after allowing samples to equilibrate for 24 hours. A subset of the samples was leached repeatedly with water and analysed for pH and electrical conductivity after hours to days. 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 by ICP-AES.

Jarosite dissolution experiments were conducted to estimate the kinetics over a range of conditions and the flux of acids and metals to solution from jarosite. Jarosite was collected from sediment cores obtained from the field site. Intact sediment core samples were air dried and then jarosite mottles were carefully scraped out from the bulk sediment. These were analysed by Scanning Electron Microscope (SEM) with Energy Dispersive X-Ray Spectrometer (EDS) detection, and X-Ray Diffraction (XRD), to confirm mineralogy and to determine bulk chemical composition. The jarosite was gently crushed in a mortar and pestle, 200 mg of jarosite powder was added to a clean polyethylene bottle and then 100 ml of solution was added. There were six experimental treatments: water; 0.1 and 1 mM HCl (ca. pH 4 and 3); 0.05 and 0.5 mM H_2SO_4 (ca. pH 4 and 3); and, 1 mM oxalic acid (ca. pH 3). Experiments were run in triplicate. 10 ml aliquots were removed from each bottle periodically over 12 days, filtered, and analysed for major ions and total dissolved sulfur by Inductively Couple Plasma-Atomic Emission Spectrophotometry (ICP-AES).

RESULTS AND DISCUSSION

The major cation concentrations in the 1:5 sediment water extracts were analysed from the four cores collected in July 2004. Four trends could be observed that describe the physical and chemical controls on the concentrations. All the major cations (Na, Mg, Ca, K) and several of the trace elements (Fe, Al, Mn, Zn) show an enrichment at the surface compared to deeper in the profile, which may be a function of evaporation of the standing water (Figure 2). In general, the highest concentrations of cations were observed in the middle of the scald, and lower concentrations in the middle of vegetated areas, indicating the salts accumulate as the
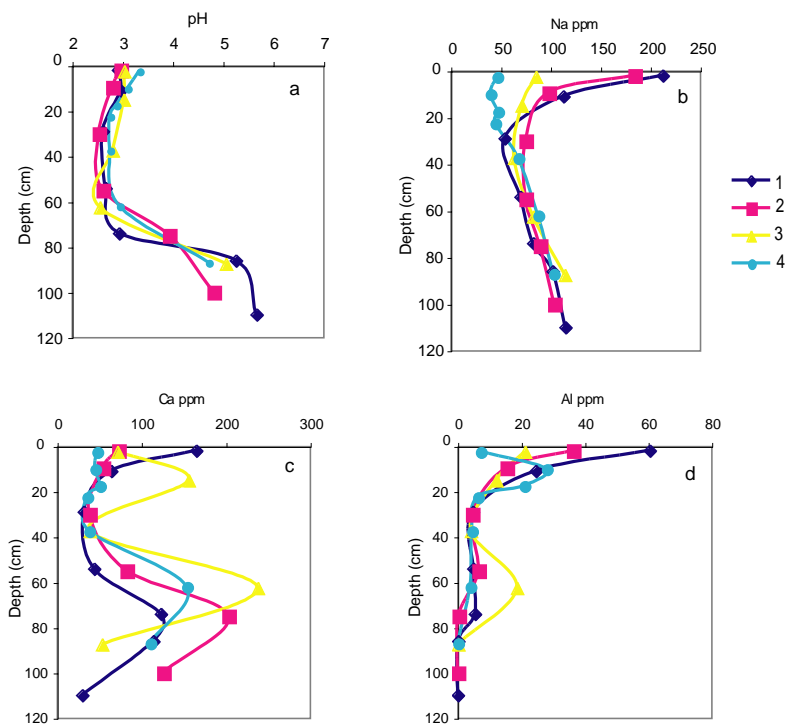

Figure 2: (a) pH, (b) Na, (c)Ca, and (d) Al in 1:5 sediment water leaches.

standing water evaporates. This process is probably instrumental in perpetuating the scalds once they form. There is a significant increase in the concentration of Ca, Sr and to some extent Mg at ca. 60-80 cm, which reflects increased dissolution of the shell layer (described in Kehoe *et al.* 2004, Somerville *et al.* 2004, Wallace *et al.* 2004) from the acidic pore water. This is consistent with the results of the mineralogical analysis that show the shells are partially dissolved, and abundant gypsum crystals in the soil matrix 10-20 cm above the shell layer. The solubilities of Fe, Al, Mn and Zn are strongly dependant on pH and concentrations of these elements are higher in the acidic pore water and decrease as pH increases.

