

EXPERIMENTAL DETERMINATION OF ACID AND SULFUR FLUXES IN AN INLAND ACID SULFATE SOIL SYSTEM

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INTRODUCTION

Acid sulfate soils (ASS) form under anaerobic conditions, where sulfate, sulfate-reducing bacteria, organic matter and minerals containing Fe are present. Potential ASS environments typically occur in low-lying coastal areas, where water logged sediments which contain Fe sulfides are present. The Fe sulfides formed as a result of past sea level rises when sulfate present in the seawater mixed with terrestrial sediments containing Fe oxides and organic-rich material. ASS can also form in inland areas that are subject to influxes of sulfate-rich waters. When topsoil is removed or disturbed, or the water table is lowered as a result of agricultural development or environmental variability, pyritic subsoils can be exposed to oxygen, thus forming sulfuric acid, and significantly lowering the pH of the soils. These acidic waters can infiltrate groundwater or flow as runoff into nearby water systems. ASS are a significant risk and impose a range of impacts on the environment: preventing growth of plant matter; forming scalds on the surface; reducing farm productivity; and, increasing the morbidity and mortality of aquatic biota. The acid generated dissolves Fe, Al and other heavy metals in the soil. As a result, these metals become bioavailable to plants in toxic levels and, when mobilised within drainage systems, additional impacts on aquatic biota occur. In addition, exposed metal and concrete can be corroded with subsequent impacts on the built environment. Emissions of sulfur dioxide, an important greenhouse gas, and reduced S gases are also associated with ASS. Wetting and drying of these sediments and subsequent oxidation have the potential to perturb the system and affect acid and sulfur fluxes. While there has been an extensive focus on the problem in coastal environments (e.g., White *et al.* 1997), less is known about sulfidic systems in inland settings (e.g., Lamontagne *et al.* 2004).

FIELD SITES

This project focussed on one of these inland sulfidic systems, the Loveday Basin near Berri, SA. The Loveday Basin was originally a natural flooded wetland adjacent to the River Murray. In the last three decades, this site has been used as a disposal basin for saline water, which has led to increased salinization of the site, and also the accumulation of S-rich sediments. The site is located between the river and an irrigated citrus orchard, which (because of irrigation recharge) is associated with a local mounding of the groundwater level. The site itself has been highly modified hydrologically through the use of floodgate structures, inlets from the irrigation area and a causeway as part of its earlier use as a salt disposal basin. The Loveday site is important because it is an inland site for sulfidic sediments and is highly degraded. It presents an emerging issue in terms of how sites that may contribute S gases to the atmosphere and acidic discharge to the River Murray may be important in relation to wetting and drying cycles imposed by both climate and riverine management (for environmental flows for example). This site has now been targeted for rehabilitation.

OBJECTIVES

The objectives of this study were to:

- Determine the spatial variability of salinity, S species, and potential acid flux from an inland sulfidic system; and,
- Determine how wetting, drying and oxidation might perturb the system and affect acid and S flux.

METHODS

Leaching experiments were designed to determine:

- The salt and acid fluxes from acid sulfate soils; and,
- The potential acid and sulfur fluxes after wetting and drying events, and subsequent oxidation of the soils.

Sediment and water samples were collected from several locations in the Loveday Basin in December 2004 by researchers from the Australian National University and CSIRO Land and Water, Adelaide. Near-surface sediment samples (< 2 m deep) were collected along a transect across the northern side of the basin, as well as from a few other sites where the researchers could gain access (Figure 1). Sediment samples were taken using shovels, hand trowels, gouge auger, and a general purpose auger. Samples were separated into five

different horizons based on physical characteristics, mainly color and texture (Luke Wallace, CRC LEME, ANU, *pers. comm.*). Samples were packaged in plastic and stored under cool conditions until returned to the lab, where they were stored in plastic at temperatures of approximately 4°C.

