THE UNIVERSITY of ADELAIDE

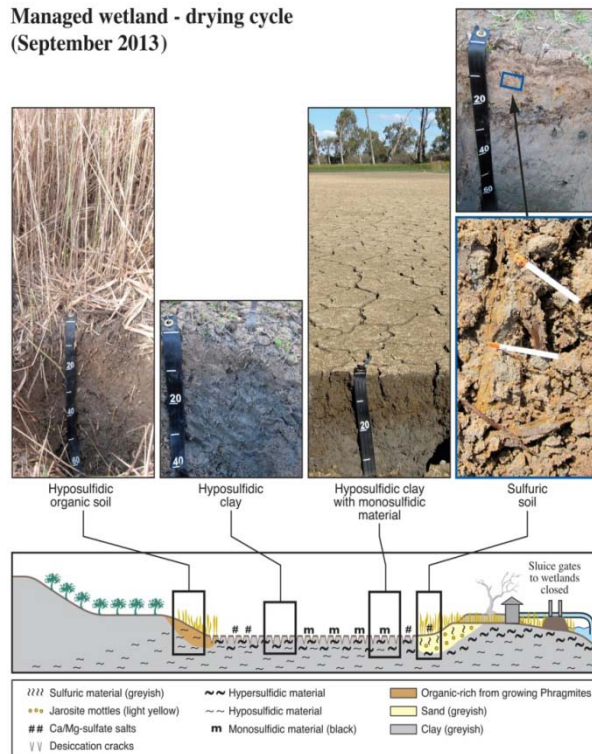# *Acid Sulfate Soils Centre*

Acid Sulfate Soil Assessment and Monitoring of the Banrock Station wetland

Managed wetland - drying cycle (September 2013)

RW Fitzpatrick, P Shand, R.H. Merry, P. Marschner, N. Jayalath and S Grocke

Enquiries should be addressed to:

Prof Rob Fitzpatrick: Acid Sulfate Soils Centre, The University of Adelaide, Private Bag No 2, Glen Osmond, South Australia

Email: robert.fitzpatrick@adelaide.edu.au
Phone: 08 8303 8511; Mobile: 0408 824 215

Citation: Fitzpatrick R.W, P. Shand, R.H. Merry, P. Marschner, N. Jayalath and S. Grocke (2015) Acid Sulfate Soil Assessment and Monitoring of the Banrock Station wetland. Acid Sulfate Soils Report No ASSC_035, 28th April 2015

Cover image

Photographs of dry landscape sections and soil profiles of the Banrock Station Wetland Complex taken in early September 2013 when the entire wetland floodplain was dry. Cross-section diagram of Acid Sulfate Soil subtypes (i.e. Sulfuric soil, Hyposulfidic organic soil, Hyposulfidic clay with monosulfidic material) sampled on 1st September, 2013 after at least 4 cycles of re-wetting and drying of the whole wetland over a 5 year period.

Photographs: Rob Fitzpatrick @ 2014 Acid Sulfate Soils Centre, The University of Adelaide

Contents

List of Figures

List of Tables

Acknowledgments

EXECUTIVE SUMMARY

Objectives

Acid sulfate soils (ASS) are soils that are either acidic (due to the generation of sulfuric acid and formation of sulfuric material), or have the potential to generate sulfuric acid when exposed to oxygen because of the presence of sulfide minerals (sulfidic material). The prime objective of this report is to:

- Assess acidification and deoxygenation/malodour hazards caused by ASS sub-types (i.e. with sulfuric, hypersulfidic, hyposulfidic & monosulfidic materials) using reliable interpretation methods in the Banrock Station wetland complex following at least 4 re-wetting and drying/part drying cycles between October 2008 and September 2013 by:
  - re-sampling on 2nd September, 2013 at six (6) previously studied representative study sites located around the margins and in the middle of the wetland to evaluate any changes associated with drying and rewetting.
- Assess the rate and extent of: (i) neutralisation of previously acidified Sulfuric soils and Sulfuric subaqueous soils and (ii) pyrite accumulation or decrease in ASS sub-types by comparing the 2nd September, 2013 ASS data (dry) with previous data for samples taken previously on 23rd May 2008 (dry) and 3rd October 2008 (re-flooded).
- Develop a revised set of soil-regolith models (cross-section diagrams and summaries of temporal and spatial variations and changes at each site) by integrating the 2nd September 2013 findings with previous findings (23rd May 2008 and 3rd October 2008) and predicted historical data (1925-1993 and 1993-2006).
- Assess the influence of organic matter addition on pH and redox potential under flooded (anaerobic) conditions and subsequent pH changes during a drying (oxidation) period.
- Provide briefings of baseline data to underpin long-term management and ongoing monitoring options.
- Publish a final report and journal papers on all findings in relation to envisaged outcomes, especially with regard to the development of revised soil-regolith models (cross-section diagrams).

Context and methods

The Banrock Station Wetland Complex is situated in a river red gum floodplain of some 1,375 ha, which includes 1,068 ha of floodplain wetland and 307 ha of an open mallee-box woodland buffer. This Ramsar site is located in the lower River Murray system about 15 kilometres west of Barmera in South Australia.

The main 'Banrock Lagoon' became permanently flooded in 1925, when lock 3 was constructed, until 1993 when partial drying phases were introduced to wetland management. However, drought conditions prevented the wetland from being flooded between June 2006 and June 2008. The wetland was re-flooded in June 2008, with a drying cycle following in January 2009. Since January 2009, there have been at least 4 re-wetting and drying/partial drying cycles.

This investigation encompassed the re-sampling of 29 soil layers, which were collected from six (6) geographically well-distributed and locally representative sites (soil profiles) and analysed using a combination of standard methods: (i) soil morphology, (ii) field pH testing, (iii) peroxide testing, (iv) acid-base accounting (ABA), (v) soil incubation (ageing), and (vi) selected samples for mineralogy. No surface water samples were collected from the floodplain wetlands due to a lack of water at the time of the survey.

Key findings

The study provides a spatial dataset for the soil condition at the time of sampling (2nd September, 2013) from which conceptual models and map legends were generated to show the presence and spatial variability of acid sulfate soil properties in Banrock Station Wetland Complex. The soil map legend illustrates the wide range of acid sulfate soil sub-types, which also incorporates soil depth, water depth, presence of monosulfidic material and information about the location of underlying clay layers/horizons. The soil map legend provides an overview of the acid sulfate soil variation that occurred when the wetland complex was surveyed on 2nd September, 2013. Moderate concentrations of iron monosulfides (monosulfidic material) were restricted to hyposulfidic clay soils in the lakebed.

The soil map legends were used as a basis to assign the Acid sulfate soil acidification and deoxygenation/ malodour hazard ratings with polygons rated as high (yellow coloured map unit), medium (brown coloured map unit) and low (blue coloured map unit). This assessment was based on field and laboratory data obtained on samples taken on 2nd September 2013. We have established that soil acidification and deoxygenation/ malodour hazard ratings in the wetlands were variable and ranged from high to low as summarized in the acidification and deoxygenation/malodour hazard rating map legends:

- Soils along the outer shoreline of the wetland in the southern segment are mainly Sulfuric soils (dry periods) and Sulfuric *subaqueous* soils (wet/flooded periods) with **high** acidification hazard ratings and **low** malodour hazard ratings.
- In contrast, soils in the lakebed of the southern and northern *segments* are mainly Hyposulfidic cracking clays (dry periods) and Hyposulfidic *subaqueous* clays (wet/flooded periods) with **low** acidification hazard ratings and **moderate** malodour hazard ratings.

The current investigation involved field sampling on 2nd September 2013 (Dry-sampling-c) at 6 (six) previously studied sites, which were sampled on 23rd May 2008 (Dry-sampling-a) and 3rd October 2008 (Wet-Sampling-b). The overall assessment, which includes a series of predictive conceptual models, involved interpreting all the field and laboratory investigations from 2008 to 2013.

Soil-regolith toposequence models in combination with the localised acid sulfate soil map legends, present an understanding of ASS distribution in three dimensions. A generalized temporal soil-regolith model has been constructed to describe the past and current understanding of the complex ASS distribution and to demonstrate the rewetting and drying scenarios of changes, which have occurred over time (i.e. progression from being drained and re-flooded.

The conceptualised temporal soil-regolith models were used to describe several progressive changes in ASS properties occurring over time (i.e. progressive drying and reflooding conditions):

(i)   Dynamic balance of the thickness and amount of sulfide formation - caused by cyclic climatic and geomorphic changes before 1880s.

(ii) Slow transformation *Hyposulfidic* clayey soils to *Hypersulfidic* subaqueous clayey soils – with monosulfidic material during the **1880s to 1930s period.**

(iii) Rapid transformation *Hyposulfidic* clayey soils to *Hypersulfidic* subaqueous clayey soils – with monosulfidic material during the **1930 to 1993 period.**

(iv) Rapid transformation of Hypersulfidic subaqueous soils to Sulfuric soils and Sulfuric subaqueous soils along the ***Shoreline.*** Increased formation of pyrite in *Hypersulfidic*

subaqueous clayey soils to *Hypersulfidic* & subaqueous clayey soils in the **Lakebed**: during the 1993 to 2006 period

(v)   Rapid transformation of Sulfuric soils to Sulfuric subaqueous soils along the ***Shoreline.*** Increased oxidation of pyrite during the transformation of *Hypersulfidic* subaqueous clayey soils to *Hypersulfidic* clayey soils in the **Lakebed** during the **June 2007 to October 2008 flooding period**

(vi)   Static/Dynamic balance of Sulfuric soils and Sulfuric subaqueous soils along the **outer** ***shoreline.*** Fast transformation of *Sulfuric* soils to *Hyposulfidic* soils along the **inner** s***horeline.*** Fast transformation of *Hypersulfidic* subaqueous clayey soils to *Hyposulfidic* clayey soils in the ***Lakebed*** during **October 2008 to September 2013 period**

A number of potential metal and nutrient contaminants were present in the extractions including Al, As, Be, Co, Cr, Cu, Ni, NH$_4$, Pb, U and Zn, but some metals are probably associated with colloidal particles in two of the samples. The main control on high metal mobilisation is likely to be pH. The simple water extractions suggest that contaminant mobilisation in the soils may be an issue following rewetting of the ponds or during any disturbance, particularly if the soils become acidic. Oxidation where acidification does not occur is likely to strongly limit metal release, but species mobile at high pH, e.g. As which forms oxyanions, should be monitored.

Summary and Recommendations

Based on the ASS map legend produced in this report, it is recommended that a follow-up field investigation be conducted during future dry and/or reflooded periods to construct Acid sulfate soil maps of the wetland complex. This spatial information will be used to assist in future land management planning options for the wetland complex.

1. INTRODUCTION

This section gives a brief and selective historical background to the Banrock Station Wetland Complex with emphasis on the soil drying and rewetting (re-flooding) cycles - as background to defining the aims and scope of this project. It also briefly defines Acid Sulfate Soils (ASS), the criteria used for the classification of sulfuric, sulfidic, hypersulfidic, hyposulfidic and monosulfidic materials and ASS Sub-types.

This section also provides a brief synopsis of previously published ASS work in the Banrock Station Wetland Complex. This historical case study describes how sulfides in anthropically modified environments are oxidised to form sulfuric acid, iron-oxide minerals and salts by processes such as draining due to the construction of locks to control water flows. This study illustrates the complexities and importance of understanding specific sites to assess particular ASS processes, implications and suitability of the different management options.

1.1 Overview and purpose

Banrock Station Wetland Complex is located in the lower Murray River system, about 15 kilometres west of Barmera in South Australia (Figure 1-1). This Ramsar site is situated in a river red gum (*Eucalyptus camaldulensis*) floodplain of some 1,375 ha, which includes 1,068 ha of floodplain wetland and 307 ha of an open mallee-box woodland buffer. The wetland is connected to the River by one meandering inlet creek, and one outlet creek (Figure 1-1). Flow control structures were installed at each creek in 1993.
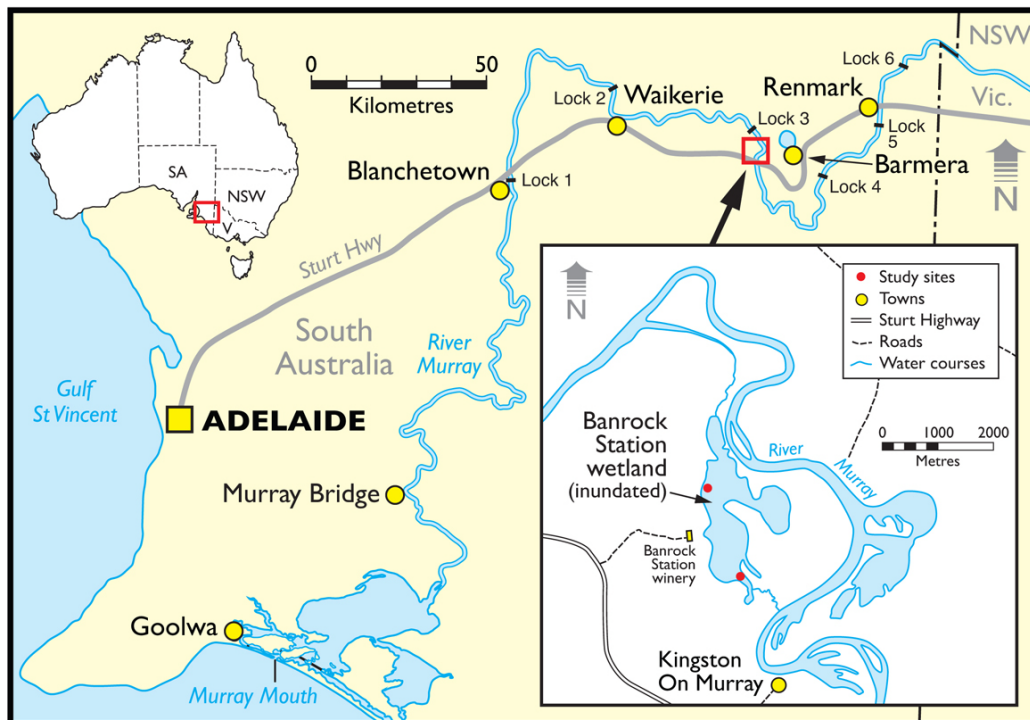
Figure 1-1 Locality map showing the Banrock Station Wetland Complex, the two groups of sites re-sampled on 2nd September, 2013 (sites RBAc-01 to RBAc-04 located in the southern section where the water enters the wetlands and sites RBAc-06 and RBAC-07, which is located in the northern section near the water exit point to the wetland complex) and the localities of Locks 3 and 4 along the River Murray.

The Murray–Darling Basin is Australia's largest river system containing locally and internationally important ecosystems, irrigation and drinking water supplies, and

recreational and cultural values. During 2007–2010, the lower reaches of the River Murray in South Australia (Figure 1-2) experienced the worst drought and lowest water levels in over 90 years of records (Mosley et al., 2012). Due to acid sulfate soil exposure, soil acidification was recorded in large areas along the River Murray, especially in floodplain wetlands of the River Murray (Fitzpatrick et al., 2009, 2010, 2011; Lamontagne et al. 2004; Shand et al. 2010a,b; 2008a,b; 2009). The oxidation of acid sulfate soils with sulfidic material (pH > 4) underlying this former floodplain occurred, due to falling river and groundwater levels during the 2006–2010 extreme "millennium" drought.

The main 'Banrock Lagoon' became permanently flooded in 1925, when lock 3 was constructed (Figure 1-2), and remained so until 1993 when "partial drying phases" were introduced to wetland management. Hence, from 1993 to June 2006 the wetland has been partially dried each winter (to introduce semi-natural wetting-drying cycles). However, the wetland remained completely dry between January 2007 and June 2008 due to the Millennium Drought (see aerial photograph in Figure 1-2, which shows a completely dry wetland in late May 2008 when eight soil profiles were sampled to assess ASS (Thomas *et al.* 2011; Fitzpatrick *et al.* 2009; 2012). The wetland was re-flooded in June 2008 and these inundated sites were re-sampled by CSIRO staff. This was followed by a drying cycle, which commenced again in January 2009 [e.g. see conceptual models in Fitzpatrick et al. (2009) and revised below].

Acid sulfate soils form naturally in wetland environments when sulfate in the water is converted by bacteria to sulfide minerals, predominantly iron pyrite (FeS_2). Soil horizons that contain sulfides with the potential to strongly acidify to pH<4 are called sulfidic material (previous definition of sulfidic: Isbell 1996, 2002; Soil Survey Staff 2003) or hypersulfidic material (new definition replacing sulfidic of Isbell 1996: see Sullivan *et al.* 2010; Isbell 2015, revised 2nd edition), and can be environmentally damaging if exposed to air by disturbance. Exposure results in the oxidation of pyrite, with each mole of pyrite yielding 4 moles of acidity (i.e. 2 moles of sulfuric acid). This process transforms sulfidic or hypersulfidic material to sulfuric material when, on oxidation, the material develops a pH of 4 or less (Isbell 1996); note that a sulfuric horizon has a pH of 3.5 or less according to Soil Survey Staff (2014), the USDA soils classification. If the pH remains above pH 4 during oxidation, they are classified as hyposulfidic. When ASS become strongly acidic, acid pore water or drainage water is produced. This acid together with toxic elements that are leached from soils and sediments can kill fish and shellfish and contaminate groundwater, and can corrode concrete and steel in homes, underground pipes and buildings. These impacts can be measured in terms of:

- poor water quality with loss of amenity, damage to wetland environments and reduction of wetland biodiversity,
- the need for rehabilitation of disturbed areas to improve water quality and minimise impacts,
- loss of fisheries and agricultural production, and
- additional maintenance of community infrastructure affected by acid corrosion.

Other hazards associated with acid sulfate soil include: (i) mobilisation of metals, metalloids and non-metals, (ii) decrease in oxygen in the water column when monosulfidic materials are mobilised into the water column, and (iii) production of noxious gases. In severe cases, these risks can potentially lead to damage to the environment, and have impacts on water supplies, and human and livestock health.

Figure 1-2 Aerial photograph showing the eight (8) sites assessed in the Banrock Station Wetland Complex, adjacent to the Banrock Station winery in late May 2008. The following six (6) sites were re-sampled on 2nd September, 2013: sites RBAc-01 to RBAc-04 located in the southern section and sites RBAc-06 and RBAc-07 located in the southern section.

Changes to the hydrology in regulated sections of the Murray-Darling Basin (MDB) system (due to higher weir pool levels), and the chemistry of rivers and wetlands have caused significant accumulation of sulfidic material in subaqueous and wetland margin soils (Fitzpatrick et al. 2009; 2011). If left undisturbed and covered with water, sulfidic material poses little or no threat of acidification. However, when sulfidic material is exposed to the air, the sulfides react with oxygen to form sulfuric acid (and sulfuric

materials where soil pH < 4). When these sulfuric materials are subsequently covered with water, significant amounts of sulfuric acid can be released into the water.

In summary, this project provides an excellent opportunity to continue to monitor and assess the 6 previously studied representative study sites located around the margins and in the middle of the Banrock Station Wetland Complex (Figure 1-2; Thomas *et al.* 2011; Fitzpatrick *et al.* 2012) to evaluate any changes associated with the drying and rewetting (i.e. subaqueous soils) cycles. This information will be used to investigate and advise on the acid sulfate soil hazards and to determine if the ASS change pattern is temporary and/or reversible.

1.2 Aims and scope of work

The Acid Sulfate Soils Centre (ASSC) was commissioned by Accolade Wines Limited to:

- Assess acidification and deoxygenation/malodour hazards caused by ASS sub-types (i.e. with sulfuric, hypersulfidic, hyposulfidic & monosulfidic materials) using reliable interpretation methods in the Banrock Station wetland complex following a drying cycle (i.e. complete drying and partial drying) by:
  - re-sampling in September, 2013 of six (6) previously studied representative study sites located around the margins and in the middle of the wetland (Thomas *et al.* 2011; Fitzpatrick *et al.* 2012) to evaluate changes associated with drying and rewetting.
- Assess the rate and extent of: (i) neutralisation of previously acidified Sulfuric soils and Sulfuric subaqueous soils and (ii) pyrite accumulation or decrease in all ASS sub-types by comparing the September, 2013 ASS data (dry) with previous data for May 2008 (dry) and June 2008.
- Develop a revised set of soil-regolith models (cross-section diagrams and summaries of temporal and spatial variations and changes at each site) by integrating the September, 2013 findings with the previously studied sites (23rd May 2008 and 3rd October 2008) and predicted historical data (1925-1993 and 1993-2006).
- Assess the influence of organic matter addition on pH and redox potential under flooded (anaerobic) conditions and subsequent pH changes during a drying (oxidation) period.
- Provide briefings of baseline data to underpin long-term management and ongoing monitoring options.
- Publish a final report and journal papers on all findings in relation to envisaged outcomes, especially with regard to the development of revised soil-regolith models (cross-section diagrams).

