THE LOVEDAY BASIN: SALINITY, ACIDITY, WATER CHEMISTRY, ISOTOPE GEOCHEMISTRY, MINERALOGY, BIOLOGY AND SQUISHY MUD

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INTRODUCTION

The Loveday Basin was previously a natural flooded wetland adjacent to the River Murray. However, in the last three decades, this site was used as a disposal basin for saline water, which led to increased salinization of the site and also the accumulation of sulfur-rich sediments. This has led to certain environmental problems, in particular noxious smells produced from the reduced S compounds, and as such, the Loveday Basin has been selected by the Murray-Darling Basin Commission to be the test case for remediation. The purpose of the project is to characterize the physical, chemical and biological properties of sediment and water at the site and to determine how these will change upon the wetting and drying of the area. Results of this work will then be used by land managers to determine remediation strategies.

METHODS

Sediment and water samples were collected along two transects that run approximately E-W north of the causeway and N-S along the long axis of the Basin (Figure 1). The sampling in December 2004 was focused primarily on the E-W transect just north of the causeway. In August 2005, the original sites were resampled in addition to selected areas in both the northern and southern parts of the Basin. A more extensive sampling was limited on both occasions by time constraints and by the extreme conditions of the field site.
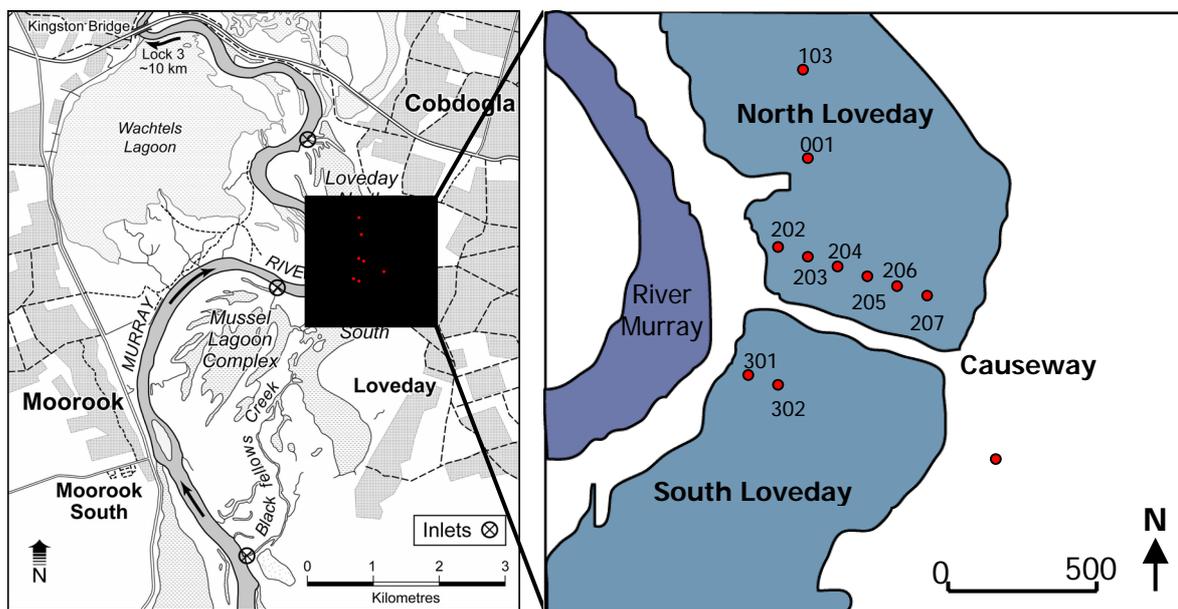

Figure 1: sampling locations.

The sediments were characterized for physical properties including water content, bulk density, linear shrinkage and distribution of cracks and pores. Selected sediments were characterized for mineralogy by light and Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). Bulk geochemistry was determined by X-ray Fluorescence (XRF) at the Waite Laboratory at CSIRO Division of Land & Water. Sediment mineralogy and geochemistry were characterized by SEM with energy-dispersive X-ray spectrometric (EDX) detection, and laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS). Estimates of salt content and acidity in sediments and pore water were done by 1:5 sediment water extracts.