To determine the potential acid flux and the kinetics of acid release from the sediments, the 1:5 sediment water extracts that were described in previous studies (Kehoe *et al.* 2004, Somerville *et al.* 2004, Wallace *et al.* 2004) were repeated several times. The results of sequential leach experiments, one from a vegetated profile and one from a scald area, are shown in Figure 3. The pH and EC were measured after 1 hour, 1 day and 6 days, supernatant was discarded and replaced with fresh water, and measurements were made again after 1 hour and 3 days, supernatant was discarded replaced with fresh water and measurements were made after an hour. The pH of the sediment water extracts with sediments from below about 80 cm in the scald are near neutral and remain near neutral with subsequent leaches. The pH of the other sediment water extracts were extremely acidic, about pH 3 to 4.5 within the first hour which then decreased about 0.1 to 0.3 over the next 6 days, Similar values were observed for the second water leach of the sediments. The pH measured after 1 hour with the third water leach were about 0.1 to 0.5 pH units higher than the

Figure 3: pH measurements from sequential leach of sediments (1:5) from **(a)** scalded and **(b)** vegetated areas. Solutions were changed after 6 and then 3 days.

first, suggesting that the pool of rapidly released acid store will be gradually reduced by continued flushing of the sediments. The results of the sequential leach data show that the pore water is extremely acidic in most of the sediment samples, and that subsequent leaches continue to leach the acid stored in the sediment. The acid stored in the sediment is released rapidly to solution, suggesting that the kinetics of acid release would be rapid compared to flushing of the sediments during flooding or rain events.
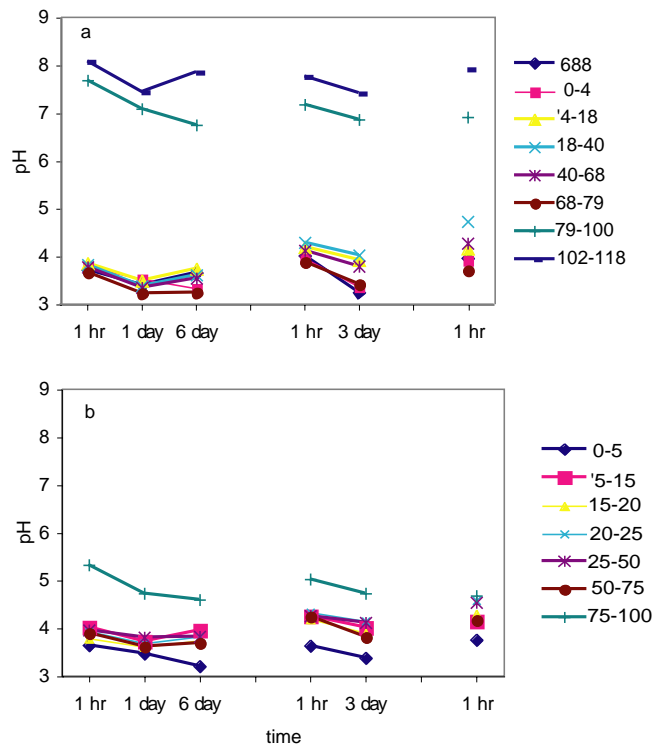
The results of jarosite dissolution experiments are shown in Figure 4. Jarosite was reacted in water, dilute hydrochloric and sulfuric acids at an initial pH of about 3 and 4, and 1 mM oxalic acid to simulate the effects of organic complexes in the infiltrating water. In all of the inorganic dissolution experiments, there is a rapid release of salts to solution within the first few hours followed by a much slower increase in concentration of major ions over time. This probably represents the dissolution of soluble salts that precipitated from the porewater as the sediment dried. The total dissolved salt concentrations released in the water, HCl, and sulfuric acid pH 4 were similar, in spite of the different initial conditions. In contrast to these, however, in the oxalate experiment, the solutes increased constantly over the duration of the experiment, and total dissolved salt concentration was approximately an order of magnitude greater than the other experiments.

The pH of the jarosite dissolution changed over the course of the experiment. In the water treatment, pH decreased from neutral to about 4.5 within minutes and then slowly decreased to about pH 4. In the experiments at pH 4, pH decreased slightly over the duration of the experiments, to about pH 3.8 to 3.9. In the experiments at pH 3, pH increased slightly during the experiments, to about pH 3.1 to 3.2.