The project will provide the Banrock Station land managers; and local, state and federal government policy makers (MDBA) with better access to scientifically based information on the September 2013 (changed) condition and future trends of Acid Sulfate Soils in this managed Ramsar wetland. It will also provide detailed quantitative data to underpin management and policy decisions regarding: (i) future/ongoing monitoring and (ii) remedial activities as the Banrock drying and/or re-flooding continues to impact the wetland and River Murray system.

This information will also be used to help refine and build improved past and current predictive soil-regolith models for this managed wetland. New ASS data will be uploaded to the Atlas of Australian ASS on ASRIS (Australian Soil Resource Information System: www.asris.gov.au).

1.3 Acid sulfate soil materials

Acid Sulfate Soils (ASS) are those soils in which sulfuric acid may be produced, is being produced, or has been produced in amounts that have a lasting effect on main soil characteristics (Pons 1973). This general definition includes: (i) potential, (ii) actual (or active), and (iii) post-active ASS, three broad generic soil types that continue to be recognised (e.g. Fanning 2002). However, definitions of these broad generic types of ASS can be confusing and the Acid Sulfate Soil Working Group of the International Union of Soil Sciences agreed to adopt changes to the classification of ASS materials (Sullivan et al. 2010), which was also adopted by the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soils Risk Assessment Project for use in detailed assessment of acid sulfate soil in the Murray-Darling Basin. This report follows these recommendations. Acid sulfate soils are essentially soils containing detectable sulfide minerals, principally pyrite (FeS_2) or monosulfides (FeS). The definitions used in this report are:

Sulfuric material: Soil material that has a pH less than 4 (1:1 by weight in water, or in a minimum of water to permit measurement as currently defined by the Australian Soil Classification, Isbell 1996).

Sulfidic materials* – soil materials containing detectable sulfide minerals. The intent is for this term to be used in a descriptive context (e.g. sulfidic soil material or sulfidic sediment) and to align with general definitions applied by other scientific disciplines such as geology and environment science (e.g. sulfidic sediment). The method with the lowest detection limit is the Cr-reducible sulfide method, which currently has a detection limit of 0.005%; other methods (e.g. X-ray diffraction, visual identification, Raman spectroscopy or infra red spectroscopy) can also be used to identify sulfidic materials.

*This term differs from previously published definitions in various soil classifications (e.g. Isbell 1996)

Hypersulfidic material – (adapted from (e.g. Isbell 1996) with modifications to *inter alia* account for recent improvements to the incubation method (Sullivan et al. 2009). Hypersulfidic material is a sulfidic material that has a field pH of 4 or more and is identified by experiencing a substantial** drop in pH to <4 (1:1 by weight in water, or in a minimum of water to permit measurement) when a 2-10 mm thick layer is incubated aerobically at field capacity. The duration of the incubation is either: a) until the soil pH changes by at least 0.5 pH unit to below 4, or b) until a stable*** pH is reached after at least 8 weeks of incubation.

Hyposulfidic material - (adapted from Isbell (1996) with modifications to *inter alia* account for recent improvements to the incubation method (Sullivan et al. 2009): Hyposulfidic material is a sulfidic material that (i) has a field pH of 4 or more and (ii) does not experience a substantial** drop in pH to <4 (1:1 by weight in water, or in a minimum of water to permit measurement) when a 2-10 mm thick layer is incubated aerobically at field capacity. The duration of the incubation is until a stable*** pH is reached after at least 8 weeks of incubation.

**A substantial drop in pH arising from incubation is regarded as an overall decrease of at least 0.5 pH unit.

***A stable pH is assumed to have been reached after at least 8 weeks of incubation when either the decrease in pH is < 0.1 pH unit over at least 14 day period, or the pH begins to increase.

Monosulfidic materials - soil materials with an acid volatile sulfide content of 0.01%S or more. Monosulfidic materials are subaqueous or waterlogged organic-rich materials that contain appreciable concentrations of monosulfides. Monosulfidic black oozes are specific materials characterised by their gel-like consistence.

Non-Acid Sulfate Soil materials

In addition, the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soils Risk Assessment Project agreed to identify "other acidic soil materials" arising from the detailed assessment of wetland soils in the Murray-Darling Basin even though these materials may not be the result of acid sulfate soil processes (e.g. the acidity developed during ageing may be the result of Fe^{2+} hydrolysis, which may or may not be associated with acid sulfate soil processes). The acidity present in field soils may also be due to the accumulation of acidic organic matter and/or the leaching of bases. Of course, these acidic soil materials may also pose a risk to the environment.

The definition of these *other acidic soil materials* for the detailed assessment of acid sulfate soils in the Murray-Darling Basin is as follows:

1. Other acidic soil materials – either:

a. non-sulfidic soil materials that acidify by at least a 0.5 pHw unit to a pH_w of <5.5 during moist aerobic incubation, or

b. soil materials with a pH_w ≥ 4 but < 5.5 in the field.

2. Other soil materials – soils that do not have acid sulfate soil (or other acidic) characteristics.

1.4 Acid sulfate soil types and subtypes

Acid sulfate soil profiles are allocated (or classified) an acid sulfate soil type and subtype according to the Acid Sulfate Soil Identification Key (Fitzpatrick et al. 2010; Fitzpatrick 2013; Appendix 1). The Key was designed for people who are not experts in soil classification systems, assisting them to easily identify five acid sulfate soil types (subaqueous, organic, cracking clay, sulfuric and hypersulfidic soils) and 18 sub-types based on the occurrence of sulfuric, hypersulfidic, hyposulfidic, or monosulfidic material, and clayey or sandy layers.

1.5 Review of previous acid sulfate soils investigations

Despite decades of scientific investigation of the ecological (e.g. Living Murray Icon Site Environmental Management Plan (Murray-Darling Basin Commission 2006a; b; c), hydrological, water quality (salinity) and pedological features of wetlands in the MDB, it was only post 2006 that a remarkably wide spectrum of acid sulfate soil subtypes and processes were identified along the MDB - especially from continued lowering of water levels (e.g. Fitzpatrick et al. 2008a,b,c,d; 2009; 2011; Lamontagne et al. 2004; 2006; Shand et al. 2010a,b; 2008a,b; 2009; Simpson et al. 2008, 2010; Sullivan et al. 2008). Hence, the MDB Ministerial Council at its meeting in March 2008 directed the then Murray-Darling Basin Commission (MDBC) to undertake an assessment of acid sulfate soil risk in key wetlands in the MDB (e.g. Thomas *et al.* 2011; Fitzpatrick *et al.* 2012, Grealish et al. 2014).

1.6 Review of Banrock Station Wetland Complex

The Wetland Complex straddles the boundary of the Mallee Trench and Mallee Gorge geomorphic tracts (Butcher et al. 2009) and supports a number of discrete depositional basins and active channels on an incised ancestral floodplain, which is approximately 5 -10 m above sea level. The largest wetland basin is referred to as the main Banrock Lagoon (Butcher et al. 2009). It is an elongate lagoon (120 ha in size) that effectively by-passes lock 3 (see Figure 1-1), providing a constant flow of water through the wetland at pool level (8.6 m AHD). A second, eastern lagoon (about 130 ha), is connected to the main 'Banrock Lagoon' but is usually dry at pool level, and only fills when weir pool levels are above 9.2 m AHD. The 'Eastern Lagoon' is joined to 'Banrock Lagoon' during high flows and together they form the major freshwater wetland area of the site. Surrounding these lagoons are significant areas of samphire and lignum dominated floodplain, much of which is affected by rising saline groundwater. Additional intermittently flooded wetlands occur on Wigley Reach. The mallee areas of the site rise to 40 - 50 m above the floodplain with the highest point on the site being 62 m above sea level (Butcher et al. 2009).

The floodplain wetlands are dominated by lignum and sedge with expanses of open water. Adjoining is an open mallee-box woodland community which provides habitat for a breeding population of the Regent Parrot *Polytelis anthopeplus* - a species listed as vulnerable nationally and within South Australia. Approximately 159 bird species, including several migratory species have been observed at the site. During dry periods the swamp acts as a drought refuge.

Banrock Station Wetland Complex is a floodplain wetland that was restored in 1992 when actions were taken to reinstate wetting and drying cycles that are semi-natural and intermittent. Banrock Station Wetland Complex is now one of only 20 sites in the Lower River Murray that has been returned to a near-natural hydrological regime.

The Ramsar Wetland Complex is located entirely on private land, and management is the responsibility of Accolade Wines Limited. The Wetland Complex is used extensively for recreation and tourism and is the subject of a range of scientific research.

2.   FIELD AND LABORATORY METHODS

Summary

This section outlines the methods used to survey, sample and analyse representative Acid Sulfate Soil samples from soil profiles and surface salt efflorescences at Banrock Station.

2.1   Field sampling of soils

Banrock Station Wetland Complex lies on the River Murray floodplain in south-eastern Australia opposite the township of Overland Corner, and is 26 km northwest of the major township of Berri. The total area of the Ramsar site is 1,375 ha, which includes 1,068 ha of floodplain wetland and 307 ha of an open mallee-box woodland buffer (Figure 1-2).

Acid sulfate soil field survey at the site involved characterisation of two toposequences, one in the up-stream (southeast) section and one at the down-stream (northwest) section of the main 'Banrock Lagoon' (Figure 1-2). The upstream toposequence was sited across the deepest part of the wetland, which in early 2008, dried completely for the first time in 83 years. The second toposequence was sampled near the outlet creek in an area that had experienced complete drying seasonally since 1993 (Figure 1-2). Both toposequences formed representative cross-sections from the high flood mark to the dry wetland bed (Figure 1-2). No surface water or groundwater was encountered at any of the toposequence locations. Light brown sandy soils were found to fringe the wetland and generally contained sulfuric material (from the near surface to about 50 cm depth) and were underlain by gleyed, grey clayey sands (Figure 1-2). The wetland bed generally contained cracked clayey surface horizons with darker grey, moist heavy clays at depth. Black mottles were evident in the near surface at site RBAc4 (the deepest point in the wetland).

A summary of methods for field data collection is presented in Table 2-1.

Sample site location coordinates were obtained using a GPS, using the WGS 84 Datum: Zone 54 South (Easting's and Northing's; Table 2-1).

Photographs were taken of all the soil profile sites and soil profiles in soil pits for each site (see electronic data base of photographs). In the field, each soil profile was photographed and horizons were sub-sampled. Soil material was described and physical properties such as colour, consistency, structure and texture follow McDonald *et al.* (1990). The presence of 'sulfidic' smells (e.g. H_2S – rotten egg gas and methyl thiols) as well as oxidising odours (SO_2) were recorded.

Representative sub-samples were collected in chip trays for: (i) soil morphological study/ description and (ii) incubation tests. Sub-samples were placed in plastic jars for acid-base accounting, electrical conductance and pH measurements. Air was excluded as far as possible when samples were collected in the plastic bottles. The analytical data for these analyses are appended to this report.

Table 2-1 List of methods for field data collection.

Data and Analysis	Objective	Method
Field Data		
Site number	uniquely identifies the site	Unique alpha numeric code (e.g. DXF2-01): D – project name; XF2 pond ID
Site location (Zone, easting, northing coordinates)	accurately places the sample site within the study area	Global positioning system (GPS) + or – 1 meters, locate to the WGS 84 Z 54S Grid.
Depth of water or depth to water table below soil surface	Current status of water level relative to the soil surface	Tape measure (National Committee on Soil and Terrain 2009)
Site description	Places the sample site within the landscape and surrounding environment, to enable extrapolation of the profile information and to estimate the proportion that it represents in study area	Refer for guidance to National Committee on Soil and Terrain (2009).
Sample depth (upper and lower)	Estimating the layer thickness and position in the profile of the soil sample	Tape measure (National Committee on Soil and Terrain 2009)
Soil Morphology Description: field texture, consistence, structure, moisture status, and other diagnostic features if present, such as mottling (redoximorphic features), odour, organic material, shell fragments, minerals such as jarosite, crystals, coarse fragments)	For characterisation and classification of the soil. To facilitate understanding of soil variability and transfer of quantitative data between profiles and layers that appear similar through this qualitative description	National Committee on Soil and Terrain (2009); Schoeneberger *et al.* (2002) – for redoximorphic features

2.2 Laboratory soil analysis methods

A summary of methods for laboratory analyses conducted is presented in Table 2-2. Following sampling, the soils were transferred to the laboratory and kept cool at ca. 4°C until analysed. Samples were stored in chip trays to conduct incubation tests to follow the course of potential acidification and determine ASS status. Oven and air dried/moist samples and chip tray samples were kept for long-term storage to allow for future re-sampling and analyses, if required.

Samples for acid-base accounting were air dried at 80°C. Moisture contents were recorded and bulk densities estimated. Samples for sulfur suite analysis were sent to the Environmental Analysis Laboratory of Southern Cross University.

As discussed previously, sulfide minerals are generally stable under reducing conditions, however, on exposure to the atmosphere the acidity produced from sulfide oxidation can impact on water quality, crop production, and corrode concrete and steel structures (Dent 1986). In addition to the acidification of both ground and surface waters, a reduction in water quality may result from low dissolved oxygen levels (Burton et al. 2006; Sammut et al. 1993; Sullivan et al. 2002a), high concentrations of aluminium and iron (Ferguson and Eyre 1999; Ward et al. 2002), and the release of other potentially toxic metals (Burton et al. 2008a; Preda and Cox 2001; Sullivan et al. 2008; Sundstrom et al. 2002).

In nature, a number of oxidation reactions of sulfide minerals (principally pyrite: FeS_2) may occur which produce acidity, including:

$$2FeS_2 + 7O_2 + 2H_2O ---> 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

$$4FeS_2 + 15O_2 + 10H_2O ---> 4FeOOH + 8H_2SO_4$$
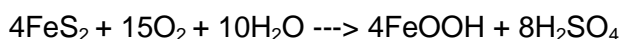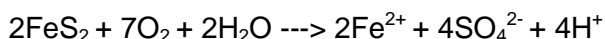
A range of secondary minerals, such as jarosite, sideronatrite and schwertmannite may also form, which act as stores of acidity i.e. they may produce acidity upon dissolution (e.g. during rewetting).

Acid-base accounting (ABA)

Acid-base accounting (ABA) is used to assess both the potential of a soil material to produce acidity from sulfide oxidation and also its ability to neutralise any acid formed (e.g. Sullivan et al. 2001; Sullivan et al. 2002b).It is a technique, which balances the potential acid generated from the sum of sulfide-S (S_{CR} or chromium-reducible S) and the titratable actual acidity (TAA) of the soil (AGP), with the total amount of potential alkalinity/acid neutralising capacity (ANC) generated. Details of the chemical methods used are given in Ahern *et al.* (2004). The ANC is usually only routinely measured when soil pH_{KCl} (measured in a high ionic strength KCl solution) is greater than pH 6.5. When pH_{KCl} is less than 4.5, this indicates that secondary less soluble acid-producing minerals such as jarosite are likely to be present. This is measured as retained acidity. The net acid generating potential (NAGP) is the acid generating potential (AGP) plus retained acidity minus ANC, which gives an indication of acid generation *if all components react fully*. Arguments against this technique include the fact that the carbonate may not be available to soil solutions (e.g. if it is coated and protected with organic material or iron oxides) or if it is in a form that is not particularly reactive (e.g. iron carbonates and dolomite (calcium magnesium carbonate) have much slower reaction kinetics than calcite). Net acidity aims to take this into account by introducing a "fineness factor", whereby net acidity is calculated by dividing the ANC by a factor of 1.5. However, the oxidation of pyrite may also cause pyrite to not react fully if it becomes coated with protective secondary minerals. Thus, it may be difficult to assess acidification scenarios effectively.

The standard ABA applicable to acid sulfate soil is as described in Ahern et al. (2004) and summarised here. The equation below shows the calculation of Net Acidity (NA):

Net Acidity = Potential Sulfidic Acidity + Existing Acidity – ANC*/Fineness Factor

*ANC = Acid Neutralising Capacity

The components in this ABA are further discussed below and by Ahern et al. (2004).

Potential Sulfidic Acidity (PSA)

The potential sulfidic acidity is most easily and accurately determined by assessing the chromium reducible sulfur (CRS or S_{Cr}). This method was developed specifically for acid sulfate soil materials (Sullivan et al. 2000) to, *inter alia*, assess their potential sulfidic acidity (PSA) also known as the 'acid generation potential' (AGP). The method is also described in Ahern et al. (2004), which includes the chromium reducible sulfur method (Method Code 22B) and its conversion to PSA.

Existing Acidity

Existing acidity is the sum of the actual acidity and the retained acidity (Ahern et al. 2004). Titratable actual acidity (TAA) is a measure of the actual acidity in acid sulfate soil material that has already oxidised. TAA measures the sum of both soluble and exchangeable acidity in acid sulfate soil material and non-acid sulfate soil material. The retained acidity (RA) is an operational term used to estimate the acidity 'stored' in minerals such as jarosite, schwertmannite and other hydroxysulfate minerals. Although these minerals may be stable under acidic conditions, they can release acidity to the environment when these conditions change. The methods for determining both TAA and RA are given by Ahern et al. (2004).

Acid Neutralising Capacity (ANC)

Soils with pH_{KCl} values > 6.5 may potentially have ANC in the form of (usually) carbonate minerals, principally of calcium, magnesium and sodium. The carbonate minerals present are calculated by titration, and alkalinity present is expressed in $CaCO_3$ equivalents. By definition (Ahern et al. 2004), any acid sulfate soil material with a pH_{KCl} < 6.5 has a zero ANC.

Fineness Factor (FF)

This is defined by Ahern et al. (2004) as "A factor applied to the acid neutralising capacity result in the acid base account to allow for the poor reactivity of coarser carbonate or other acid neutralising material. The minimum factor is 1.5 for finely divided pure agricultural lime, but may be as high as 3.0 for coarser shell material". Fine grinding of soil materials may lead to an over-estimate of ANC when carbonates are present in the form of hard nodules or shells. In the soil environment, they may provide little effective ANC when exposure to acid may result in the formation of surface crusts (iron oxides or gypsum), preventing or slowing further neutralisation reactions. For reasons including those above, the use of the "Fineness Factor" also applies to those naturally occurring alkalinity sources in soil materials as measured by the ANC methods.

pH testing after peroxide treatment

Hydrogen peroxide (H_2O_2) is a strong oxidising agent and is used to encourage the oxidation of sulfide minerals (principally pyrite: FeS_2) and the subsequent production of acidity. Since peroxide is a strong oxidising agent, it can be argued that the resultant pH measured is a worst-case scenario. In nature, the presence of carbonate minerals such as calcite ($CaCO_3$) may neutralise acid produced, however, in some cases the carbonate may not fully dissolve due to slow dissolution rates (reaction kinetics). The dissolution rates of individual minerals may be controlled by a number of factors, hence additional tests based on measuring the carbonate content are recommended.

Table 2-2 List of methods for laboratory analysis conducted.

Data and Analysis	Objective	Method
Laboratory Analysis		
pH_{water}	Measures the current sampled status of the soil acidity or alkalinity	pH meter; 1:1 soil:water (Rayment and Higginson 1992)
$pH_{peroxide}$	Measures the potential end oxidized status of the soil pH	pH meter; Method 4E1 (Rayment and Higginson 1992)
$pH_{incubation}$	Represents a scenario for soil sample on exposure to air (oxygen) for a specified period of time	Fitzpatrick _et al._ 2008
Electrical conductivity	Measure of the soil salt content	(Rayment and Higginson 1992)
Soil texture	Assessment of texture to assist with interpretation of acid base accounting results	Hand texture determination placed into 3 classes – coarse, medium, fine
pH_{KCl}	pH value. Provides trigger value (pHKCL >6.5) for deciding to test for acid neutralising capacity.	pH meter. Method 23A (Ahern _et al._ 2004)
Chromium reducible sulfur (S_{CR})	Identifies presence of sulfides. For acid base accounting	Method 23B (Ahern _et al._ 2004)
Titratable actual acidity (TAA)	Identifies soil acidity. For acid base accounting.	Method 23F (Ahern _et al._ 2004)
Acid neutralising capacity (ANC) (where pH_{KCl} >6.5)	Identifies neutralising capacity of soil. For acid base accounting.	Method 19A2 (Ahern _et al._ 2004)
Retained acidity (RA)	Identifies stored soil acidity. For acid base accounting.	Method 20J (Ahern _et al._ 2004)
Net acidity (NA)	Identifies the soil acidity (or alkalinity)	Calculated (Ahern _et al._ 2004)

For coastal and inland acid sulfate soils in Australia, the action criteria or trigger values for the preparation of an ASS management plan are shown in Table 2-3.