Water content, Electrical Conductivity (EC) and pH of extracts were determined using standard laboratory methods (described below). Water content was determined by carefully weighing several grams of wet sediment, drying the sample overnight at < 100°C, and then reweighing the sample, assuming weight loss equals water content. The pH and EC were determined on 1:5 (sediment:water) and 1:1:4 (sediment:peroxide:water) extracts on wet samples. Five grams of wet sediment was placed in a 50 ml tube, and then either 25 ml of MilliQ water, or 5 ml of 30% peroxide and 20 ml of water was added to the tubes. Tubes were sealed and placed on an orbital shaker overnight. The sediment was allowed to settle for several hours, and then the pH and EC was measured on the suspension. The pyrite content, and the potential for acid flux from oxidation of the sediment, can be estimated by the difference in pH in the water verses peroxide treatment.

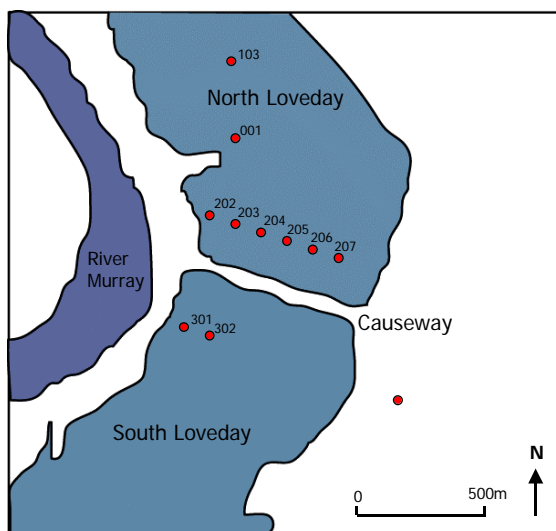


Figure 1: sampling sites from the Loveday Basin. (Map courtesy of Luke Wallace, CRC LEME, ANU).

Sulfide oxidation slurry experiments were conducted using methods similar to those described by Kehoe (2004). The Loveday site is characterised by sediments that experience periodic wetting and drying. This appears to have imposed a very well developed pedal structure on the sediments. The polygonal peds are approximately 20 cm in diameter and are separated from each other by wide cracks within which a highly organic slurry occurs. These experiments used sediments collected from the top 20 cm of the sediment profile, the surface of the ped, the surface of the crack and middle of the ped, since these samples were identified as likely to be the most biologically active. Five grams of wet sediment were added to a clean 250 ml Erlenmeyer flask that had been acid washed and then autoclaved. One hundred millilitres of filtered MilliQ water was added to each flask, and the flasks were loosely capped to allow air exchange, and placed on an orbital shaker. Experiments were run in triplicate with seven different sediment samples.

Aliquots of approximately 10 ml were removed from each flask periodically—6 time points spaced over a month and samples were filtered with a 0.45 µm filter. The solution pH of a small aliquot of the filtered sample was then analysed for pH using an Orion pH meter and electrode. Major cations and S were measured by ICP-AES and the mineral saturation index was calculated using PHREEQC.

RESULTS AND DISCUSSION

The results of the 1:5 sediment:water extracts showed that salt content varied significantly with depth and over the surface of the site. The electrical conductivity ranges from approximately 2 to 40 mS/cm. In general, the EC measured for the surface sediments was greater than deep samples. The pH of the 1:5 sediment:water extracts for most of the samples was near-neutral pH, ranging from approximately 6 to 8.5. The one exception to this was for sediment samples collected from a site approximately 400 m north of the main transect, where pH in the water extracts was about 4, and jarosite mottles were evident. The pH and EC for two of the samples sites, 203 and 204, are depicted in Figure 2.

Experiments were conducted with seven sediment samples that were collected from the top 20 cm from sites 203 (drier) and 204 (wetter). The sediments were collected from the top of a ped (approximately 0-10 cm), the middle of a ped (approximately 10-25 cm), from an adjacent crack surface (approximately 5-15 cm) and from a salty crust. With the exception of Si, the concentration of all the major elements increased rapidly within the first day of the experiment and then concentrations increased much more slowly or else were approximately constant over the duration of the experiment (Figure 3).

In the experiments with sediments from the top of the peds, cracks, and the salt crust, the major element concentrations in the replicate experiments is fairly reproducible, within approximately 10%. This is in contrast to the treatments with the material from the peds, where concentrations varied by about a factor of

two. In the ped experiments, the ped samples remained as intact lumps of sediment for about one week, whereas the other sediments disaggregated within about 1 day.