The dissolution of jarosite is nonstoichiometric in all of the experiments, suggesting that there are other mineral phases intermixed with the jarosite, that the chemistry of the jarosite is variable, or that the reaction is incongruent. Based on the SEM analysis of the solid phase and the solution chemical analysis, it is likely
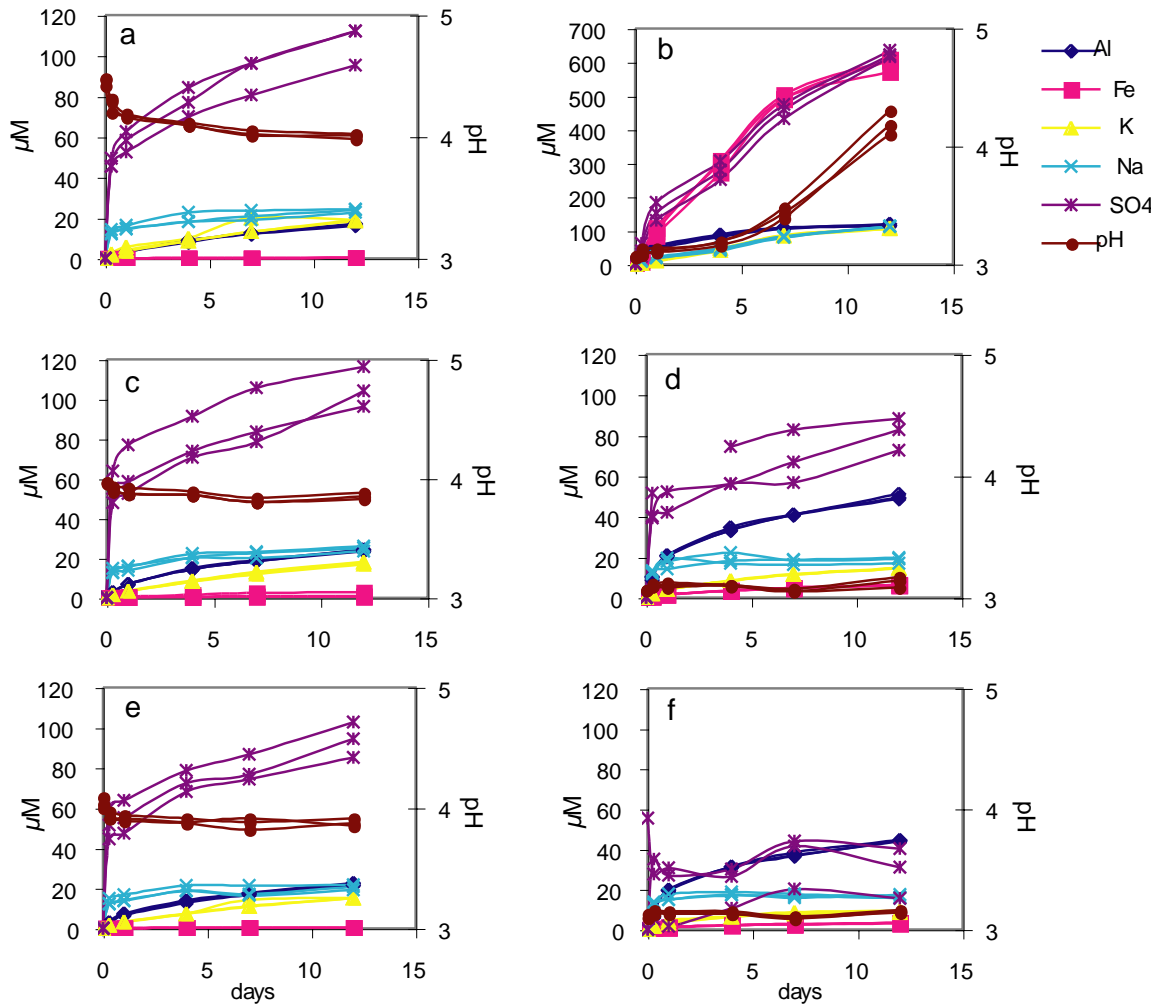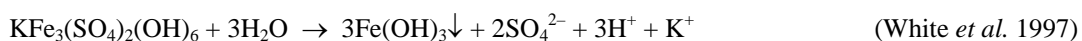
Figure 4: Concentrations of major ions from jarosite dissolution in **(a)** water, **(b)** oxalate, and **(c)** HCl pH ca. 4, **(d)** HCl pH ca. 3, **(e)** H_2SO_4 pH ca. 4 and **(f)** H_2SO_4 pH ca. 3.

that all three occur. The initial rapid release of Na, Mg, Ca and SO_4 to solution is probably the result of the dissolution of soluble chloride and sulfate salts that precipitated within the jarosite when the core was dried. Based on results of the 1:5 sediment:water extracts, the Na, Ca and Mg contents should be about 0.5 to 1 ppm (about 10-40 µM) which is about half the concentrations of these ions measured in the jarosite dissolution experiments. However, based on visual inspection of the core, the porosity of the jarosite mottles is greater than the surrounding clay material, which could account for the higher initial salt concentration. If the Ca came from dissolution of gypsum, the approximately 10% of the total sulfate concentration in the water and HCl treatments could be from dissolving gypsum.