Table 2-3: Criteria indicating the need for an ASS management plan based on texture range and chromium reducible sulfur concentration and amount of soil material disturbed (Dear et al. 2002).

Texture range	S_{CR} (%S)	
	<1000 t disturbed soil	>1000 t disturbed soil
Coarse: Sands to loamy sands	0.03	0.03
Medium: Sandy loams to light clays	0.06	0.03
Fine: Medium to heavy clays	0.10	0.03

Incubation (ageing) experiments

The third method used, which is often considered to represent a more realistic scenario for ASS testing is based on the 'incubation' of soil samples. A number of specific techniques are employed, but all are based on keeping the sample moist for a specified period (usually a number of weeks or months), which allows a more realistic oxidation of sulfide minerals to occur than that produced during peroxide testing. Although this may mimic nature more closely and does not force reactions to occur (as in the peroxide test) or rely on total 'potential' reaction, it can be argued that the complex processes occurring in the field are not represented e.g. exchange with sub-surface waters (containing ANC) or biogeochemical reactions. These should also be assessed, where possible, but often require a thorough understanding of water movement.

The current practice in CSIRO Land and Water/ Acid Sulfate Soil Centre (ASSC) is to use all of the above techniques and, where possible, to monitor changes in the field during periods of drying to assess the most likely scenarios of acid generation and neutralisation.

This test used for these acid sulfate soil protocols is a modification of this incubation procedure which involves the following steps:

- Incubate mineral or organic soil materials, which have a natural pH (1:1 soil:water) value > 4, as a layer ca. 1 cm thick under moist conditions, while maintaining contact with the air at room temperature.

- Measure the pH and observe whether there is a drop in pH of 0.5 units or more to a value of 4.0 or less, including wetting and drying cycles.

- The duration of incubation shall continue for a "minimum of 8 weeks" until a stable pH is reached (differs from the "fixed 8 weeks" in the formal Australian Soil Classification definition) as described in Sullivan *et al*. 2009.

- Collection and storage of moist samples in plastic chip trays produces similar conditions, and thus chip trays are suitable for incubation testing as described and used in Fitzpatrick *et al*. (2008, 2009a; 2010).

2.3 Acid Volatile Sulfur

Iron-monosulfides, defined operationally as acid-volatile sulfur (AVS) is readily extracted by the diffusion method described by Hsieh et al. (2002) using a modified apparatus (Burton et al. 2006; 2007). Approximately 2 g of wet sample is equilibrated (orbital shaking at 150 rpm for 18 hrs) with 10 ml of 6M HCl/0.1M ascorbic acid in gas-

tight 55 cm^3 polypropylene reactors. The evolved $H_2S(g)$ is trapped in 7 ml of 3% Zn acetate in 2 M NaOH, and subsequently quantified via iodometric titration. The quantitative recovery of acid volatile sulfur using this method is 96 ± 4%. Pyrite-S is not extracted by the acid volatile sulfur analytical method employed here (Hsieh et al. 2002). The slurry remaining after acid volatile sulfur extraction is diluted to 50 ml with deionised water and centrifuged (4000 g, 10 minutes).

2.4 Total carbon and nitrogen

Samples were analysed by the Environmental Analysis Laboratory, Southern Cross University for total carbon and nitrogen using a high temperature combustion method (LECO CNS2000 Analyser) described in Rayment and Lyons (2010). Electrical Conductivity (1:5, soil:water) was determined using the standard method described in Rayment and Lyons (2010).

2.5 Rapid metal release test methods

Soil samples were air dried at 40 ^{0}C, and 25 g of each sample was weighed into clean acid-washed 250 mL Nalgene extraction bottles and resuspended in 250 mL of deionised water for a period of 24 hours in an end over shaker. Water blanks were run with the batch extraction to monitor water quality throughout the experiment. After 1 hour, a 25 ml aliquot was sampled to measure water quality at the start of the extraction, with the measurements repeated at the end of extraction (24 hours). Water quality measurements included dissolved oxygen, pH, alkalinity/acidity, redox potential (Eh), and specific electrical conductance (SEC).

At the completion of the extraction phase, the samples were centrifuged to settle solids and allow the supernatant to be filtered for chemical analysis using Millex 0.45 micron PVDF syringe filters. Analyses for a suite of major and trace elements including metals, metalloids nutrients were run on the filtered water extracts to provide a detailed profile of each sample's chemistry.

Nitrogen species, Cl and PO_4 were analysed by colorimetric analysis using an Auto Analyser; Br, F and SO_4 by ion chromatography; and NPOC by a TOC Analyser in the Adelaide Waite laboratories at CSIRO. For cation analyses, water samples were transported to the CSIRO laboratory at Lucas Heights, Sydney by courier and analysed for a range of major and trace elements.

A subsample of each water sample was taken for direct metals analysis using an inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Varian730 ES or Agilent 700 series) fitted with an argon sheath torch using in-house method C-229 and operating instructions recommended by the manufacturer. High salinity samples were analysed using the method of standard additions for the determination of aluminium, iron, manganese and zinc. Calcium, sodium, potassium, magnesium, sulfur and strontium were analysed by diluting the sample then analysing against matrix matched calibration standards prepared from certified stock solutions (Accustandard, USA). The remaining elements were analysed by inductively coupled plasma-mass spectrometry (ICP-MS) (Aglient 7500 CE) using in-house method C-209 and operating instructions recommended by the manufacturer. Samples were diluted and analysed against matrix matched standards which were prepared from a set of three multi-element stock solutions (High Purity Standards, USA).

2.6 Mineralogical analyses by x-ray diffraction

The soil samples (bulk and <2µm fractions), gypsum crusts and salt efflorescences were ground in an agate mortar and pestle The resulting fine powders were either gently back pressed into stainless steel sample holders or lightly front pressed onto silicon low background holders for X-ray diffraction analysis (XRD) analysis. XRD patterns of samples were collected with a PANalytical X'Pert Pro Multi-purpose Diffractometer in "standard" configuration mode using iron filtered Co $K\alpha$ radiation, automatic divergence slit and X'Celerator Si strip detector. The diffraction patterns were recorded in steps of 0.017° 2 theta with a 0.5 second counting time per step.

Analysis of the XRD patterns were performed using in-house developed XPLOT software and commercial software, HighScore Plus from PANalytical. Mineralogical phase identification was made by comparing the measured XRD patterns with the International Centre for Diffraction Data (ICDD) database of standard diffraction patterns using computer aided search/match algorithms.

2.7 Water analyses

Various methods were used for water analyses as shown in Table 2-4.

Table 2-4 Methods used for analyses of water

Analyte	Method
Dissolved metals by ICP-AES	Dissolved metals were measured by ICP-AES (CIROS, SPECTRO). The sample is converted to an aerosol and transported into the plasma. Atoms and ions of the plasma are excited and emit light at characteristic wavelengths. The light emitted by the sample passes through the entrance slit of the spectrometer. The different wavelengths are measured and converted to a signal and quantified by comparison with standards.
Dissolved metals by ICP-MS	Dissolved metals were measured by ICP-MS (Agilent 7500 CE). Analyte species originating in a liquid are nebulised by a Micromist nebuliser and a cooled double-pass spray chamber. The ions are detected by an electron multiplier. The ions are quantified by comparison with prepared standards.
Alkalinity and Acidity as calcium carbonate	APHA 21st ed., 2320 B This procedure determines alkalinity by both manual measurement and automated measurement (PC Titrate) using pH 4.5 for indicating the total alkalinity end-point. Acidity is determined by titration with a standardised alkali to an end-point pH of 8.3.
Major anions - filtered	APHA 21st ed., 4500 Cl - B. Automated Silver Nitrate titration.
Chloride	APHA 21st ed., 3120; USEPA SW 846 - 6010 The ICP-AES technique ionises filtered sample atoms emitting a characteristic spectrum. This spectrum is then compared against matrix matched standards for quantification.
Nitrite and nitrate as N	APHA 21st ed., 4500 NO_3^- I. Nitrate is reduced to nitrite by way of a cadmium reduction column followed by quantification by FIA. Nitrite is determined separately by direct colourimetry and result for Nitrate calculated as the difference between the two results.
Reactive phosphorus - filtered	APHA 21st ed., 4500 P-E Water samples are filtered through a 0.45um filter prior to analysis. Ammonium molybdate and potassium antimony tartrate reacts in acid medium with orthophosphate to form a heteropoly acid -phosphomolybdic acid - which is reduced to intensely coloured molybdenum blue by ascorbic acid. Quantification is achieved by FIA.
Total organic carbon (TOC)	APHA 21st ed., 5310 B, The automated TOC analyser determines Total and Inorganic Carbon by IR cell. TOC is calculated as the difference.
Moisture content	A gravimetric procedure based on weight loss over a 12-24 h drying period at 110±5ºC.
Paste pH, conductivity	Paste pH (USEPA 600/2-78-054): pH determined on a saturated paste by ISE. Electrical Conductivity of Saturated Paste (USEPA 600/2-78-054) - conductivity determined on a saturated paste by ISE.

3. SOIL PROFILE ASSESSMENT

This section presents the soil profile assessment data from the field survey campaign conducted in September, 2013 – comprising 6 soil profiles and 29 soil layers/horizons.

3.1 Field sampling of soils

The field investigation was undertaken on the 2nd September, 2013 (dry-sampling-c). The approach adopted was to resample 6 of the 8 sites that were previously sampled on 23rd May 2008 (dry-sampling-a) by Thomas et al. (2008) and on 23rd October 2008 (wet-Sampling-b). The sites sampled on 2nd September 2013 are shown in Figure 1-2 and briefly described in Table 3-1. Summary soil profile descriptions for all soil profiles, as well as acid sulfate soil material designations for all soil layers identified, pH after peroxide treatment and Carbon Nitrogen (C:N) ratios are given in Table 3-3. The information gained from this data and the accompanying pH incubation and acid base accounting data will be used to assist in quantifying soil changes associated with the ongoing water level fluctuations following cyclic reflooding and drying.

At the time of the field investigation on 2nd September 2013, the wetland surfaces were generally dry, as shown in Figure 3-2 by shallow cracking patterns near the soil surface (10 to 15 cm deep) with only a few localised wet or muddy patches, which were restricted to low lying areas.

The distribution of the site locations (see Figure 1-2 and Table 3-1) were grouped into the following two sections or segments of the wetland:

- Southern wetland section near the wetland inlet for profiles RBAc01 to RBAc04

- Northern wetland section near the wetland outlet for profiles RBAc06 to RBAc07

Sample site location coordinates were obtained with a GPS, using the WGS 84 Datum: Zone 54 South (Easting's and Northing's; Table 3-1). Soil profile sampling was carried out by observable horizon and not fixed sampling depths and was achieved by digging with a spade. Accompanying soil profile photographs (e.g. Figure 3-1, Figure 3-2) are presented in a separate electronic data base (Appendix 2).

On the 2nd September 2013 field investigation, **6 soil profile** sites were investigated and **29** soil layers/horizons were described, sampled in chip trays and underwent laboratory pH incubation analyses (Figure 3-3; Appendix 4). The pH peroxide testing (Table 3-3) and Acid Base Accounting (Appendix 5) was conducted on all samples in the laboratory.

Selected samples were taken of salt efflorescences and salt crusts for X-ray diffraction analysis (Appendix 3).
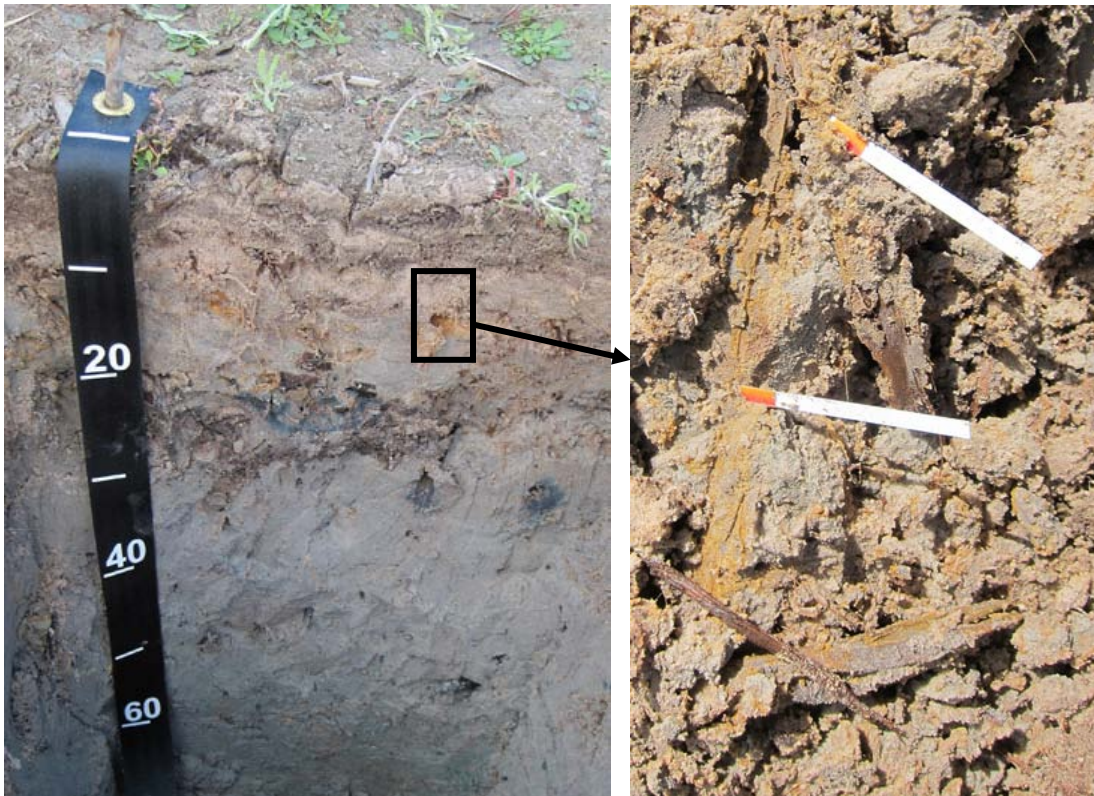
Figure 3-1 Photograph of Sulfuric soil (RBAc 01) taken on 2nd September 2013 showing: (i) Acid Sulfate Soil with sulfuric material between 5 – 20 cm overlying hypersulfidic material (20 to 50 cm) (*left hand side*) and (ii) close-up views of the sulfuric material (pH <3.5) with bright yellow jarosite mottles (pH <3.5: see "red" coloured pH strips clearly indicating low pH values of 3.0) (*right hand side*)

Figure 3-2 Photograph of soil profile RBAc 03 showing cracked, dark grey clay overlying a light grey heavy clay with sporadic very thin, white salt efflorescences at the surface. Hyposulfidic material occurs throughout the soil profile.

Table 3-1 Soil profile locality, profile codes and GIS coordinates (WGS 84 datum, zone 54 south). Three wetland components / landscape types were targeted during this study (2nd September, 2013 sampling) and included – (i) Dry shoreline, ii) Dry bed and iii) Dry bed – lowest position.

[1]Section topo-sequence	Site No	Site Landscape Position	Sample type (near surface)	Date Sampled	Easting	Northing
RBAc 1-5 (south: near wetland inlet)	[2]RBAc 1	Dry shoreline	Clayey sand	02/09/2013	439334	6214987
	RBAc 2	Dry shoreline	Clayey sand	02/09/2013	439291	6214963
	[3]RBAc 3	Dry lakebed	Cracking clay	02/09/2013	439275	6214946
	RBAc 4	Dry lakebed (lowest)	Cracking clay	02/09/2013	439273	6214945
	RBAc 5	Dry lakebed	Cracking clay	Not sampled	439240	6214949
RBAc 6-8 (north: near wetland outlet)	RBAc 6	Dry lakebed (lowest)	Sandy loam	02/09/2013	438732	6216464
	RBAc 7	Dry shoreline	Organic-rich	02/09/2013	438738	6216472
	RBAc 8	Dry shoreline	Clayey sand	Not sampled	438606	6216568

[1]See Figure 1-2 for site locality
[2] See photographs in Figure 3-1
[3]See photograph in Figure 3-2

3.1.1 Soil acidity and classification

As shown in Figure 3-3 and Table 3-3 the pH (T=zero or commencement of incubation) data confirmed the identification of hyposulfidic materials with a pH (T=zero) >4 for most sites in the low lying lakebed landscapes (Table 3-1).

Only one profile, namely RBAc-01 (see Figure 3-1) out of 6 soil profiles comprising 29 samples contained sulfuric material (layer RBAc-01.4 at a depth of 5 to 20 cm) with pH <4.0 and classified as a "Sulfuric soil" in accordance with the Australian ASS classification key (Fitzpatrick et al. 2008; Fitzpatrick 2013) (Figure 3-1; Table 3-3; Table 3-4). The two layers below RBAc-01.4, namely RBAc-01.5 (20–30cm) and RBAc-01.6 (30–60cm), contained hypersulfidic material. This site is adjacent to *Phragmites stands* and the associated areas have sandy clay textured topsoil layers. When this profile was sampled on 23rd May 2013, after being completely dried during the Millennium drought, it also classified as a "Sulfuric soil" (Table 3-4) and as a Typic Sulfaquept in accordance with Soil Taxonomy (Soil Survey Staff, 2014; Table 3-5). Interestingly, after the wetland complex was reflooded and inundated for 5 months between June to October 2008, the soil layers below the water remained as sulfuric material and did not reduce to hypersulfidic material. Consequently, when this soil (RBAb-01) was sampled on 3rd October, 2008 (see photograph in Figure 3-5) it classified as a "Sulfuric subaqueous soil" using the Australian ASS classification key (Fitzpatrick et al. 2008; Fitzpatrick 2013). Currently, no subgroup exists in Soil Taxonomy (Soil Survey Staff, 2014) that adequately describes a subaqueous soil with a sulfuric horizon, as observed at this sampling location on 3rd October, 2008. This presents little issue if these soils exist in a transient state for a short period of time. However, in some instances such as in this soil, it is expected that the sulfuric horizon will persist for a number of years. In these cases, it would be appropriate to have the ability to classify these soils accurately within Soil Taxonomy. Fitzpatrick et al. (2015) have proposed the subgroups Typic Sulfowassept to describe the active subaqueous ASS in the Banrock station wetland complex (Table 3-4; Table 3-5). This involves the creation of the Inceptisol sub order, Wassepts, and the great group Sulfowassepts. These proposals are currently being drafted by Fitzpatrick et al. 2015 for

USDA-NRCS for consideration to be included in revised versions of the US Keys to Soil Taxonomy.

In contrast, profile RBAc-02 (closer to lower lying lakebed), which contained sulfuric material when sampled previously (23rd May and 3rd October 2008) contained layers with an initial pH ranging between 4.89 and 5.42, which did not decrease below pH 4.00 on incubation for 16 weeks (i.e. pH 4.64 for sample RBAc-02.3 at a depth 5-15 cm). Consequently, this profile only contained layers with hyposulfidic material and although it classified as a Hyposulfidic soil (Table 3-3; Table 3-4) the pH after incubation for 16 weeks did decrease to a pH of 4.89 (Figure 3-3; see Table 3-3). In addition, the pH after oxidation with hydrogen peroxide decreased to pH 3.26, 2.94 and 2.09 and therefore also represents a potential acidification hazard. Currently no subgroup exists in Soil Taxonomy (Soil Survey Staff, 2014) that adequately describes this Banrock soil because this soil will not qualify as having: (i) "sulfidic material" as defined in Soil Taxonomy and (ii) hyposulfidic material because this term does not yet exist in Soil Taxonomy. Consequently, it is best described as a Typic Hydraquent using Soil Taxonomy (Soil Survey Staff, 2014) because the material does not qualify as having "sulfidic material" (Table 3-5).