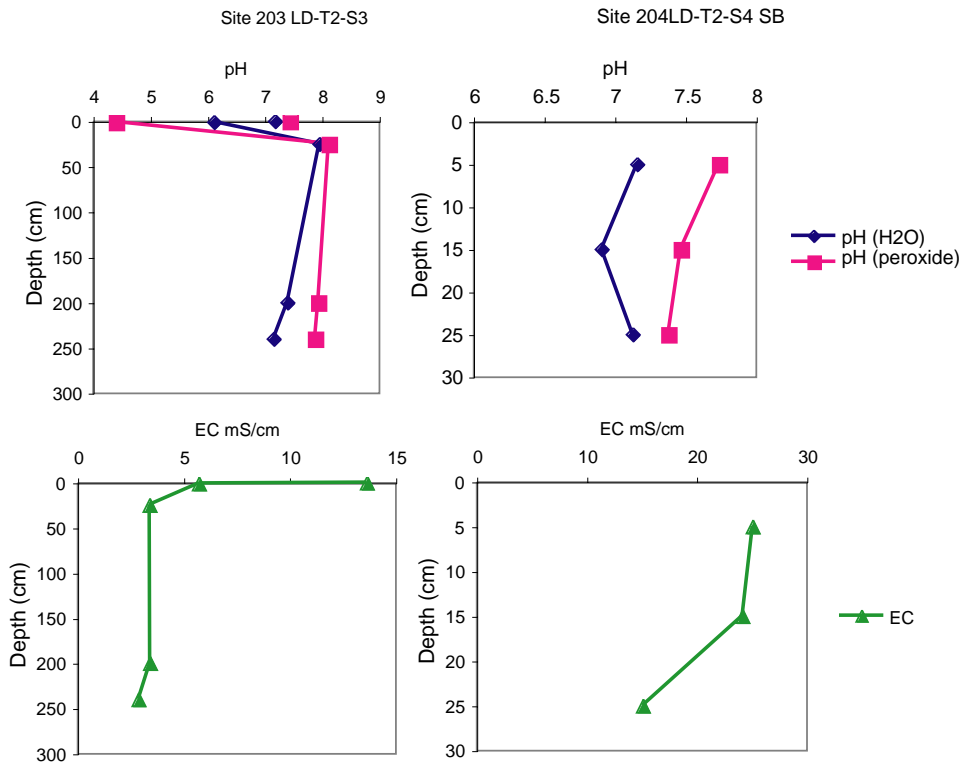


Figure 2: pH, pH after peroxide addition, and electrical conductivity EC versus depth for two sites from the Loveday Basin

In general, total salt release was slightly higher in the crack samples than in the sediments from the top of the peds, and much greater than from the center of the peds. Salt concentrations were also slightly higher at site 4 (wetter) than site 3 (drier).

In the experiments with sediments from site 3, the Ca/SO_4 ratios and Ca and SO_4 concentrations reflect gypsum dissolution and gypsum solubility. This is consistent with the results of light microscopy, SEM and XRD analysis of the sediments.

In contrast, in the experiments using crack and ped surface sediments from site 4, although Ca and SO_4 concentrations are approximately at gypsum saturation, the Ca/SO_4 ratio is lower than 0.4 suggesting either an additional source of sulfate or else a sink for Ca. One potential source of sulfate is from the oxidation of sulfides, which is also consistent with the relatively high sulfate concentrations in these two experiments. Iron monosulfides and pyrite are abundant in these sediments, as evident from the color, the odor and from SEM and chemical analysis (Luke Wallace and Susan Welch, CRC LEME, ANU, *pers. comm.* 2004). However, none of these experiments ever became acidic, with pH ranges from approximately 6 to 8, and Fe concentration are below detection, < 0.05 ppm. If the additional sulfate came from sulfide oxidation, this should have released enough acid to decrease pH below 3, and solubilize about 300 ppm of Fe. Therefore, if sulfide oxidation is occurring in these experiments, there has to be another reaction buffering acidity and limiting Fe release to solution.

CONCLUSIONS

Analysis of the pH, EC and peroxide tests of the sediments demonstrate that the Basin has very high salt content, with salt stores in the pore water. Although the site is a potential ASS site, most of the sediments are not acidic, even after oxidation of the sulfidic material by the peroxide. Based on results of the leaching experiments, the S flux from the near surface sediments appears to be dominated by gypsum dissolution.