Na and H^+ can substitute for K, and Al can substitute for Fe in the jarosite structure, and be released via dissolution. Sodium-rich jarosite, hydro-jarosite, and alunite are all more soluble than jarosite. Since Log K from the Wateq4f database for these minerals are -9.21 for jarosite, -5.28 for Na-jarosite, -5.39 for H-jarosite and -1.4 for alunite, they should dissolve faster. Therefore the Na and Al released to solution should be at least in part due to reactions of Na and Al substituted jarosite.

The Fe concentration in solution is about an order of magnitude higher at pH 3 than at pH 4, but is still much lower than predicted for stoichiometric jarosite dissolution based on sulfate concentration. Assuming that all of the Al measured in the experiments was substituted into the Fe^{3+} site in jarosite, the $(Fe^{3+} + Al^{3+})/SO_4^{-2}$ ratio in solution is 10-30% of the expected value 1.5 for stoichiometric dissolution, indicating that under the experimental conditions, jarosite dissolution is incongruent. The overall reaction can be described as:

$$KFe_3(SO_4)_2(OH)_6 + 3H_2O \rightarrow 3Fe(OH)_3\downarrow + 2SO_4^{2-} + 3H^+ + K^+ \qquad \text{(White } \textit{et al.} \text{ 1997)}$$

Thermodynamic calculations on the solution composition at the end of the experiments, using PHREEQC and the Wateq4f database (Parkhurst), show that the solutions were:

- Greatly undersaturated with respect to jarosite;
- Undersaturated with respect to amorphous $Fe(OH)_3$; but,
- Saturated with respect to goethite.

Although goethite should eventually form from jarosite weathering, nanocrystalline Fe-oxyhydroxide phases such as ferrihydrite and schwertmanite form as meta-stable intermediates in acid sulfate soil environments. These phases are more soluble than goethite and are probably controlling Fe solubility in our jarosite dissolution experiments.

The kinetics of jarosite dissolution can be estimated from the change in solute concentration over time. For these estimates, it was assumed that the rapid increase in solutes in the first day of the experiments was largely due to other salts, and only the data from day 1-12 were used for estimating jarosite dissolution rate. Jarosite dissolution rates based on the increase in sulfate concentration ranged from about 0.5 to 2 µmole jarosite/g-day in the inorganic solutions, and approximately 20 µmole jarosite/g-day in oxalate. Dissolution rates based on K release were roughly 70% slower, suggesting substitution of other ions for K.

CONCLUSIONS

The results of the experimental work indicates that acid stored in the sediment is released rapidly to solution. The kinetics of acid release would be rapid compared to flushing of the sediments during flooding or rainfall events where the sediments are unsaturated (such as during prolonged or seasonal drought). Under saturated conditions, however, acid release and mobilisation could be commensurate.

The results of the inorganic dissolution experiments demonstrate a rapid release of salts to solution within the first few hours followed by a much slower increase in concentration of major ions over time, as a function of dissolution of soluble salts present within the soil pore spaces. Notably, the total dissolved salt concentrations released were similar, regardless of the different initial conditions. By contrast, in the organic dissolution experiment, the solutes increased constantly over the duration of the experiment, and total dissolved salt concentration was approximately an order of magnitude greater than the inorganic experiments. This may be responsible for the persistent acidic conditions that occur in the subcatchment. Organic compounds can solubilize high concentrations of Fe and Al that are slowly hydrolyzed and continue to release acid over longer periods of time.

REFERENCES

KEHOE M., BEAVIS S. & WELCH S. 2004. Investigating the role of biotic versus abiotic processes in the generation of acid sulfate soils in coastal NSW. *In:* ROACH I.C. ed. *Advances in Regolith.* CRC LEME, pp. 171-174.

SOMERVILLE P., BEAVIS S. & WELCH S. 2004. Spatial and temporal variability of acidity at a coastal acid sulfate soil site. *In:* ROACH I.C. ed. *Advances in Regolith.* CRC LEME, pp. 335-339.

WALKER P.H. 1972. Seasonal and stratigraphic controls in coastal floodplain soils. *Australian Journal of Soil Research* **10**, 127-142.

WHITE I., MELVILLE M., WILSON B.P. & SAMMUT J. 1997. Reducing acidic discharges from coastal wetlands in eastern Australia. *Wetlands Ecology and Management* **5**, 55-72.

WALLACE L.J., WELCH S.A., BEAVIS S. & MCPHAIL D.C. 2004 Trace metal partitioning in acid sulfate soils, Mayes Swamp, Kempsey, NSW. *In:* ROACH I.C. ed. *Advances in Regolith.* CRC LEME, pp. 385-390.