All the other soils sampled on 2nd September, 2015 contained Hyposulfidic material and classified as Hyposulfidic cracking clay soils (e.g. Figure 3-2) or Hyposulfidic organic soils (profile RBAc-08) in accordance with the Australian ASS classification key (Fitzpatrick et al. 2008b; Fitzpatrick 2013).
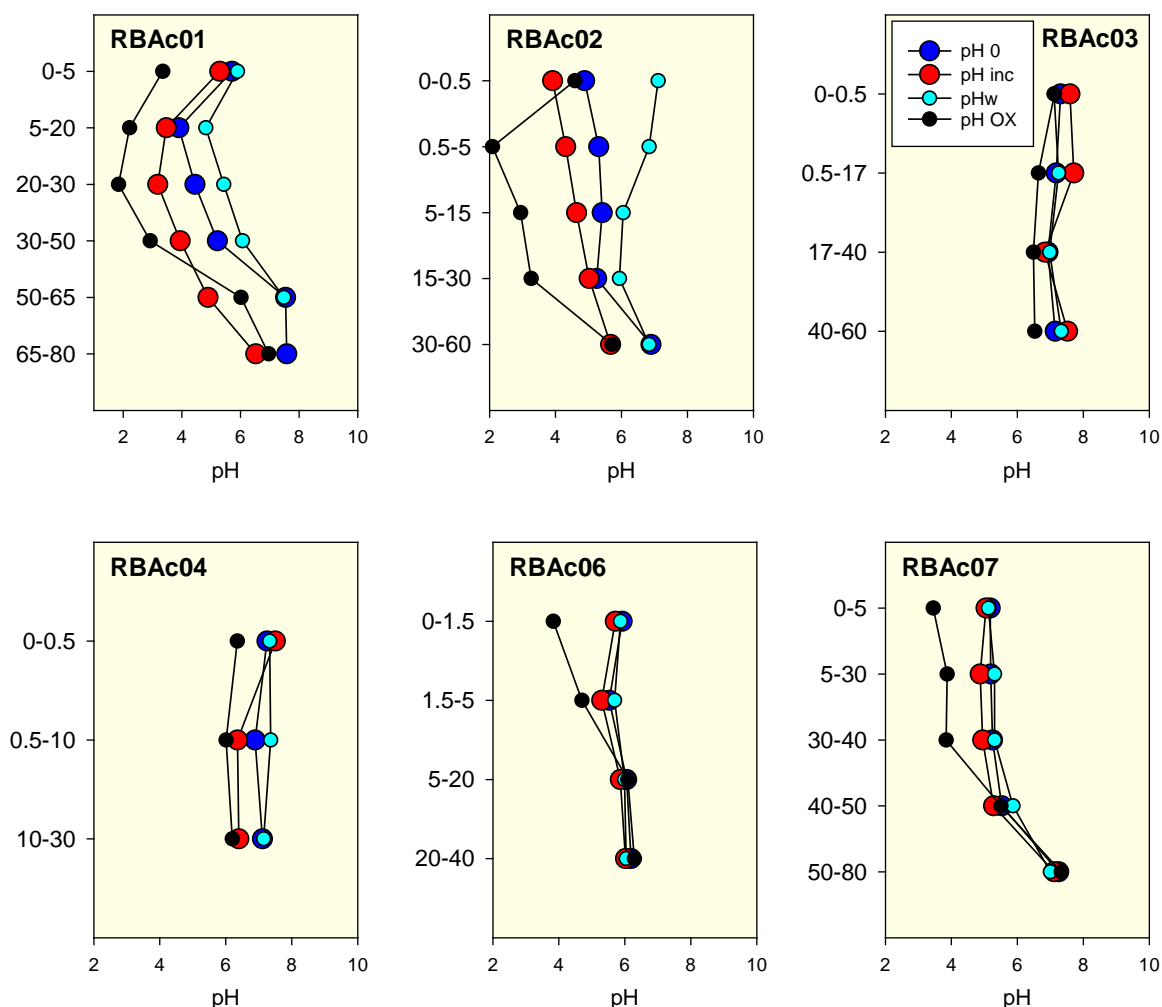
Figure 3-3: Initial incubation pH (pH 0; time zero), incubation pH after 16 weeks (pH inc), pH after oxidation with hydrogen peroxide (pH OX; $pH_{peroxide}$), pH measured in 1:1 soil:water ratio (pHw or pH_{water} plotted against depth for each profile collected.

3.1.2 Acid-base accounting

Acid-base accounting was carried out according to the methods described in Section 2.2 and comprised analyses for sulfide-S (S_{CR} or Cr-reducible S), Retained Acidity (RA), Titratable Actual Acidity (TAA), Acid Neutralising Capacity (ANC) and Net Acidity (NA).   Acid-base accounting and pH data (pH_W and pH_{INC}) for each soil layer are presented in Figure 3-4. These data were used to inform the acidification hazard assessment that is presented in Table 3-3. The total amount of non-organic reduced-S (or reduced inorganic sulfur – RIS), contained mainly within sulfide minerals (S_{CR}), is determined by the Cr-reducible S technique (Ahern et al. 2004). The total amount of acid generated, assuming complete oxidation, can be quantified, usually in mol H^+ tonne^{-1}, or taking into account the bulk density as mol H^+ m^{-3}.

As described above, the soil profile (RBAc 01) on the "outer edge" of the wetland complex when re-sampled on 2nd September 2013 classified as a "Sulfuric soil" because it contained both bright yellow coloured jarosite-rich mottles between 5-20 cm with *in situ* measurement of pH being <3.5 as shown in Figure 3-1 and at commencement of incubation (Figure 3-4 Figure 3-4, Table 3-3). The net acidity values exceeded zero for all the soil layers in six (6)

out of 8 layers sampled for RBAc 01 and reached a maximum of 69 moles H+/tonne (Figure 3-4). The pH before incubation (time zero) and after 16 weeks incubation did not change significantly (i.e. materials were not re-classified) with high acidification hazard (Table 3-3). Values decreased towards the soil surface and at depth (Figure 3-4). There was generally a small amount of ANC in the subsoil layers as shown in Figure 3-4. The pH before incubation (time zero) and after 16 weeks incubation did not change significantly and remained remarkably similar to when this profile was originally sampled on 23rd May 2008 (Thomas et al. 2008). As a consequence, this profile again classified as a Sulfuric Soil (i.e. the sulfuric material classification remained unchanged) (Table 3-3). This profile classified as a "Sulfuric subaqueous soil" when sampled on 3rd October 2008 after being inundated (reflooded) for 5 weeks (see photograph in Figure 3-5).

Profile RBAc 03 and RBAc 04 re-sampled on 2nd September 2013 were both classified as Hyposulfidic clay with monosulfidic material (i.e. *low* acidification hazard rating and *medium* deoxygenation/malodour hazard) (Table 3-3). Acidity comprised a combination of mainly RIS (S_{CR}) and some TAA (Figure 3-4). Profile RBAc 03 contained mainly hyposulfidic material (Table 3-3) with relatively high organic carbon (2.66 4% organic carbon), with large negative net acidity and moderate levels of ANC and no TAA and minor RIS (SCR) (Figure 3-4).
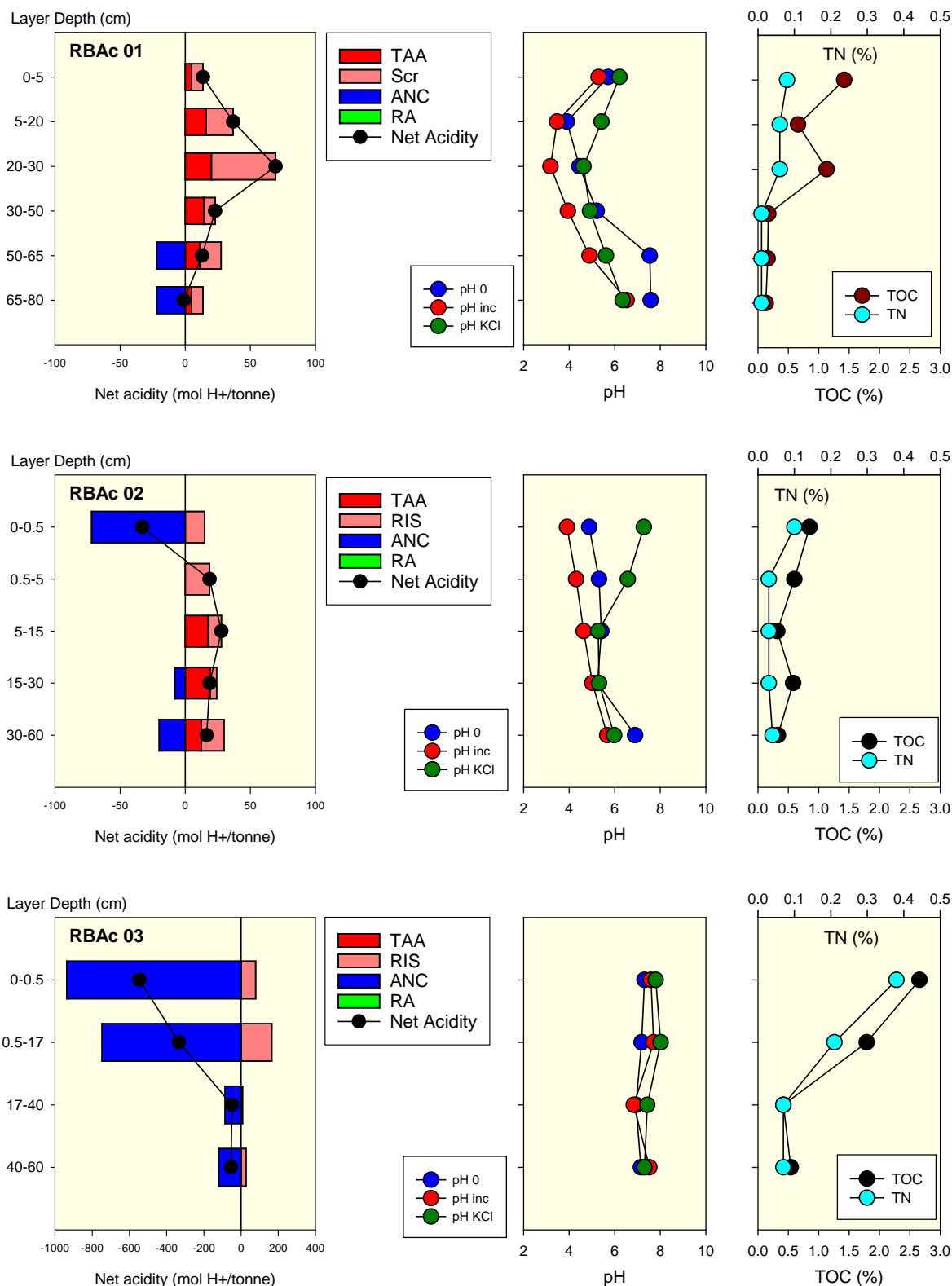
Figure 3-4 Acid base accounting [Titratable Actual Acidity (TAA), Reduced Inorganic Sulfur (RIS or sulfide-S or S_{CR} or Cr-reducible S), Acid Neutralising Capacity (ANC), Retained Acidity (RA) and Net Acidity (NA)], initial incubation pH (pH 0; time zero), incubation pH after 16 weeks (pH inc) and pH measured in KCl:1 soil:water ratio (pH KCl), total organic carbon (TOC) and total nitrogen (TN) data plotted against depth for each soil profile collected on 2nd September 2013.
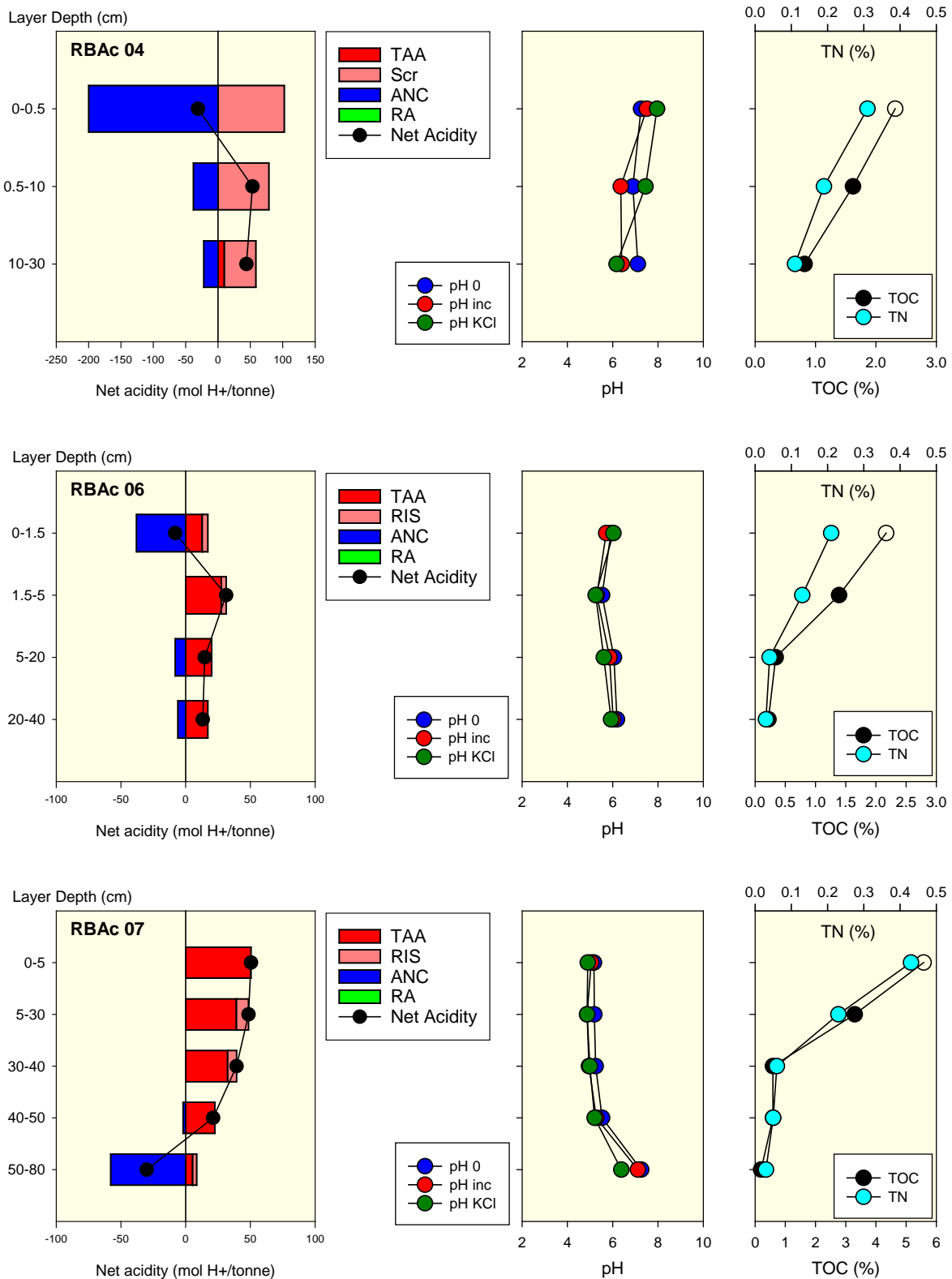
Figure 3-4 *continued*: Acid base accounting [Titratable Actual Acidity (TAA), Reduced Inorganic sulfur (RIS or sulfide-S or S_{CR} or Cr-reducible S), Acid Neutralising Capacity (ANC), Retained Acidity (RA) and Net Acidity (NA)], initial incubation pH (pH 0; time zero), incubation pH after 16 weeks (pH inc) and pH measured in KCl:1 soil:water ratio (pH KCl), total organic carbon (TOC) and total nitrogen (TN) data plotted against depth for each soil profile collected on 2nd September 2013.

Figure 3-5 Photograph of the "Sulfuric subaqueous soil" (RBAb 01) profile showing sulfuric material between 25-40 cm with diffuse yellow jarosite mottles (pH <3.5: see "red" coloured pH strips indicating low pH values of 3.0) (*left hand side*) sampled under water using a shovel and placed on the boardwalk on 3rd October 2008 when the wetland was inundated (*right hand side*).

In summary, in the present survey on 2nd September 2013, soil profile (RBAc 01) on the "outer edge" of the wetland complex the southern segment remained classified as a "Sulfuric soil" because the pH in at 5-20 cm remained at a pH < 4., As well, the pH before and after incubation for 16 weeks had not changed significantly indicating that the materials originally classified as either hyposulfidic and hypersulfidic did not change (Table 3-3).

In contrast, the present survey a higher proportion of soils in the lower lying southern segment of the wetland classified as Hyposulfidic soils, indicating that these soils had changed from Hypersulfidic ASS subtypes when investigated during the previous investigations on 23rd May and 3rd October 2008.

3.1.3 Mineralogy of salt efflorescences and surface precipitates

Soils on the banks and on the edge of the Banrock Station Wetland Complex, especially under the boardwalks, which protects the highly soluble minerals from dissolving, contained abundant white salt efflorescences as a result of high evapotranspiration rates from a likely combination of groundwater seepages and salt concentration in pore-waters, which evaporates at the soil surface.

The semi-quantitative determination of minerals by X-ray diffraction (XRD) of salt efflorescences under the overhanging bank edges and beneath the boardwalk is presented in Table 3-2. X-ray diffraction (XRD) patterns are presented in Appendix 3.

Table 3-2 Mineralogical composition of salt efflorescence

Sample ID	Sample type	Konyaite	Gypsum	Bloedite	Thenardite	Hexahydrite	Epsomite
RBA 1.1a	**White salt**	CD	M	T	SD	CD	SD

The values are estimated from the strongest diffraction line of the particular phase and relate to the approximate concentration levels. D = Dominant — >60%, CD = co-dominant — two or more components of equal quantity, SD = sub-dominant — 20–60%, M = minor — 5–20% and T = trace — <5%. If more than one phase is present in a class, they are listed in decreasing abundance

The very fluffy white efflorescences on sides and base of the wooden pylon supporting the boardwalk (RBA 1.1a) comprised co-dominant konyaite [$Na_2Mg(SO_4)_2 \cdot 5H_2O$] and hexahydrite ($MgSO_4.6H_2O$) with subdominant epsomite ($MgSO_4.7H_2O$) and thenardite (Na_2SO_4), followed by minor amounts of gypsum ($CaSO_4.2H_2O$) and trace amounts of bloedite ($Na_2Mg(SO_4)_2.4H_2O$). These salts are likely to form from the combination of groundwater seepages and surface water evaporation. In the white efflorescences on the soil surface (RBA 1.1b), bloedite and hexahydrite are co-dominant with gypsum and konyaite being subdominant with thenardite being minor and epsomite occurring in trace amounts.

These efflorescent salts (mostly sulfate containing salts) formed very loose and fluffy salts on the sides and base of the wooden posts and soft crusts on soil surfaces, which accumulated above thin pyrite-containing subsoils or sulfuric materials where localised water collects or ponds, enabling salts to precipitate from solution as pore-waters and surface waters evaporate.

3.1.4 Organic carbon and nitrogen

Details of trends in the amount of organic carbon and nitrogen in soil profiles are given in Figure 3-4 . Nitrogen data was used to calculate carbon to nitrogen ratios to assist in determining the organic carbon origins (Table 3-3).

Most surface and near surface layers within the wetland lakebed, namely RBAc03 to RBAc06 (in contrast to those surface layers along the sandy shoreline, which are closely associated with Phragmites) had C:N ratios <10 indicating organic carbon derived from non-vascular aquatic plants e.g. algae or perhaps soil microbial biomass. For those samples collected at depth, where the C:N ratios were low and mainly <10 indicating that the organic matter was not derived from terrestrial vascular plants and was likely formed under conditions that were relatively nutrient rich (Table 3-3).

Samples from several profiles along the sandy shoreline, which are closely associated with Phragmites, namely RBAc01, RBAc02 and RBAc07, have C:N>10 on the surface and at depth, which probably represents humic material consistent with organic bands observed in these profiles (Table 3-3).

3.1.5 Classification and acidification and **deoxygenation/smell hazard** assessment

ASS material and profile classification was carried out for each soil sample collected, according to the definitions and methods presented in Section 2.2.

A summary of the ASS materials for each layer/horizon and subtype classification for each profile is presented in Table 3-3. Acid sulfate soil subtype classification was achieved using the key described in Appendix 1 (Fitzpatrick *et al.* 2008; 2010). The ASS subtype classification was carried out for each soil profile collected during the September sampling campaign and used as a basis for determining the "Acidification and deoxygenation/malodour hazard assessment" in chapter 7.

In summary, the Acidification and deoxygenation/malodour hazard assessment in chapter 7 is derived from the following criteria:

(i)   landscape position (Figure 3-2),

(ii)   soil morphology (Table 3-3),

(iii)   pH data (Figure 3-1; Figure 3-4; Appendix 4),

(iv)   acid base accounting (Figure 3-4; Appendix 5) and AVS data (see Appendix 5)

(v)   ASS material and subtype classification Table 3-3.

The following Acidification and deoxygenation/malodour hazard categories were developed for map legends with: high (Yellow), medium (Brown) and low (Blue).

Table 3-3 Samples from Banrock wetland complex: summary of ASS material classification, ASS subtype soil profile classification, other major soil morphology features used to determine acidification hazard ratings (where a sulfuric soil** has a high rating, hypersulfidic soil* has medium rating and hyposulfidic soil has a low rating), pH peroxide and C:N ratios.