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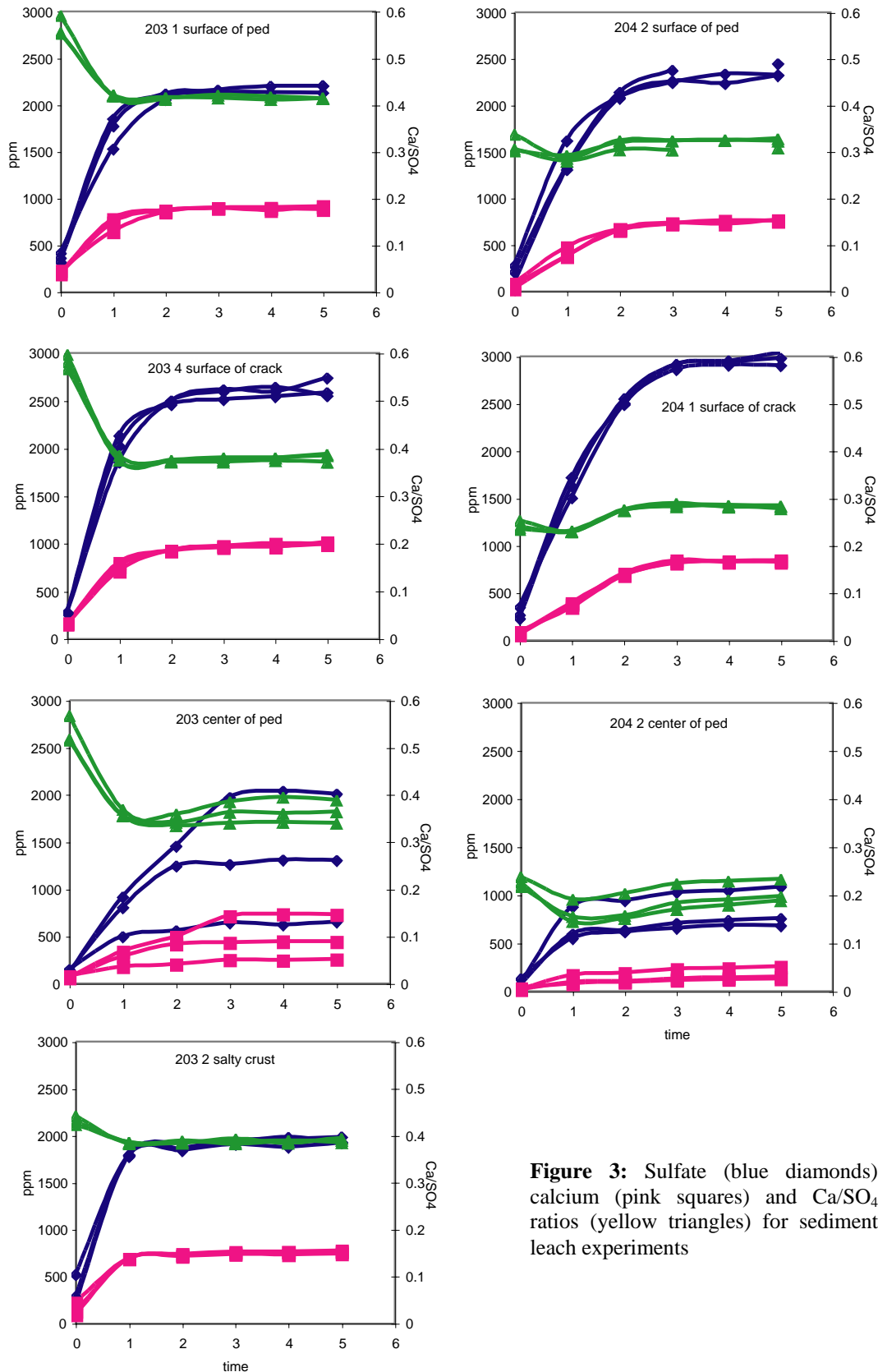


Figure 3: Sulfate (blue diamonds) calcium (pink squares) and Ca/SO₄ ratios (yellow triangles) for sediment leach experiments