Water samples were collected from standing surface water, pit water that accumulated from the sediment sampling sites and shallow groundwater from temporary piezometers. Water samples were analysed for pH, redox potential, electrical conductivity, dissolved oxygen, alkalinity and ferrous iron during or shortly after collection. Water samples were filtered and then analysed for major and trace species by ICP-Atomic Emission Spectrophotometry (ICP-AES) and ion chromatography. Water samples were analysed for isotopes of O and H in H_2O, S and O in SO_4 and C and O in CO_3.

In August 2005 we attempted several field experiments along with sample collection. Hydraulic conductivity was determined using a disc permeameter. Estimates of salt flux from the surface sediments were determined by microcosm experiments. We also did some fine scale measurements of pH, electrical conductivity, and redox potential with micro-electrodes at some sites.

RESULTS AND DISCUSSION

Soil mineralogy and physical properties

As a result of the dry conditions, a large area of the surface of the Loveday basin is dominated by a system of peds and deep cracks that have been partially infilled with sediments (Figure 2). This has resulted in extreme physical and chemical heterogeneity over short, ~ cm scale, horizontal and vertical distances. The structure of the large columnar peds comprises a 'nested system' of large peds – small peds – micropeds which are defined by discontinuities in the soil matrix and associated staining by iron oxides and oxyhydroxides, fine aggregates of gypsum and higher concentrations of framboids. This can be explained by results of linear shrinkage and micromorphological analyses which indicate secondary porosity imposed by complex crack/discontinuity systems. Preliminary bulk density results are lower than anticipated for fine clayey material (0.6 – 1.4g/cc), indicating relatively high porosities. The bulk densities of crack material is significantly lower than pedal material, suggesting a higher organic and clay content.

Shrink-swell behaviour of these sediments showed increasing shrinkage from the surfaces to the interior of the large columnar peds, and increasing shrinkage downprofile, suggesting the ped structure (and oxidation of the sediment), will propagate with continued wetting and drying (Figure 3).
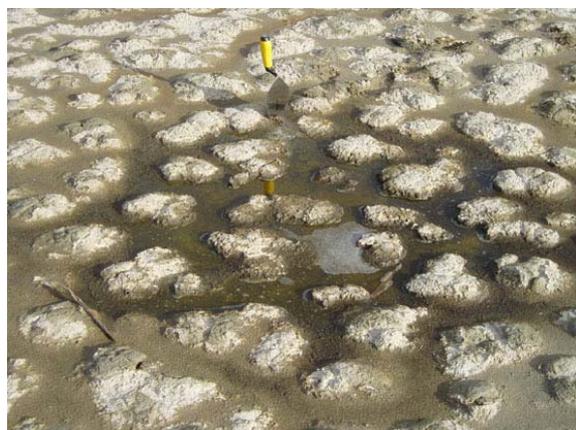
Figure 2: The surface of the Loveday Basin is dominated by ca. 10-20 cm sized columnar peds with infilled cracks. The surfaces of the peds are often covered by a gypsum crust and endolithic alga. The surfaces of the cracks are covered by alga that serve as a source of organic matter for the sulfate reducing bacteria. The infilled cracks typically contain abundant 'black ooze' or reduced Fe-S minerals.
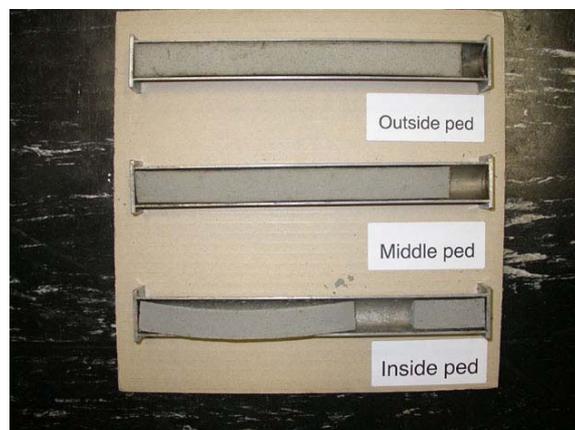
Figure 3: Linear shrinkage of sediment samples from a ped. The increased shrinkage from the inner ped material indicates that the ped structure will propogate with subsequent wetting and drying events.