Sample ID.	Depth	Material	Profile	Other soil morphology features	Monosulfidic Material	pH ox	C:N Ratios
RBAc 01.1	0-0.02	Other soil	Sulfuric	Salt eff, white			
RBAc 01.2	0-0.5	Other soil		Salt eff, white		5.32	15.80
RBAc 01.3	0-5	Hyposulfidic		CS, light grey		3.35	17.75
RBAc 01.4	5-20	Sulfuric		SCL, light grey m- j-yel		2.22	11.00
RBAc 01.5	20-30	Hypersulfidic		MC, grey-brown, m-yel		1.84	18.83
RBAc 01.6	30-50	Hypersulfidic		LC, gr-grey, m-br		2.92	17.00
RBAc 01.7	50-65	Hyposulfidic		LC, gr-grey, m-br		6.02	16.00
RBAc 01.8	65-80	Other soil		HC, gr-grey, m-yel		6.96	13.00
RBAc 02.1	0-0.5	Other soil	Hyposulfidic	Salt eff, white	Monosulfidic (H)	4.59	8.50
RBAc 02.2	0.5-5	Hyposulfidic		CS, light grey	Monosulfidic (H)	2.09	20.00
RBAc 02.3	5-15	Hyposulfidic		SCL, light grey m-yel	Monosulfidic (M)	2.94	10.67
RBAc 02.4	15-30	Hyposulfidic		LC, gr-grey, m-br		3.26	19.33
RBAc 02.5	30-60	Hyposulfidic		HC, gr-grey m-yel		5.71	8.25
RBAc 03.1	0-0.5	Hyposulfidic	Hyposulfidic	LC, light grey	Monosulfidic (H)	7.13	7.00
RBAc 03.2	0.5-17	Hyposulfidic		HC, light grey	Monosulfidic (H)	6.64	8.52
RBAc 03.3	17-40	Hyposulfidic		HC gr-grey m-br ss		6.49	6.00
RBAc 03.4	40-60	Hyposulfidic		HC gr-grey m-ol ss gyp		6.53	7.71
RBAc 04.1	0-0.5	Hyposulfidic	Hyposulfidic	LC; olive-grey	Monosulfidic (H)	6.35	7.48
RBAc 04.2	0.5-10	Hyposulfidic		LC; dark-grey	Monosulfidic (H)	6.01	8.53
RBAc 04.3	10-30	Hyposulfidic		HC gr-grey m-yel ss gyp		6.20	7.45
RBAc 06.1	0-1.5	Hyposulfidic	Hyposulfidic	SCL, light grey m-yel	Monosulfidic (H)	3.83	10.33
RBAc 06.2	1.5-5	Hyposulfidic		SCL, light grey m-yel	Monosulfidic (H)	4.70	10.69
RBAc 06.3	5-20	Hyposulfidic		LC, gr-grey,		6.09	8.50
RBAc 06.4	20-40	Other soil		HC, gr-grey, m-yel		6.29	7.33
RBAc 07.1	0-5	Hyposulfidic	Hyposulfidic	br,90% organic matter		3.45	12.98
RBAc 07.2	5-30	Hyposulfidic		br,80% organic matter		3.87	14.35
RBAc 07.3	30-40	Hyposulfidic		MC, dark-grey, m-br		3.84	9.83
RBAc 07.4	40-50	Hyposulfidic		HC, dark-grey, m-yel		5.50	11.80
RBAc 07.5	50-80	Other soil		HC, dark-grey, m-red		7.33	6.67

Where the soil classification is a **Sulfuric soil, **sulfuric material** (pH <4 at time zero incubation) has been identified in a layer or horizon (at least 10cm thick) within 150 cm of the soil surface.

*Where the soil classification is a **Hypersulfidic soil**, **hypersulfidic** material (pH decreased to <4 after incubation of at least 16 weeks) has been identified in a layer or horizon (at least 10cm thick) within 150 cm of the soil surface.

Monosulfidic material: High (H); Medium (M) and Low (all others) determined visually in the field

Other soil: Other soil material

Texture: S = Sand (i.e. Medium Sand), CS = Clayey Sand; LS = Loamy Sand; SL = Sandy Loam; L = Loam; SCL = Sandy Clay Loam; ; CL = Clay Loam; ZCL = Silty clay Loam; LC = Light Clay; LMC = Light Medium Clay; MC -= Medium Clay; MHC = Medium Heavy Clay; HC = Heavy Clay. S = Medium sandy; K = coarse sandy; F= fine sandy and Z = silty McDonald and Isbell (2009; page 164)

Salt Ef = Salt efflorescences, m = mottles, j = jarosite; gr = greenish; ol = olive; br = brownish; yel = yellowish; red= reddish; ss = slickensides; gyp = gypsum; n= n-Value (see appendix)

Table 3-4: Soil classification in accordance with the Australian Acid sulfate soil key for soils sampled previously (23rd May 2008 and 3rd October 2008) and in the current investigation (2nd September, 2013)

[1]Dry 23rd May 2008 (a)		[2]Reflooded 3rd October 2008 (b)		[3]Dry 2nd September 2013 (c)	
Profile No	Identification key[4]	Profile No	Identification key[4]	Profile No	Identification key[4]
RBAa 1	Sulfuric soil	RBAb 1	Sulfuric subaqueous soil	RBAc 1	Sulfuric soil
RBAa 2	Sulfuric soil	RBAb 2	Sulfuric subaqueous soil	RBAc 2	"acidic" Hyposulfidic soil
RBAa 3	Hypersulfidic cracking clay soil	RBAb 3	Hypersulfidic subaqueous clay	RBAc 3	Hyposulfidic cracking clay soil
RBAa 4	Hypersulfidic cracking clay soil	RBAb 4	Hypersulfidic subaqueous clay	RBAc 4	Hyposulfidic cracking clay soil
RBAa 5	Hypersulfidic cracking clay soil	RBAb 5	Hypersulfidic subaqueous clay	RBAc 5	Hyposulfidic cracking clay soil
RBAa 6	Hypersulfidic cracking clay soil	RBAb 6	Hypersulfidic subaqueous clay	RBAc 6	Hyposulfidic cracking clay soil
RBAa 7	Hypersulfidic cracking clay soil	RBAb 7	Hypersulfidic subaqueous clay	RBAc 7	Hyposulfidic cracking clay soil
RBAa 8	Hypersulfidic organic soil	RBAb 8	Hypersulfidic subaqueous organic soil	RBAc 8	Hyposulfidic organic soil

[1]. Sampling location label used in previously published works (Thomas et al. 2011)
[2.] Sampling location label used in previously published works (Fitzpatrick, personal communication)
[3.] Acid sulfate location label used in this paper
[4.] Acid sulfate soil profile classification (soil Identification key) used in Australia (Fitzpatrick 2013; Fitzpatrick et al. 2008)

Table 3-5: Soil classification in accordance with Soil Taxonomy for soils sampled previously (23rd May 2008 and 3rd October 2008) and in the current investigation (2nd September, 2013)

[1]Dry on 23rd May 2008 (a)		[2]Reflooded on 3rd October 2008 (b)		[3]Dry on 2nd September 2013 (c)	
Profile No	Soil Taxonomy[4]	Profile No	Soil Taxonomy[4]	Profile No	Soil Taxonomy[4]
RBAa 1	Typic Sulfaquept	RBAb 1	[5]Typic Sulfowassept	RBAc 1	Typic Sulfaquept
RBAa 2	Typic Sulfaquept	RBAb 2	Typic Sulfowassept	RBAc 2	Typic Hydraquent
RBAa 3	Typic Sulfaquent	RBAb 3	Typic Sulfiwassent	RBAc 3	Typic Hydraquent
RBAa 4	Typic Sulfaquent	RBAb 4	Typic Sulfiwassent	RBAc 4	Typic Hydraquent
RBAa 5	Typic Sulfaquent	RBAb 5	Typic Sulfiwassent	RBAc 5	Typic Hydraquent
RBAa 6	Typic Sulfaquent	RBAb 6	Aeric Sulfiwassents	RBAc 6	Typic Hydraquent
RBAa 7	Typic Sulfaquent	RBAb 7	Aeric Sulfiwassents	RBAc 7	Typic Hydraquent
RBAa 8	Typic Sulfihemists	RBAb 8	Fibric Sulfiwassists	RBAc 8	Hydric Haplofibrist

[1]. Sampling location label used in previously published works (Thomas et al. 2011)
[2.] Sampling location label used in previously published works (Fitzpatrick, personal communication)
[3.] Acid sulfate location label used in this paper
[4]. Acid sulfate soil profile classification used by Soil Survey Staff (2014)
5. Typic Sulfowassept is new subgroup proposal to Soil Taxonomy. A new proposal is currently being submitted by Fitzpatrick et al. (2015) to USDA-NRCS to consider for inclusion in revised versions of the US Keys to Soil Taxonomy: (i) Inceptisol Suborder: Sulfowassepts, (ii) Inceptisol Great Groups & Subgroups for Typic Sulfowassept.

4. RAPID METAL RELEASE

Summary

Rapid metal release tests were undertaken on 4 samples from Banrock Station wetlands using a water extraction to determine the potential mobility and bioavailability of nutrients, metals and metalloids.

The soil extractions varied in water quality in terms of the master variables pH and Eh, as well as SEC. Only one sample had a low pH. They were chemically of mixed cation type, but with SO_4 dominating as the major anion. High SO_4/Cl ratios suggest an additional source of SO_4 to that derived from cyclic salts, either pyrite oxidation or gypsum dissolution.

A number of potential contaminants, including metals and reduced N-species were present in the extractions including Al, As, Be, Co, Cr, Cu, Ni, NH_4, Pb, U and Zn, but some metals are probably present as colloidal particles in two of the samples. The main control on high metal mobilisation is likely to be pH. The simple water extractions suggest that contaminant mobilisation in the soils may be an issue following rewetting of the ponds or during any disturbance, particularly if the soils become acidic. Where oxidation occurs without acidification, metal release is likely to be limited, but species mobile at high pH, e.g. As which forms oxyanions, should be monitored.

4.1 Introduction

The pH and Eh of soil porewater and surface water are the most important master variables controlling the solubility and sorption characteristics of metals and metalloid contaminants. In acid sulfate soil areas, pH is typically the main control on metal cation mobility with high concentrations being common especially at pH < ca. 4.5 (Shand *et al.* 2010; Simpson *et al.* 2010). Predicting the quantities of contaminant release is difficult, especially in oxidised soils, because contaminants are often associated with a range of mineral fractions as well as organic matter (Shand *et al.* 2012).

A number of soil samples were selected to determine the potential availability of nutrients and metal/metalloid contaminants from the Banrock Station wetland soils. This was undertaken as a dilute water extraction based on the methodology of Simpson *et al.* (2010), with samples selected from the ponds from a range of soil depths. The technique was designed to simulate the rewetting of dried soils or to assess the potential mobility of contaminants in a weak (water) extract. A total of 4 soil samples from 3 profiles were selected for these tests and analyses: samples RBAc 01.5, 01.7, 03.2 and 07.2. Details are provided in Sections 2 and 3 above.

4.2 Methodology and analytical techniques

Soil samples were air dried at 40 ^{0}C, and 25 g of each sample was weighed into clean acid-washed 250 mL Nalgene extraction bottles and resuspended in 250 mL of deionised water for a period of 24 hours in an end over shaker. Water blanks were run with the batch extraction to monitor water quality throughout the experiment. After 1 hour, a 25 ml aliquot was sampled to measure water quality at the start of the extraction, with the measurements repeated at the end of extraction (24 hours). Water quality measurements included dissolved

oxygen, pH, alkalinity/acidity, redox potential (Eh), and specific electrical conductance (SEC).

At the completion of the extraction phase, the samples were centrifuged to settle solids and allow the supernatant to be filtered for chemical analysis using Millex 0.45 micron PVDF syringe filters. Analyses for a suite of major and trace elements including metals, metalloids nutrients were run on the filtered water extracts to provide a detailed profile of each sample's chemistry.

Nitrogen species, Cl and PO_4 were analysed by colorimetric analysis using an Auto Analyser; Br, F and SO_4 by ion chromatography; and NPOC by a TOC Analyser in the Adelaide Waite laboratories at CSIRO. For cation analyses, water samples were transported to the CSIRO laboratory at Lucas Heights, Sydney by courier and analysed for a range of major and trace elements.

A subsample of each water sample was taken for direct metals analysis using an inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Varian730 ES or Agilent 700 series) fitted with an argon sheath torch using in-house method C-229 and operating instructions recommended by the manufacturer. High salinity samples were analysed using the method of standard additions for the determination of aluminium, iron, manganese and zinc. Calcium, sodium, potassium, magnesium, sulfur and strontium were analysed by diluting the sample then analysing against matrix matched calibration standards prepared from certified stock solutions (Accustandard, USA). The remaining elements were analysed by inductively coupled plasma-mass spectrometry (ICP-MS) (Aglient 7500 CE) using in-house method C-209 and operating instructions recommended by the manufacturer. Samples were diluted and analysed against matrix matched standards which were prepared from a set of three multi-element stock solutions (High Purity Standards, USA).

4.3 Soil extraction data

The water samples had a range of pH from 3.94 (RBAc 01.7) to 8.20 (RBAc 03.2). A summary of selected parameters and solute concentrations is shown on (Table 4-1). The pH of the soil extractions correlated negatively with alkalinity (r^2=0.97) and Eh (r^2=0.91). Higher SEC was found in the low and high pH samples (Figure 4-1). There is, thus, a large degree of heterogeneity in the soils in terms of these master variables.

The extraction waters are plotted on a Piper Plot which displays the relative proportions of major cations and anions (Figure 4-2). Cations vary from Ca dominant in RBAc 03.2 to Na dominant in RBAc 01.5. The anions, however, are dominated by SO_4 for all samples, with the waters varying from Ca-SO_4 type to Na-SO_4-type. The Ca-SO_4 type waters comprised the highest and lowest pH samples, but all had very high SO_4/Cl ratio, much higher than seawater indicating a non-cyclic salt addition of sulfate (Figure 4-1). This is likely to be due to sulfide oxidation (cause of low pH in one sample) or possibly gypsum dissolution (which may itself be derived from the oxidation of pyrite in a highly buffered system:

$$H_2SO_4 + CaCO_3 + H_2O \rightarrow CaSO_4.2H_2O + CO_2$$
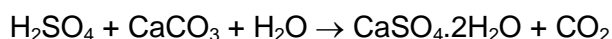
Nitrogen species and phosphate are shown on Figure 4-3. Ammonium concentrations were above detection limit in two samples with a maximum of 0.8 mg l^{-1}. Oxidised N-species were typically low compared to total N, suggesting that most of the dissolved N was present as organic bound N. This is consistent with high DOC present in the samples.

The pH control for many metals, particularly the transition metals, has been well established, with high concentrations at low pH, whilst it is known that metalloids (e.g. As, Mo, Sb) form negatively charged oxyanions, which can be mobile at neutral to high pH due to limited sorption as pH increases.

Table 4-1 Concentrations of physicochemical parameters and selected solutes in Banrock Station water extractions.

Element	RBAc 01.5	RBAc 01.7	RBAc 03.2	RBAc 07.2
pH	6.23	3.93	7.66	6.18
Eh (mV)	442	538	399	414
SEC (μS cm^{-1})	0.204	0.582	0.742	0.257
Alkalinity (meq l^{-1})	0.16	-	1.05	0.13
Acidity (meq l^{-1})	-	0.68	-	-
Ca (mg l^{-1})	7	40	96	11
Mg (mg l^{-1})	8	17	20	10
K (mg l^{-1})	14	12	12	15
Na (mg l^{-1})	20	20	30	20
Cl (mg l^{-1})	8	11	13	29
SO$_4$ (mg l^{-1})	67	281	377	95
Al (μg l^{-1})	33100	398	8.9	36400
Co (μg l^{-1})	40	153	26	14
Cu (μg l^{-1})	52	29	8.0	13
Fe (μg l^{-1})	19300	250	18	20500
Mn (μg l^{-1})	252	1630	31	152
Ni (μg l^{-1})	21	38	8.3	19
W (μg l^{-1})	128	76	65	29
Zn (μg l^{-1})	89	193	22	62
SO$_4$/Cl	8.9	24	28	3.3
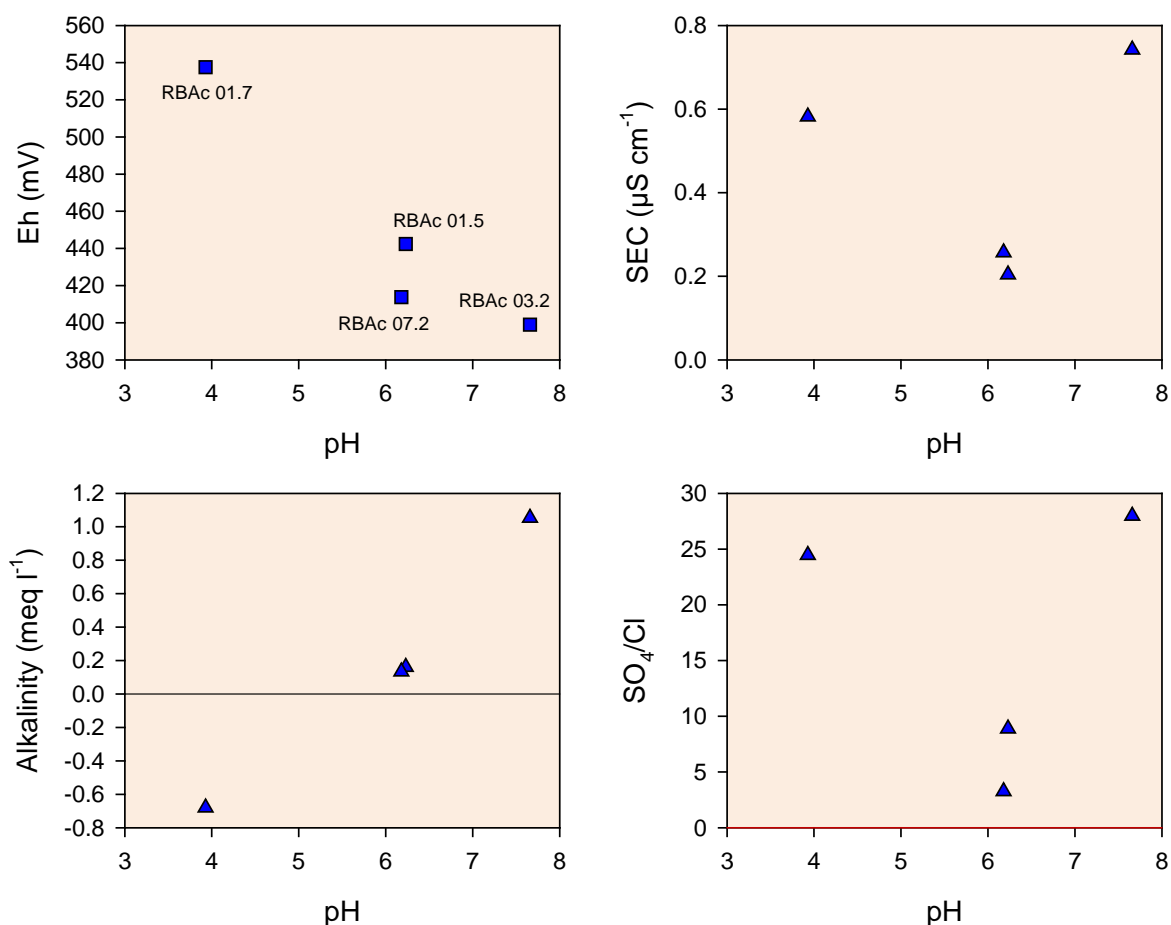
Figure 4-1 Plots of Eh, SEC and SO4/Cl ratio plotted as a function of pH. Acidity is plotted as negative alkalinity on the alkalinity plot. The SO4/Cl ratio for sweater)red line) is 0.142.

Selected trace elements are shown along with the ANZECC guideline values for 95% ecosystem protection on Figure 4-1. The dilutions used in the extraction provide only a guide to those contaminants released and soluble at this specific dilution. However, previous studies using this technique hove shown that the concentrations derived are useful as a guide to real impacts (Shand et al. 2010).

The very high Al and Fe (Table 4-1 and Figure 4-4) in the intermediate pH samples (RBAc 01.5 and 07.2) is unlikely to be due to dissolved Al, as solubility is low at the these pHs. It was noted that some samples remained cloudy even after filtering, therefore, the high Al (and Fe) is likely to be in the form of colloids that are smaller than the pore size of the industry standard filters used (0.45 µm). For these samples, elevated concentrations of several typically insoluble metals were present including Ba, Cr, Pb, Sc and the rare earth elements which are likely to be present on the colloids.

Several metals do correlate negatively with pH as commonly found in acid sulfate soil environments (Figure 4-4), including Be, Co, Mn, Ni and Zn. Arsenic (As) was present in the most acidic sample at a concentration of 9 µg l^{-1} (ANZECC guideline value of 13 or 24 µg l^{-1} for As(V) or As (III) species respectively). Uranium was present up to 1.3 µg l^{-1}, and correlated positively with pH (Figure 4-4). The following solutes were below the detection limit of analysis (detection limits in brackets µg l^{-1}): Bi (10), Cd (0.3), Eu (1), Ho (1), In (5), Ir (1), Pt (2), Re (0.1), Rh (1), Ru (0.4), Se (10), Te (10).
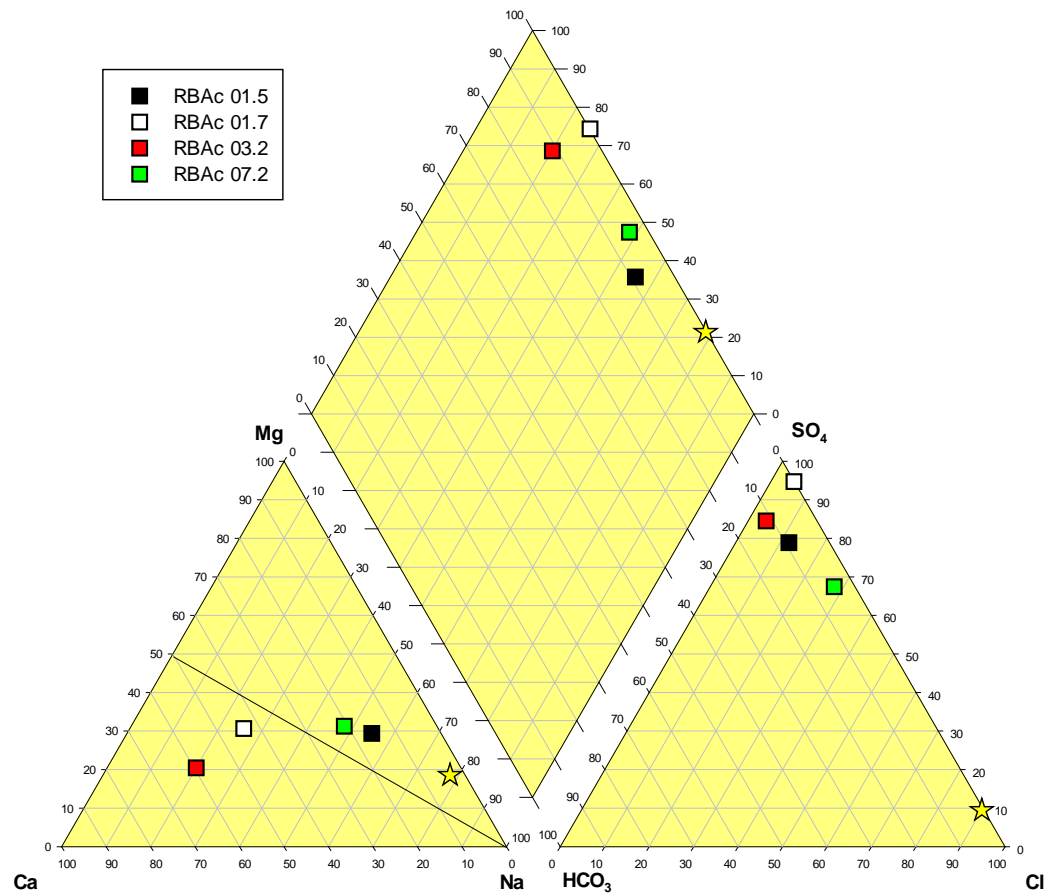
Figure 4-2 Piper plot showing the relative proportions of major elements in soil extractions. Seawater is shown for comparison (yellow star).

The simple water extractions suggest that contaminant mobilisation in the soils may be an issue for some metals and nutrients following rewetting of the ponds or during any disturbance. The data have been compared to ANZECC Guideline values only as a guide as the likely concentrations of rewetting soils will be highly scenario dependent. Some contaminants have algorithms derived to take water hardness into account (Cd, Cr(III), Cu, Pb, Zn). Sample water hardness (calculated as $[4.11 * Mg] + [2.47 * Ca]$) varies in the samples from 50 (moderate) to 319 (very hard), which also needs to be taken into account. This summary simply indicates which contaminants are likely to be present and the conditions under which they may be mobile. The effect of saline addition to the ponds has not been tested but may be significantly different in terms of what solutes are mobilised and how much is released.
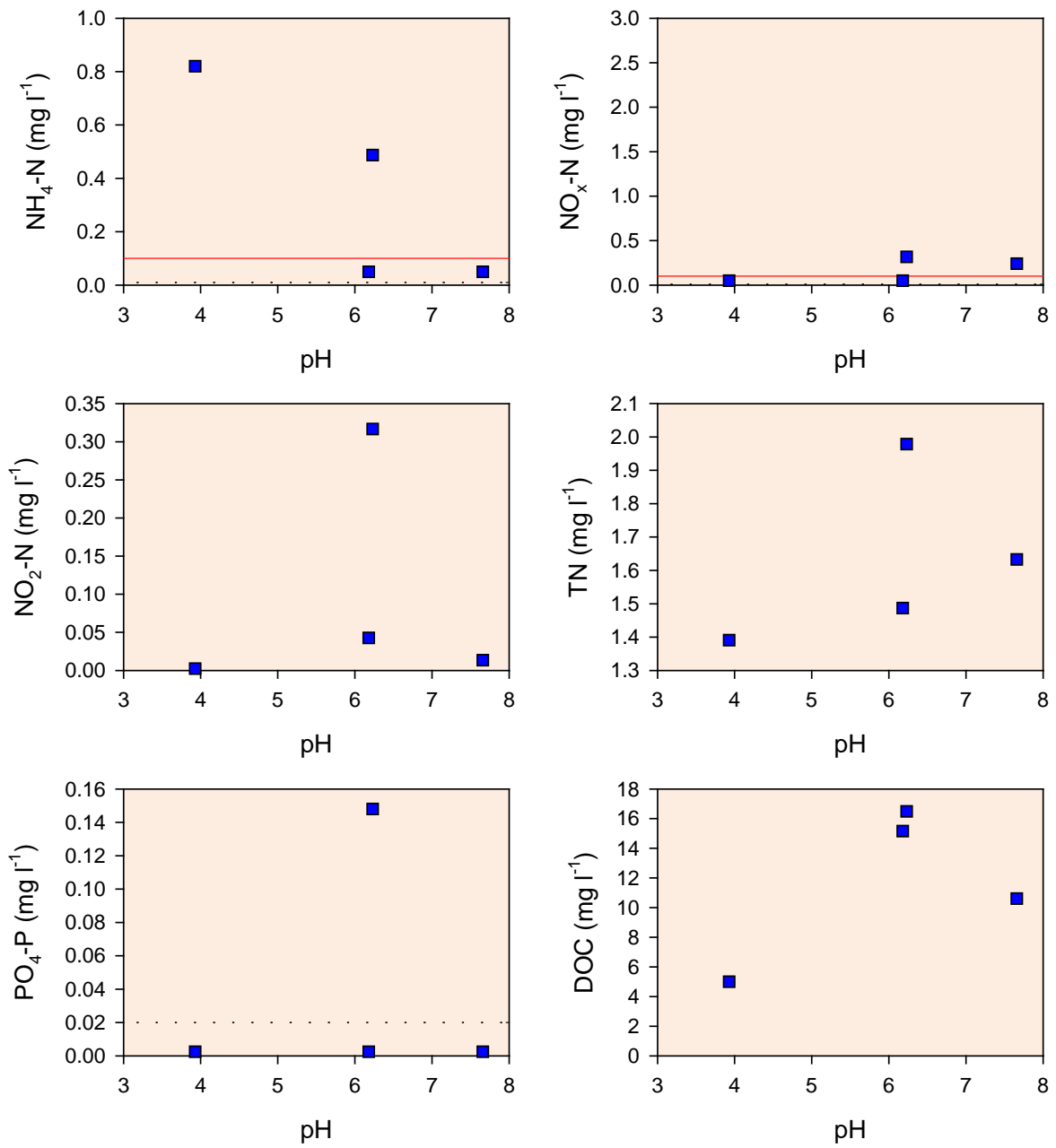
Figure 4-3 Plots of nutrient concentrations plotted as a function of sample pH. ANZECC Guideline values shown as dashed line and detection limits highlighted by red line
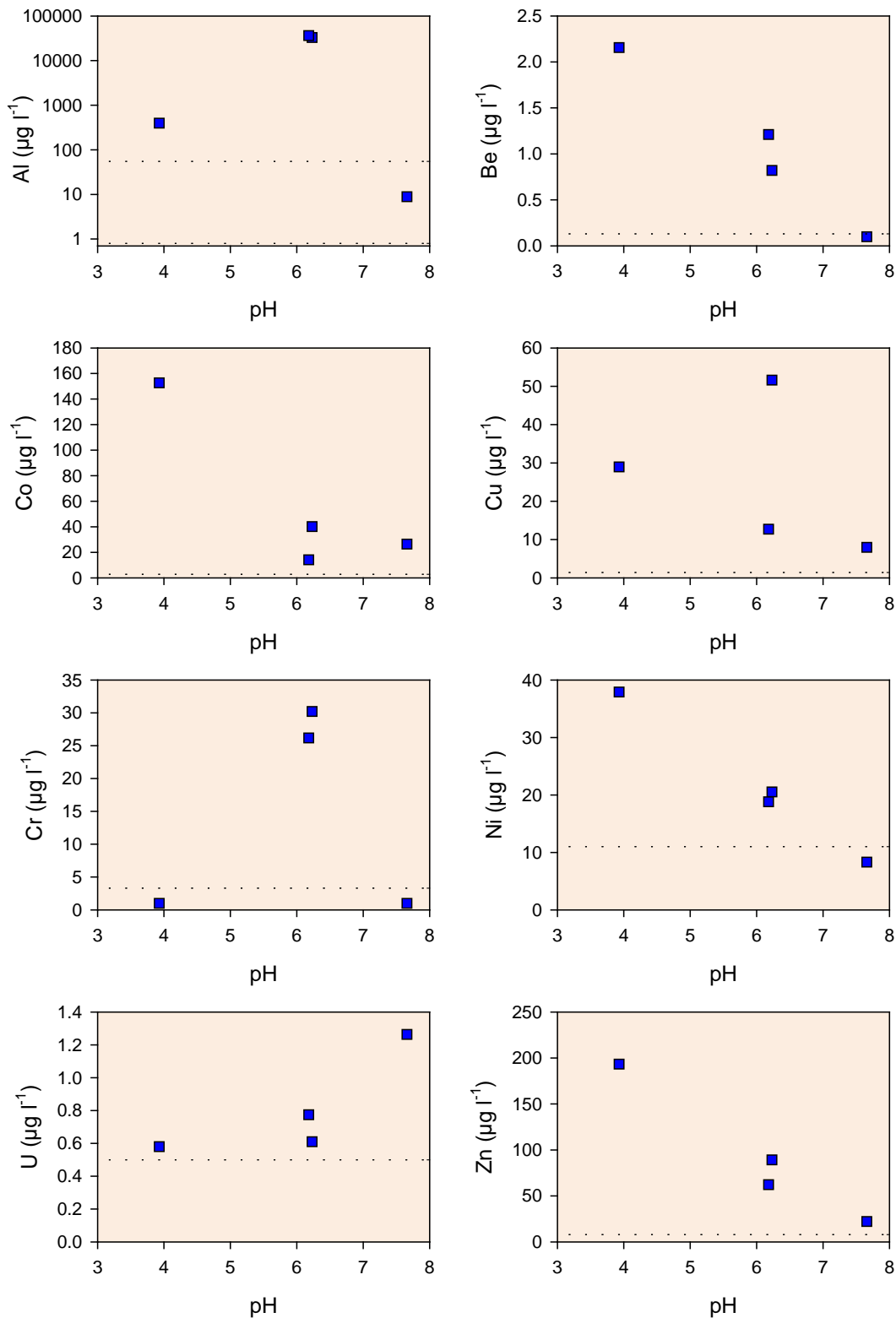
Figure 4-4 Plots of nutrient concentrations plotted as a function of sample pH. ANZECC Guideline trigger values shown as dashed line (for Al, upper line pH >6.5; lower line pH>6.5). Note log scale for Al plot.

5.   INCUBATION EXPERIMENTS TO ASSESS THE INFUENCE OF ORGANIC MATTER ADDITION

Summary

The prime objective of the incubation experiments outlined in this chapter was to assess the influence of organic matter addition on pH and redox potential under flooded conditions and subsequent pH changes during a drying period.

The results suggest that addition of plant residues can stimulate sulfate reduction during submergence and thereby increase pH. Plant residue addition at the start of the first submergence period can also result in higher pH at the end of the oxidation period and seems to further stimulate pH increase in the second submergence period. This indicates that plant residues could be used to ameliorate acid sulfate soils by first increasing and then stabilising the pH.

The promising results from the laboratory incubation experiments would need to be followed up with experiments in the field to test if addition of plant residues can ameliorate acid sulfate soils effectively and in an environmentally and economically sustainable manner.

5.1 Background

Organic matter addition may not only stimulate sulfate reduction upon re-flooding, but also minimize acidification upon oxidation of sulfidic materials by binding of protons, competition for oxygen between decomposers and sulfide oxidizers and coating of pyrite (Bronswijk et al., 1993; Bush and Sullivan, 1999; Rigby et al., 2006; Ward et al., 2010). Microbial sulfate reduction after re-saturation of sulfuric material could result in pH increase and therefore be considered as a more economical and environmentally-friendly amelioration strategy for acid sulfate soils (ASS) than applying agricultural lime.

However, microbial sulfate reduction is constrained by environmental factors such as redox conditions, availability of sulfate and organic carbon (as energy source for sulfate-reducing bacteria), and pH (most sulfate reducers are inactive at pH<5). Sulfate concentrations are usually high in terrestrial ASS that have experienced oxidation. The observation that in many subaqueous sulfuric soils, even after several years of flooding (e.g. Creeper et al., 2015; Mosley et al., 2014) pH does not increase suggests that availability of native organic matter for sulfate reducers may be low or limiting.

Management of wetlands often involves introduction of wet-dry cycles to restore ecosystem health (e.g. Banrock Station wetlands complex). Little is known about the influence of organic matter addition on sulfate reduction and acidification in wet-dry cycles, particularly with respect to organic matter composition. The aim of this study was to determine the effect of different organic matter forms on pH and redox potential under flooded/reduced conditions and on pH during the following dry/oxidised period in the three wetland soils shown in Table 5-1.

5.2 Soils

At the time of sampling, the ASS materials in the soil profile RBAc1 were classified as sulfuric, hypersulfidic and hyposulfidic materials (Sullivan et al. 2010) and the soil profile was classified as a Sulfuric soil in accordance with the Australian ASS classification key (Fitzpatrick et al. 2008; Fitzpatrick 2013) (Table 5-1). The profile was classified as a Typic Sulfaquept in accordance with Soil Taxonomy (Soil Survey Staff, 2014).

The samples collected from the sulfuric material (5-20cm), hypersulfidic material (20-30cm) and hyposulfidic material (50-65cm) were air-dried and sieved to <2 mm and used separately for each incubation experiment described below. As a consequence, they are referred to as: sulfuric soil (Soil 1), hypersulfidic soil (Soil 2) and hyposulfidic soil (Soil 3) in accordance with the Australian ASS classification key (Fitzpatrick, 2013) as shown in Table 5-1. A summary of particle size and selected chemical properties ($pH_{1:1\ H2O}$, Total organic carbon and calcium carbonate content) is shown in Table 5-2. These three ASS subtypes are representative of ASS soil occurrence in the Banrock wetland complex and in other inland wetlands in general (Fitzpatrick 2013; Fitzpatrick et al. 2009).

Table 5-1. Soil classification of acid sulfate profile and three soil subtypes used for incubation experiments

Soil Profile (*in situ*)						Soil in experiments	
Sample number[1]	Depth	Australian Acid sulfate soil classification		Soil Taxonomy		Soil Label[6]	ASS Subtype[7]
		Material[2]	ASS Subtype[3]	Horizon[4] *Material*[4]	Soil Profile[5]		
RBAc 1.4	5-20	**Sulfuric**		**Sulfuric**	Typic	Soil 1	Sulfuric soil
RBAc 1.5	20-30	**Hypersulfidic**	Sulfuric soil	*Sulfidic*	Sulfaquept	Soil 2	Hypersulfidic soil
RBAc 1.7	50-65	Hyposulfidic				Soil 3	Hyposulfidic soil

[1]Sampling location label (this report: Fitzpatrick et al. 2015) and from previous works (Fitzpatrick et al. 2009; Thomas et al. 2011)
[2]Acid sulfate soil material classification used in Australia (Sullivan et al., 2010; Isbell and the National Committee for Soils and Terrain, 2015): See Table 3-3 for soil morphology, pH incubation data and soil classification
[3]Acid sulfate soil profile classification in accordance with Australian ASS identification key (Fitzpatrick 2013; Fitzpatrick et al. 2008b)
[4]Acid sulfate soil horizon / material classification used by Soil Survey Staff (2014 (NOTE – hyposulfidic material does not qualify as sulfidic material in Soil Taxonomy)
[5]Acid sulfate soil profile classification used by Soil Survey Staff (2014)
[6]Soil label used in this chapter
[7]ASS Sub-type (Fitzpatrick 2013) after each ASS horizon or material was sampled from the soil profile and used separately for incubation experiments

The wetland became permanently inundated in 1925 after construction of lock 3 on the River Murray. However, large parts of this wetland dried during the severe drought in the last decade. As a consequence, wetland drying has oxidized the pyrite-bearing minerals in the hypersulfidic and hyposulfidic soils to sulfuric soils. To enhance its biodiversity, the wetland managers implemented wet and dry cycles with each dry and wet period lasting approximately 6 months. Several laboratory experiments were conducted on the three ASS subtypes (Table 5-1; Table 5-2). The prime objective of the laboratory experiments is to investigate the effect of organic matter addition on: (i) pH and redox potential during submergence (reflooding) and (ii) on pH in a subsequent dry period.

Table 5-2 Soil samples used in the organic matter addition and water inundation and drying experiments[1]

Soil locality name	ASS Subtype[2]	Depth	pH	Total organic C	Sand	Silt	Clay	Calcium carbonate
		cm	(1:1 H_2O)	(mg g^{-1})	%			% CaCO$_3$
Soil 1	Sulfuric	5-20	4.1	6	85	5	10	0.6
Soil 2	Hypersulfidic	20-30	5.3	8	85	0	15	0.4
Soil 3	Hyposulfidic	50-65	6.9	2	70	7	23	0.2

[1]The soils were air-dried and sieved to <2 mm.
[2]Acid sulfate soil profile classification in accordance with Australian ASS identification key (Fitzpatrick 2013; Fitzpatrick et al. 2008) (Table 5-1).

5.3 Experiment 1

Aim: Assess the influence of: (i) different forms of organic matter on sulfate reduction under flooded conditions and (ii) pH changes at 100 % water holding capacity (WHC) during the subsequent oxidation period.

The three soils were amended with four organic C sources added at a rate of 10 g C/kg soil: glucose, wheat straw, pea straw and *Phragmites* litter collected in the Banrock wetland complex (Table 5-2). The residues were dried and ground to particle size < 2 mm. A control without organic C addition was included.

There were three periods: (i) a wet (submerged or inundation) period of 18 weeks, (ii) followed by a drying or oxidation period of 16 weeks and (iii) a second submergence period, which is ongoing and will be completed when pH and redox are stable.

To start, the first submergence or inundation period, 30 g dry soil was added to 70 ml plastic containers. After mixing the organic C forms into the soils, reverse osmosis water was added until the soil surface was covered by approximately 2 cm of water. The lids of the containers were screwed on tightly to minimize entry of air. Soil pH and redox potential were measured every two weeks. After 18 weeks submergence, the soils were dried in a fan-forced oven to 100% of maximum water-holding capacity. This water content was maintained during the 11-week oxidation period. The pH was measured every 2 weeks during the oxidation period. At the end of the oxidation period, the soils were submerged again and the second submergence period was carried out as described for the first submergence period. The second wet period is ongoing.