Water chemistry and isotope results

In December 2004, 11 water samples from standing water, shallow pits dug at the surface and temporary piezometers were collected from the northern part of the basin for analysis. Samples were analysed for major, minor and trace species composition as well as isotopes of O and H in H_2O, S and O in SO_4 and C and O in CO_3. The waters are saline with chloride content ranging from 9,000 to 58,000 mg/l suggesting the

groundwaters, near-surface waters and surface water are compositionally distinct. The sulfate in the pit waters have sulphur and oxygen isotopic signatures typical of sulphide oxidation, while the groundwaters generally have isotopic composition that suggests they are a residual of sulfate reduction.

Actual and Potential Acidity

Although there is abundant sulfidic material in the uppermost sediments at the site, along with evidence of oxidation, analysis of water samples and sediment-water extracts from samples collected at the site in December 2004 show that most of the material analysed was not acidic, with pH ranging from ca. 6.5 to 9 (Figure 4). Although trace levels of jarosite were observed in many of the locations sampled, suggesting acidic micro-environments, jarosite mottles and acidic conditions (pH < 5) in the sediment water extracts and pH 3.2 in the pit water were only found at one site (001 5mw) along the western side in association with decaying woody material. This is an area along the edge of the basin with a high organic content from decaying trees, high reduced S content and relatively high elevation, ca. 20 cm above the current standing water level.

In August 2005, the site was more extensively sampled including a transect along the drier southern side of the basin. Jarosite was much more abundant on the southern side, and acidic water, pH ca. 3 to 5, was collected from shallow pits about 25 cm deep in two locations in the south Loveday Basin. Although the water collected from pits was acidic, standing surface water and shallow groundwater was near neutral pH, ca. 6.5 to 9. Abundant jarosite mottles were also found at one of the drier sites (203), north of the causeway. Analysis of sediment pH with micro-pH electrode (Figure 4a) showed that pH was near neutral in the top ca. 3 cm, and then decreased rapidly from ca. 3 to 4.5 between ca. 4 and 20 cm. pH measurements on 1:5 sediment water extracts of samples

Figure 4a: pH measurements with micro pH electrode along 3 pit walls at site 203. **b:** pH of 1:5 sediment water extracts (blue diamonds) and peroxide treated sediments (pink squares).

collected in December 2004 from this sampling site were all near neutral pH (Figure 4b). It is not clear if this acidification represents a change in conditions over the 9 months or if it simply reflects heterogeneity in the sediments.

The potential acidity stored in sediments was estimated from the rapid oxidation of sulfidic material by the peroxide test, and from incubating sediments under intermittent wetting and drying for weeks. The results of the rapid oxidation showed that although the sediments contained abundant sulfidic material, only sediments collected from ca. 5-25 cm below the surface (ped material) or the sediments that were infilling the cracks routinely became acidic (pH 2-5) upon oxidation (Figure 4b). This is consistent with the results of the sediment incubation experiments (Beavis *et al* 2005) and with results of surface and groundwater pH measurements.