5.3.1 Results

During the submergence period, the pH increased (sulfuric soil and hypersulfidic soil) or remained the same (hypersulfidic soil) only in soils amended with wheat and pea straw and *Phragmites* litter (Figure 5-1). In contrast, the pH decreased in unamended soils or those with glucose additions. After 18 weeks, the pH in plant residue-amended soils ranged between 6 and 7 whereas the unamended soils and glucose-amended soils had a pH of 4-5. The redox potential of amended soils decreased sharply in the first 2 weeks whereas it remained the same in unamended soils (Figure 5-1). Later the redox potential then remained low or only slightly increased in soils amended with plant residues. In glucose-amended soils, the redox potential increased after 6-8 weeks. At the end of the submergence period, the concentration of acid volatile sulfur (AVS), which is a measure of monosulfides was higher in the hypersulfidic soil (soil 2) than in the sulfuric soil (Figure 5-2). In all soils, the AVS concentration was low in the unamended control and soil amended with glucose and *Phragmites* litter. Addition of wheat or pea straw increased the AVS concentration, particularly in the sulfuric soil (soil 1).

At the start of the oxidation period, the pH was higher in plant residue-amended soils than unamended and glucose-amended soils (Figure 5-3). The pH decreased in all soils during the oxidation period, but the decrease was small in unamended and glucose-amended soils. In plant residue-amended soils, the pH decreased less in soils with pea straw than with *Phragmites* litter. At the end of the oxidation period, the pH plant residue-amended soils was highest in pea straw-amended soils and lowest in soils with *Phragmites*. However, the pH in all plant-residue amended soils was higher than in unamended soils and those with glucose.

5.3.2 Conclusion

Addition of organic C as plant residues stimulates sulfate reduction and therefore pH increase during submergence. Pea straw (low C/N ratio) was more effective than Phragmites

litter. The maintenance of a low redox potential indicates that the plant residues are decomposed slowly throughout the submergence period providing energy to sulfate reducers and thereby leading to pH increase during submergence. Glucose, which is soluble and readily available does not increase sulfate reduction compared to the unamended soil. The strong decrease in redox potential at the start of the submergence period shows that glucose is utilised by microbes, which consume oxygen, but the following increase in redox potential indicates that glucose C is rapidly depleted and oxygen is no longer consumed. We assume that sulfate reducers have lower growth rates than other microbes active under submerged conditions. Glucose C is rapidly depleted by fast-growing microbes leaving insufficient organic C for sulfate reducers.

Figure 5-1: Soil pH and redox potential for sulfuric soil (soil 1), hypersulfidic soil (soil 2) and hyposulfidic soil (soil 3) and unamended (control) or amended soils with wheat straw (WS), pea straw (PS), glucose (GL) and *Phragmites* litter (pH) during 18 weeks submergence (n=4).

Therefore sulfate reducers need a steady supply of organic C. The pH decrease during the oxidation period was greater in soils with plant residue addition than in unamended soils or amended with glucose. The pH at the end of the oxidation period is still higher than in unamended soils or amended soils with glucose because at the end of the submergence period, submergence was higher in soils with plant residues.

Figure 5-2 Acid volatile sulfur concentration for sulfuric soil (soil 1), hypersulfidic soil (soil 2) and hyposulfidic soil (soil 3) and unamended (control) or amended soils with wheat straw (WS), pea straw (PS), glucose (GL) and *Phragmites* litter (pH) after 18 weeks submergence (n=4)

Figure 5-3 Soil pH for sulfuric soil (soil 1), hypersulfidic soil (soil 2) and hyposulfidic soil (soil 3) and unamended (control) or amended soils with wheat straw, pea straw, *Phragmites* litter glucose during 11 weeks oxidation at 100% of maximum water holding capacity (n=4).

5.4 Experiment 2

This laboratory experiment consisted of the following three successive periods: wet-dry-wet. Thirty grams of air-dried soils were placed into 70 mL plastic containers. Mature wheat straw (total organic C 423 g kg^{-1}, C/N 108, ANC 0.3 % CaCO$_3$ equivalent, finely ground and sieved to < 2 mm) was added to the soils at the rate of 10 g C kg^{-1} of soil and mixed thoroughly. Soil without addition of wheat straw was used as a control.

To initiate the first wet period, reverse osmosis water was added first to saturate the soils and the soils were mixed thoroughly with the water. Then more water was added so that the soil surface was covered with a 2-cm thick water layer. The vials were closed and the lid

screwed on tightly to minimize entry of air. The water layer was maintained throughout the wet period by adding water if required. The containers were incubated in the dark at 25 $^\circ$ C; pH and redox potential were measured every 2 weeks. After 10 weeks, when the pH was stable for about 4 weeks, the overlying water was removed to start the dry period. The open vials were placed in a fan-forced oven at 30 $^\circ$ C and the soils dried to 100, 80, 60 or 40% of maximum water holding capacity. After reaching the desired water content, the vials were removed from the oven and incubated at 25 $^\circ$ C in the dark with lids loose to allow sufficient air exchange. During the dry period, the water content was maintained by weight, pH was measured every two week. After the pH had been stable for 2-4 weeks which occurred after 10 weeks, the second wet period was initiated by adding water and mixing as described above for the first wet period. This second wet period is ongoing.

5.4.1 Results

First wet period

The initial pH of the hyposulfidic soil (soil 3) (pH 7) was higher than that of the sulfuric soil (soil 1) (pH 4.1) and hypersulfidic soil (soil 2) (pH 4.5) (Figure 5-4). The pH of the unamended soils decreased over the 10 weeks of the first submergence period. This decrease was greater in the hyposulfidic soil (about 1 unit) than in the sulfuric and hypersulfidic soils (about 0.5 units). The pH of the amended sulfuric and hypersulfidic soils increased during the wet period by about 1.5 units to pH 6. The increase was gradual in the sulphuric soil but in the hypersulfidic soil the pH increased in the first 2 weeks, then remained stable until week 6 after which it increased more strongly to week 10. The pH of the amended hyposulfidic soil was similar at the start and the end of the wet period, but it changed over time. The pH decreased by about 1 unit in the first 2 weeks and then increased by 1 unit to week 6 after which it remained stable.

The redox potential of the unamended soils at the end of the wet period was about 100 mV higher than at the start (Figure 5-4). In the sulfuric soil, the redox potential steadily increased during the wet period, but in the hypersulfidic soil, it decreased in the first 2 weeks followed by a steady increase until week 10. The redox potential of the hyposulfidic soil fluctuated, increasing in the first 4 weeks, decreasing between weeks 6 and 8 and then increasing again. At the end of the wet period, the redox potential was lower in the hyposulfidic soil (200 mV) than in the sulfuric and hypersulfidic soils (about 300 mV). The redox potential of the amended soils decreased strongly in the first 2 weeks to about -250 mV and increased again from week 4 to week 10 when it was about -120 mV.

The AVS concentration was higher in the hypersulfidic soil than in the other two soils (Figure 5-4). Wheat straw addition increased the AVS concentration 2-fold in the sulfuric and hyposulfidic soils, but only by about 25% in the hypersulfidic soil.

Dry period

At a given percentage of WHC, the air-filled pore space was greatest in the sulfuric soil and smallest in the hyposulfidic soil. For example, at 80% WHC, air-filled pore space was 70% in the sulfuric soil, 47% in the hypersulfidic soil but only 27% in the hyposulfidic soil. Approximately half of the pore space was air-filled at 60% WHC in the hyposulfidic 3 and 80% WHC in the hypersulfidic soil. Addition of wheat straw did not influence air-filled porosity. The percentage air-filled pores increased with decreasing water content, with the strongest increase in the hyposulfidic soil where the percentage air-filled pores increased about 6-fold from 100 to 40% WHC whereas it increased only by about 30% in the sulfuric soil. 1.
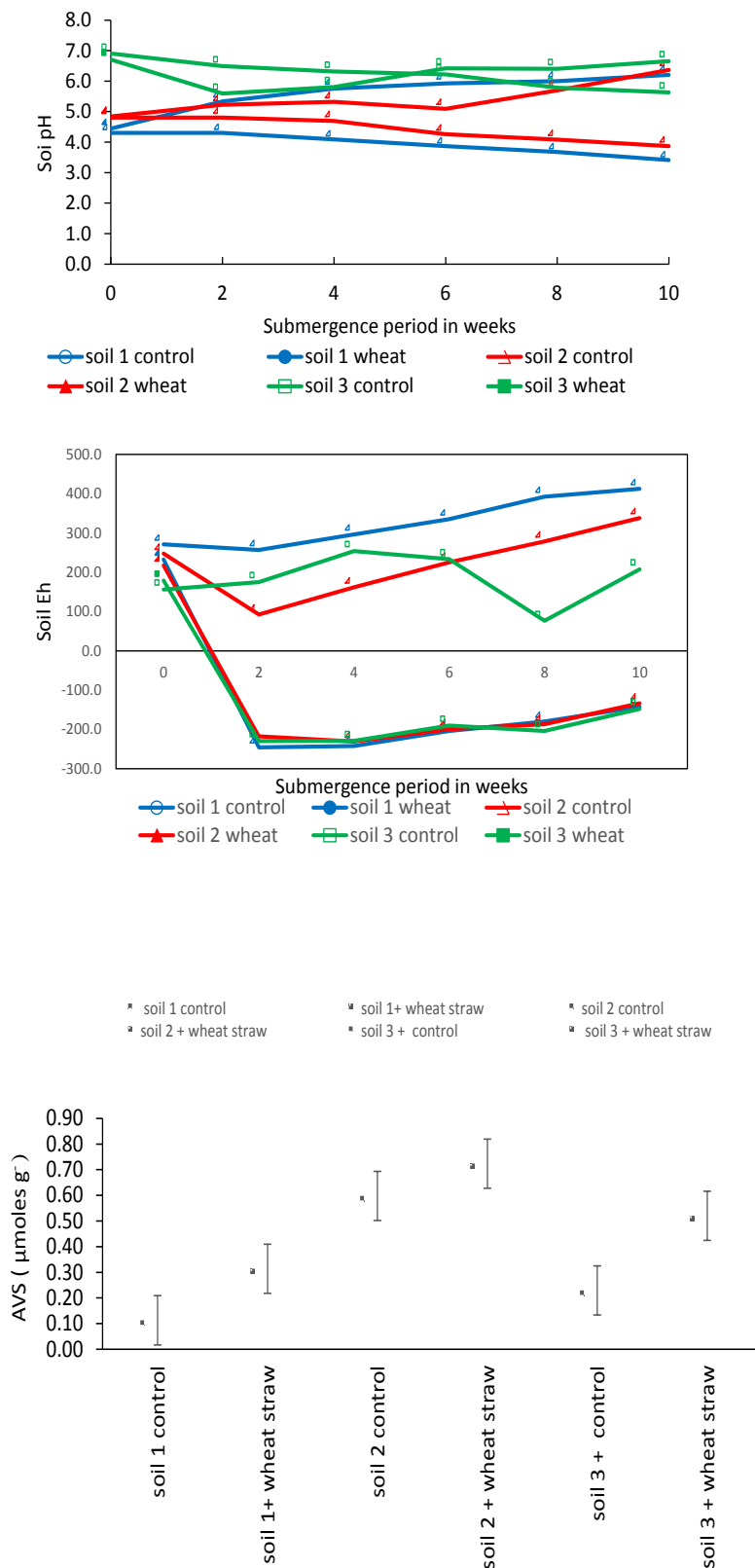
Figure 5-4 Soil pH, redox potential for the sulfuric soil (soil 1), hypersulfidic soil (soil 2) and hyposulfidic soil (soil 3) and unamended (control) or amended soils with wheat straw (WS) during 10 weeks submergence and acid volatile sulfur concentration at the end of the first submergence period (n=4).

The initial pH was higher in the amended soils (pH 6-7) than in the unamended soils (pH 4-6.5, Figure 5-5) with greater differences in the sulfuric and hypersulfidic soil

soils than in the hyposulfidic soil. The initial pH differed among adjusted water contents by 0.5 to 1 pH units being higher at the lower % WHC than at 80 or 100% WHC. The pH decrease during the oxidation period was greater in the amended (1-2.5 units) than the unamended soils (0.5-1 units). In the amended soils, the pH decrease was greatest in soil 2 and least in soil 3. The pH deceased gradually over the first7-8 weeks and then remained stable until week 10 with some fluctuations over time. In all soils with or without wheat amendment, the pH decline in the oxidation period was greater at 100 or 80% WHC than at 40% WHC. The differences among water contents were greater in amended than in unamended soils. At the end of the oxidation period, the pH was 0.5 to 1 unit higher in the amended soils in the treatment incubated at 40% WHC than at the other water contents, but there were no differences in pH among water contents in the 7-8 weeks and then remained stable until week 10 with some fluctuations over time. In all soils and without or with wheat amendment, the pH decline in the oxidation period was greater at 100 or 80% WHC than at 40% WHC. The differences among water contents were greater in amended than in unamended soils. At the end of the oxidation period, the pH was 0.5 to 1 unit higher in the amended soils in the treatment incubated at 40% WHC than at the other water contents, but there were no differences in pH among water contents in the unamended soils.

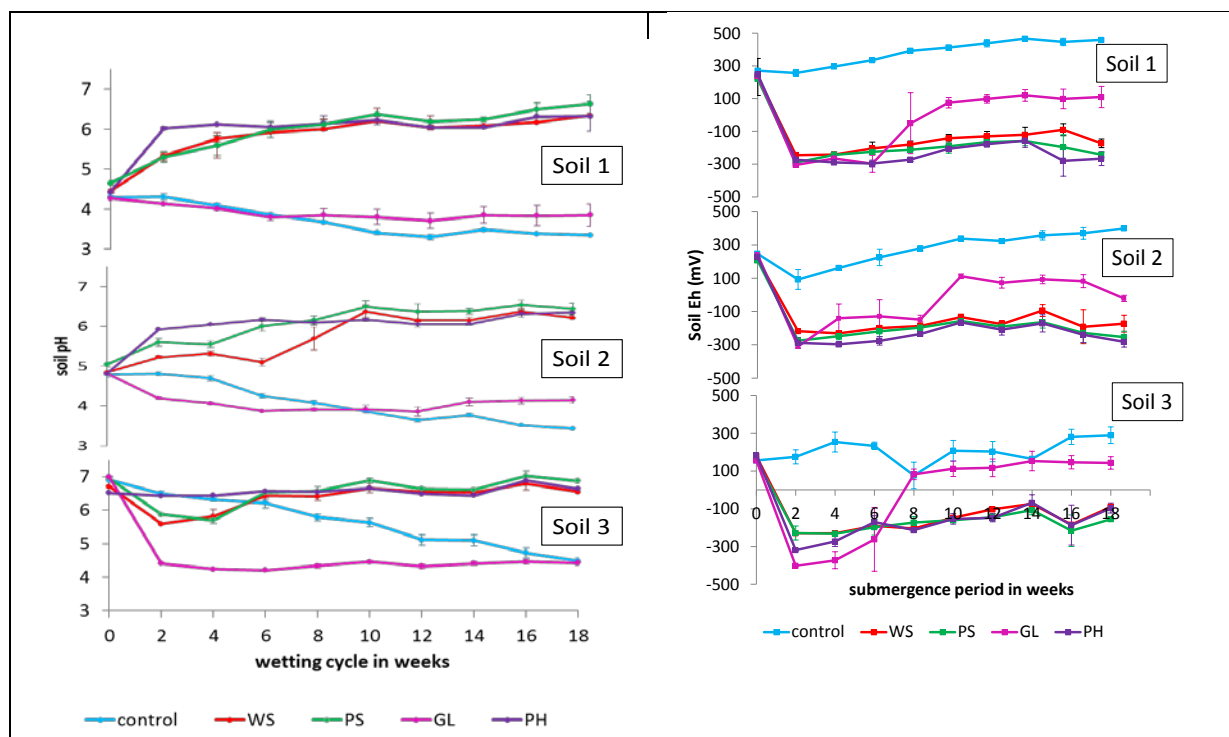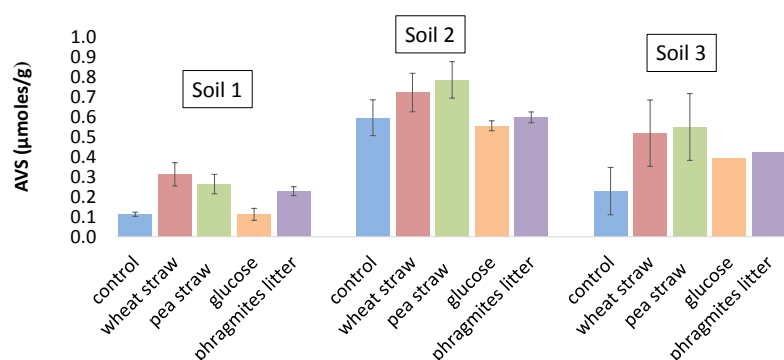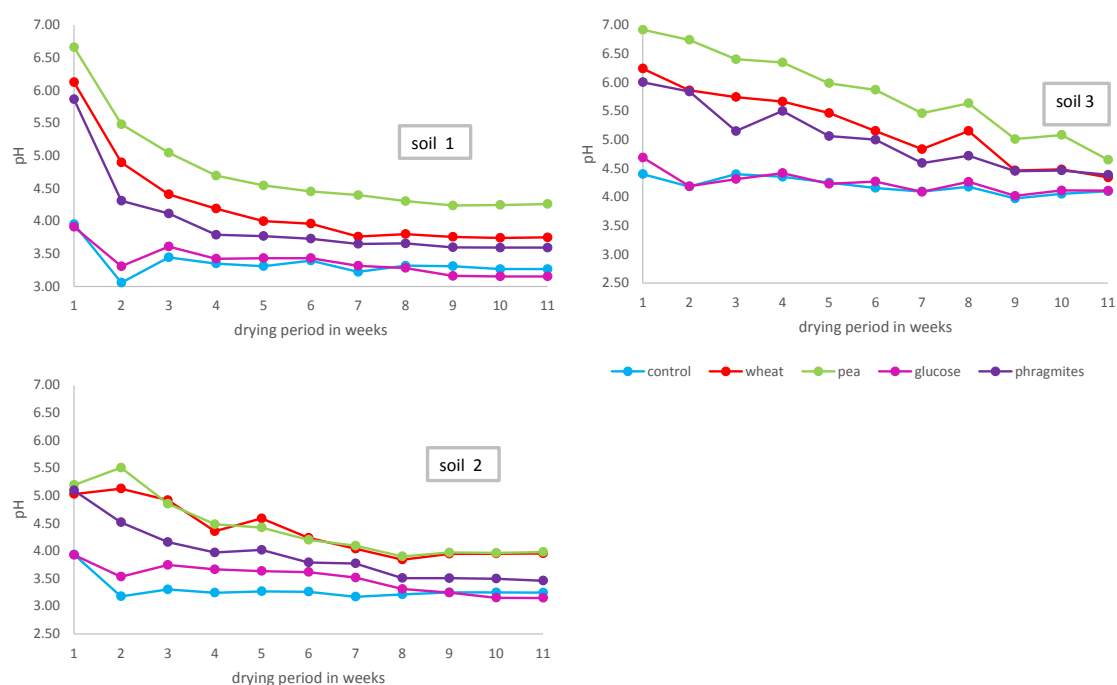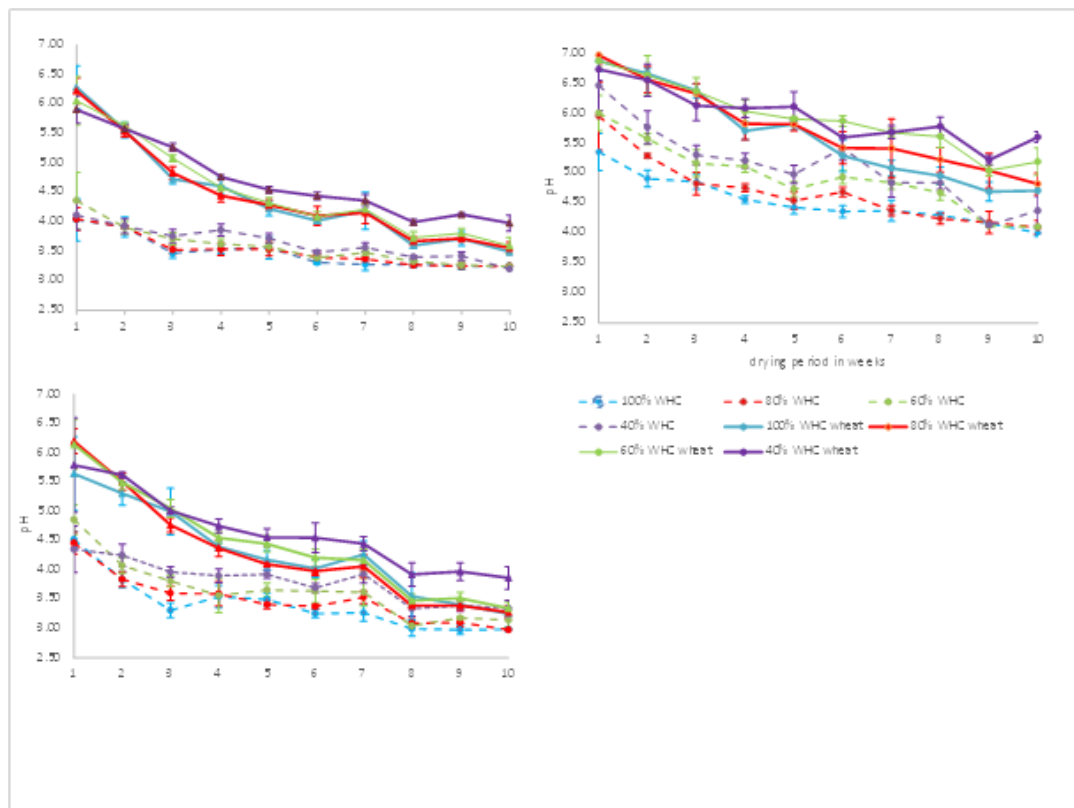Figure 5-5 Soil pH of sulfuric soil (soil 1), hypersulfidic soil (soil 2) and hyposulfidic soil (soil 3) and unamended (control) or amended soils with wheat straw (WS) during 10 weeks oxidation at 40, 60, 80 and 100% of maximum water holding capacity (n=4).