Biogeochemistry results

Preliminary culture experiments using media targeted for acidophilic sulfur and iron oxidizing bacteria showed evidence for growth. However, the organisms in the enrichment cultures were not identified. Results indicate that if the sulfidic material is exposed to oxygen, then the microbial communities could increase the rate of sulfide oxidation and acidification. In the preliminary slurry experiments, however, this did not occur (Beavis *et al.* 2005). Currently the most important biogeochemical processes are likely to be related to primary productivity and Fe and SO_4 reduction at this location. There is abundant organic matter at the site from the macroflora (dead trees), which provide organic matter to fuel Fe and SO_4 reduction to form framboidal pyrite, and there are also micro-flora that are controlling S redox chemistry. Intense algal growth is apparent anywhere there is standing water in the basin, with algal-cyanobacterial mats forming within hours of a rainfall event. There are also endolithic algae on the ped surface below the gypsum crusts and even within dead bivalve shells. The algae are associated with the black ooze that is abundant within the cracks between the peds. The high AVS concentrations in the sediments are strongly correlated with algal growth.
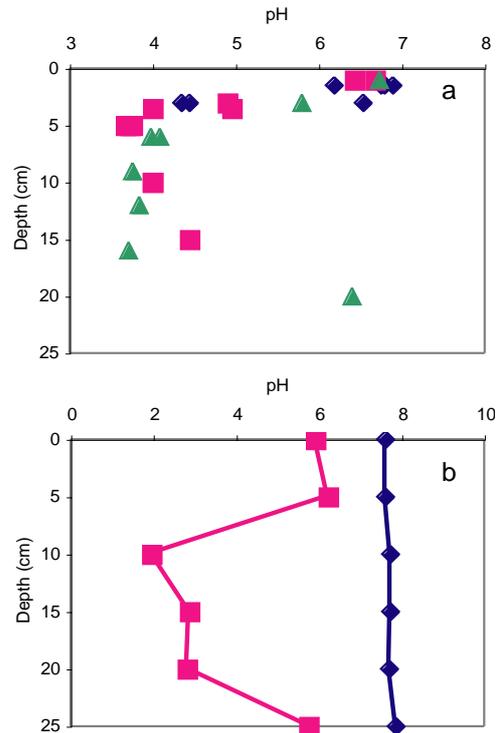
Given the average NO_3 and PO_4 concentration in the surface and pit waters of ca. 20 and 1 ppm respectively, this is enough to produce 30 mg/l of algal biomass (assuming phosphate limitation). The dissimilatory SRB are reducing sulfate via the reaction:

$$2H^+ + SO_4^{-2} + 2CH_2O \rightarrow 2CO_2 + H_2S + 2 H_2O$$
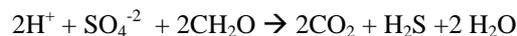
This would result in removal of ca. 50 mg/l SO_4^{-2}, representing only a small fraction (ca. 1%) of total dissolved sulfate in these waters. However, degradation of organic matter and Fe and SO_4 reduction should release nutrients back to solution, resulting in increased algal growth and subsequently in further sulfate and iron reduction.

SUMMARY AND CONCLUSIONS
Results of the preliminary surveys show that the site is physically and chemically heterogeneous both vertically and horizontally over a range of scales, from µm to m, which makes characterization of the basin difficult. Preliminary analysis has been biased, based on accessibility, and has focused predominately on 'drier' areas of the basin.

Sulfur is concentrated in the upper 40 cm of sediments as gypsum, pyrite, monosulfides and jarosite. Gypsum is prominent at the sediment surface along sediment cracks and as salt efflorescence and comprises up to 10% of the surface sediments in the 'drier' areas of the basin. The distribution of reduced sulfur species is highly variable with framboidal pyrite found in the peds, associated with microcracks and roots. AVS, predominately FeS, is abundant in the infilled cracks and is associated with decaying alga. Reduced sulfur concentrations are up to 1 wt. % in the sediments (Wallace *et al.* 2005).

Although there is abundant sulfidic material, most of the sites sampled were not currently acidic, although the upper ca. 25 cm ped and crack material will likely become acidic if allowed to oxidize. Acidic conditions (pH < 5) were found at several of the drier sites in the basin. This has implications for further degradation of the site. Although O_2 will oxidize pyrite, the reaction is kinetically slow. However, ferric Fe, which is stable under acidic oxidizing conditions, will accelerate pyrite oxidation and, therefore, once acidification occurs it may result in accelerated oxidation and acidification of the site.

Possible remediation strategies
- Flooding - keeping the site flooded will allow for continued algal growth. This will provide a source of organic matter to promote sulfate and iron reduction and accumulation of sulfides in the sediment.
- Drying - keeping the site dry will allow for the propagation of the ped structure and increased oxidation of the sulfidic material and risk of acidification. If the site becomes reflooded, such as in a rainfall event, this will result in algal growth within the cracks, sulfate reduction, and noxious odours.
- Flushing flows - flushing the system at optimal intervals will create short-term problems downstream from the site with periods of high salinity and reduced oxygen concentration. However, flushing will remove the salts and nutrients from the basin and thereby possibly limit further accumulation of sulfidic material.

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