Second wet period

At the start of the second submergence period, the pH in amended soils was highest in soils incubated at 40% WHC during the oxidation period (Figure 5-6). In the submergence period, the pH remained low in the unamended soils. The pH increased in amended sulfuric and hyposulfidic soils, but in the hypersulfidic soil the pH only increased in soil that was maintained at 40% WHC during the oxidation

period. The effect of the water content during the previous oxidation period on pH changes in amended soils during the submergence period varied among soils. In the sulfuric soil, the pH increase in amended soils in the first 6 weeks was greatest in soil incubated in the oxidation period at 40% WHC and the pH remained highest until week 14. The pH increase was slower in soils incubated in the oxidation period at 80 and 100% WHC. In the amended hypersulfidic soil, the pH only increased slightly in soils incubated in the oxidation period at 40% WHC, but did not change in the other treatments. In the hyposulfidic soil, the pH increased more strongly in amended soils incubated in the oxidation period at 60, 80 and 100% WHC than in that incubated at 40% WHC. In week 14, the pH was similar in all treatments in amended soil.
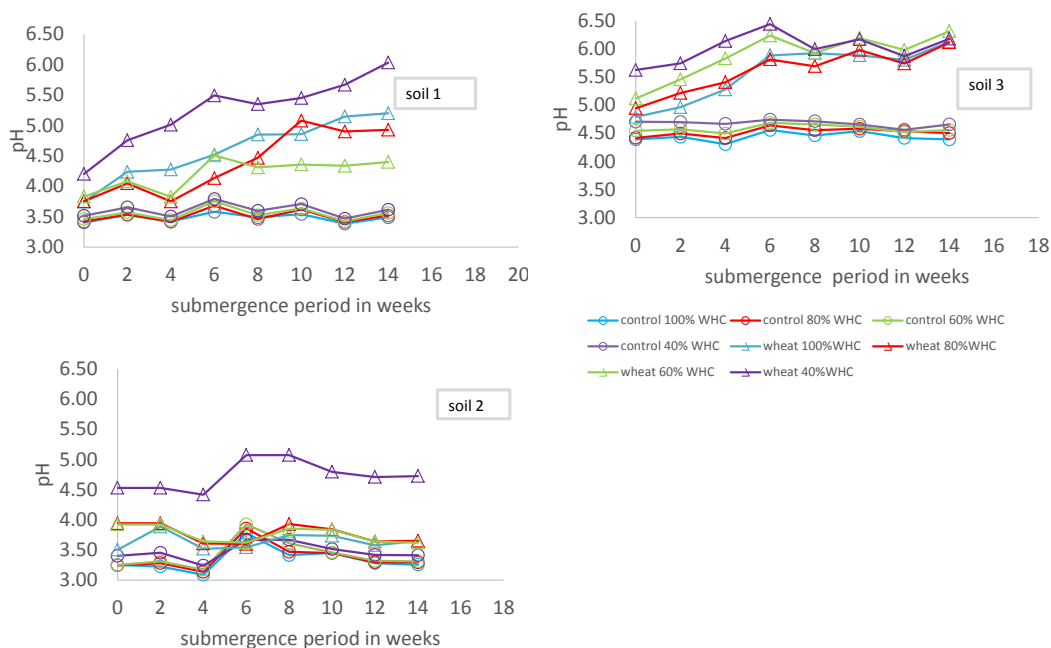
Figure 5-6 Soil pH for sulfuric soil (soil 1), hypersulfidic soil (soil 2) and hyposulfidic soil (soil 3) and unamended (control) or amended soils with wheat straw (WS) during 14 weeks under submergence after oxidation at 40, 60, 80 and 100% of maximum water holding capacity (n=4)

5.4.2 Conclusion

The second experiment confirmed that plant-residue addition stimulates sulfate reduction and therefore pH increase during submergence. As in the first experiment, the pH decrease in the oxidation period was greater in plant residue-amended soils than in unamended soils. However, because of the combination of acidity sources and buffering capacities at the start of the oxidation period, the pH at the end of oxidation period was still higher in plant residue-amended soils. The pH decrease in amended soils during the oxidation period was greater at higher water contents (80 or 100% WHC) than at 40% WHC. We assume that the higher water content at 80 or 100% WHC allowed sufficient aeration of the soils to stimulate sulfur oxidation but also provided sufficient water for microbial activity. In contrast, the rapid drying to 40% WHC at the start of the oxidation period is likely to limit water availability to microbes. Therefore, although oxygen supply was high, sulfide oxidation was limited by low water availability.

Further incubation experiments are needed to investigate if this effect is also observed in other acid sulfate soils.

5.5 Implications for wetlands

The results suggest that addition of plant residues can stimulate sulfate reduction during submergence and thereby increase the pH. Plant residue addition at the start of the first submergence period can also result in higher pH values at the end of the oxidation period and seems to further stimulate pH increase in the second submergence period. These experiments indicate that plant residues could ameliorate acidity in acid sulfate soils with sulfuric material (sulfuric soils) by first increasing and then stabilising the pH.

The promising results from the laboratory incubation experiments would need to be followed up with experiments in the field to test if addition of plant residues can ameliorate the extreme acidity in sulfuric soils (pH <4) effectively and in an environmentally and economically sustainable manner.

6. SOIL-REGOLITH HYDRO-TOPOSEQUENCE MODELS TO EXPLAIN AND PREDICT CHANGES IN SOILS OVER TIME AND SPACE

A sequence of ten soil-regolith hydro-toposequence models in the form of cross-sections were constructed to describe, explain and help predict the spatial and temporal heterogeneity of: (i) acid sulfate soil properties comprising a range of ASS materials and Subtypes, (ii) near surface features such as salt efflorescences, cracks and surface water ponding, (iii) organic-rich layers derived from *phragmites australis,* and sandy layers, which occur mainly on the edge of the wetland complex.

These models also help to visualise the temporal changes in soil morphology and soil chemical data; and illustrate the complexities and importance of understanding specific sites to assess:

- detailed behaviour (changes and/or stability) and implications of the various ASS materials (i.e. sulfuric, hypersulfidic, hyposulfidic and monosulfidic),
- deep features in soil horizons and layers (organic-rich, clayey and sandy layers)
- shallow features (i.e. salt efflorescences & wet/dry monosulfidic material)
- surface water ponding
- temporal changes in acid sulfate soil transformations from: (i) before 1880s (with partial drying and wetting/flushing cycles), (ii) during the 1880s to 1930s (mainly rewetting and part drying), (iii) during the 1930s to 1993 period (mainly wet), (iv) during the 1993 to 2006 period (partial drying and substantial rewetting), (v) during the January 2007 to June 2008 period (extreme drying), (vi) June 2008 to October 2008 period (re-wetting), (vii) during October 2008 to September 2013 period (4 cycles of wetting and drying).

Following several reflooding and part drying events between 2006 and 2013 this has: (i) not changed the nature and classification of the previously formed Sulfuric soil on the "very outer edge" (RBA-01) of the wetland complex", (ii) transformed the Sulfuric soil on the "inner edge" of the wetland complex to a Hyposulfidic soil but with low pH (4.89 and 5.42), (iii) transformed the Hypersulfidic soils in the centre of the wetland complex to Hyposulfidic soils. The progressive transformation of the "inner edge" Sulfuric soil to a Hyposulfidic soil with low pH and the Hypersulfidic soils to Hyposulfidic soils is likely due to either the oxidation of sulfides and/or an increase in the amount of carbonate (i.e. high neutralising capacity) in the near surface layers (~0-50cm).

Finally, an overall conceptual model has been constructed to explain the various pedogenic pathways and processes of soil evolution (i.e. extrinsic and intrinsic pedogenic thresholds, pedogenic rates and acid sulfate soil processes, such as the formation of monosulfidic, hypersulfidic and hyposulfidic materials).

6.1 Soil-regolith hydro-toposequence models

An understanding of the detailed behaviour of various ASS materials (e.g. sulfuric, hypersulfidic, hyposulfidic and monosulfidic) and features (e.g. surface salt efflorescences and underlying clays) in layers, horizons and deep regolith is fundamental to the successful local site characterisation of ASS in the Banrock Station Wetland Complex. Soil-regolith hydro-toposequence models help to describe and predict the spatial heterogeneity of ASS properties and processes that occur as a consequence of fundamental shifts in the "environmental equilibrium" brought about by the impact of management practices such as the building of locks and the establishment of large permanently inundated adjacent wetlands along the River

Murray and subsequent drying/draining or re-flooding. ASS in such fluctuating water environments are not stable and therefore may undergo rapid change when water levels are dropping or rising. ASS materials change depending on the water status of the soil (saturated or unsaturated), which exerts controls on whether chemical processes are oxidising or reducing, and the acid status.

Conceptual soil-regolith hydro-toposequence models in the form of cross-sections enable workers to develop and present a mechanistic understanding of complex spatial and temporal soil-regolith environments (e.g. Fritsch and Fitzpatrick 1994). The regolith is the weathered and/or unconsolidated earth material present above bedrock and includes the upper soil layers. These soil-regolith models are cross-sectional representations of soil-regolith profiles that illustrate vertical and lateral changes across wetland hydro-toposequences. They also tell a story explaining the complex soil, hydrological and biogeochemical interactions that have led to the development of an ASS problem (e.g. Fitzpatrick and Merry 2002). These models may also incorporate various management options linked to different scenarios. This can be achieved by mapping the wide distribution of acid sulfate soil materials by classification of soil types and subtypes (see Appendix 1).

To highlight the spatial heterogeneity of acid sulfate soil properties and ground/surface water interactions in the Banrock Station Wetland Complex, soil landscape cross-sections, in the form of soil-regolith toposequence models (e.g. Figure 6-1 to Figure 6-9) have been constructed to help visualise the large quantity of results from the studies discussed in the previous chapters and reports (Thomas et. al 2011; Fitzpatrick et al. 2012). In these soil-regolith models, the spatial variation of ASS materials identified are displayed in detail using a standard set of graphic symbols such as for hypersulfidic, hyposulfidic and monosulfidic materials. They also display other related features formed as a consequence of the formation of soil cracks and salt efflorescences caused as a consequence of the drying of the Banrock Station Wetland Complex between during the following periods: 1993 to 2006 period (wetting and drying), January 2007 to June 2008 period (extreme drying), June 2008 to October 2008 period (re-wetting), October 2008 to September 2013 period (4 cycles of re-wetting and drying).

In the model, the spatial extent (distribution) of the various ASS sub-types (e.g. sulfuric soils and hyposulfidic clayey soils) are indicated, which is based on numerous observations in the field from soil pits and auger samples collected.

Finally, these soil-regolith models can also be used as a framework or basis to explain some of the key intrinsic features and external drivers that render the various acid sulfate soils identified to be either relatively stable or susceptible to rapid change (Fitzpatrick et al. 2012a). For example, Fitzpatrick et al. (2012) define Extrinsic and Intrinsic pedogenic thresholds (Muhs 1984) rather loosely as a circumstance by which a "relatively modest change" in an environmental driver can cause a major change in **soil subtype** (e.g. soil evolution from a Hypersulfidic/Hyposulfidic clay soil to a Sulfuric clay soil) and soil properties.

6.2 **Generalised conceptual model illustrating sequential transformation of ASS materials under drought conditions**

A generalised conceptual model (Figure 6-1) was developed to describe three sequential drying phases during Australia's Millennium drought from 1997 to 2009 and the development of different acid sulfate soil subtypes (Fitzpatrick et al. 2008a; Fitzpatrick et al. 2008b; Fitzpatrick et al. 2009). Applying this model, Fitzpatrick et al. (2008b,c) integrated locally detailed field survey and laboratory data and used the

Australian Soil Classification (Isbell 1996) to derive 14 subtypes of ASS conforming
to the map legend of the Atlas of Australian Acid Sulfate Soils (Fitzpatrick et al.
2008c; 2010).

Under normal or natural wetting and drying cycles, build up of ASS materials is
minimised. However, since the completion of locks, weirs and barrages in the pursuit
of river regulation, sulfide minerals e.g. pyrite are likely to have accumulated in
subaqueous or submerged soils. Drought conditions between 2006 and 2010 led to
a considerable drop in water levels in the river channel, especially below Lock 1,
resulting in the progressive exposure of sulfidic material along the river bank and
wetlands in waterlogged soils, which in turn leads to the formation of sulfuric material
(pH <4) in ASS (Figure 6-1).
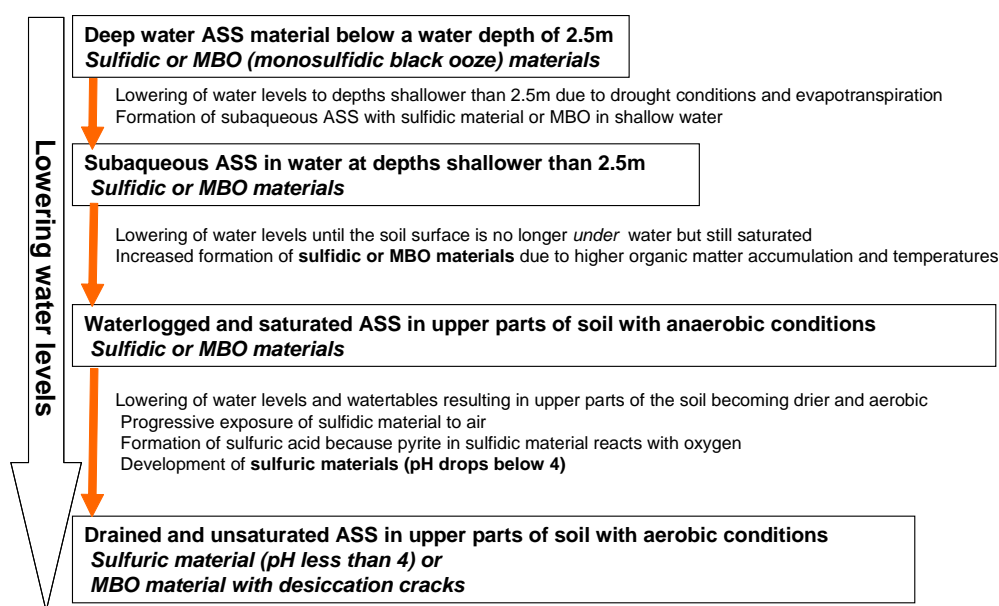
Figure 6-1 Generalised conceptual model showing the sequential transformation of four classes of ASS
due to lowering of water levels from: "Deep-water ASS" to → "Subaqueous ASS" to → "Waterlogged
and saturated ASS" (all containing sulfidic / hypersulfidic material with high sulfide concentrations and
pH>4) to → "Drained and unsaturated ASS" containing sulfuric material (pH<4) in the upper soil layers
(from Fitzpatrick et al. 2008a,b; Fitzpatrick et al. 2009)

6.3 Specific soil-regolith models for acid sulfate soil transformations over time and management

The explanatory hydro-toposequence model displayed in Figure 6-2 illustrates in
detail the spatial distribution the major horizons/layers (vertical scale exaggerated) to
display and integrate the following features:

- Topography from West to East (horizontal scale less exaggerated), including
  sluice gates on the raised river bank.
- Vegetation – vineyards and *phragmites australis* on the margins of the
  wetland.
- Colour photographs showing landscape views and detailed soil profiles
- Major soil horizons/sediment layers (vertical scale exaggerated scale): soil
  colour (greyish), texture (sands and clays) and salt efflorescences of Ca/Mg-
  sulfates salts.

- Acid sulfate soil materials (monosulfidic, hypersulfidic and hyposulfidic materails), which integrates the incubation data (16 weeks) and Acid Base Accounting data.
- Acid sulfate soil classification (e.g. Hyposulfidic clay with monosulfidic material; sulfuric soils)
- Desiccation cracks.

In summary, explanatory soil-regolith models such as shown in Figure 6-2 are constructed to characterise known sequential lateral and vertical changes to layers, horizons, ASS materials and ASS subtypes. The models also display other features such as: (i) surface layers of organic-rich material derived from *Phragmites australis*, (ii) near surface occurrences of "dry" white salt efflorescences caused by drying (droughts) and subsequent re-wetting (re-flooding). The specific soil-regolith model shown in Figure 6-2 illustrates the complex and varied distribution of ASS Subtypes in the Banrock wetland Complex in September 2013 after the lowering of water levels due to release of water as a management strategy. This soil-regolith description will change when the water flow regulator is opened to permit water flow into the wetland (rewetting).
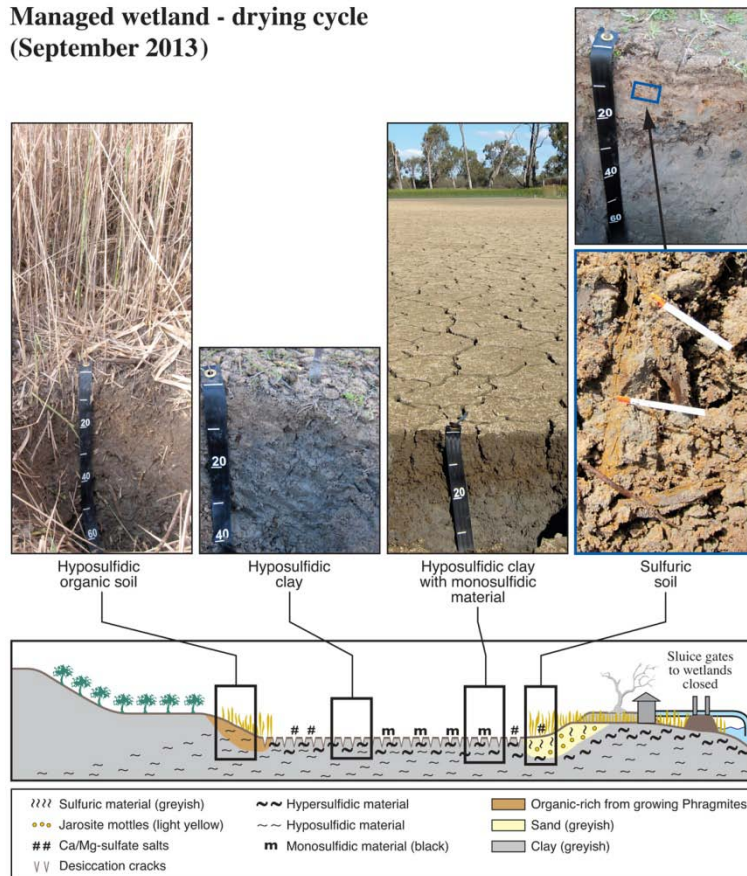
Figure 6-2: Explanatory soil-regolith model for the Banrock wetland with soil profile photographs and cross-section diagram of Acid Sulfate Soil subtypes (i.e. Sulfuric soil, Hyposulfidic organic soil, Hyposulfidic clay with monosulfidic material) sampled on 2nd September, 2013 after at least 4 cycles of re-wetting and drying of the whole wetland over a 5 year period.

The main Banrock lagoon wetland was permanently flooded between 1925, when Lock 3 was constructed, and 1993 when partial drying phases were introduced as a wetland management tool. From 1993 to September 2013 the wetland has been partially dried each winter (to introduce semi-natural wetting-drying cycles). The

wetland almost completely dried from 2007 to June 2008 (18 months) during extreme drought conditions. The wetland was re-flooded in June 2008 and a drying cycle introduced in October 2008. From October 2008 to September 2013 (~5 years; as shown in Figure 6-2) the wetland underwent at least 4 cycles of re-wetting and drying of the whole wetland.

To illustrate these sequential changes as well as the historical/geological changes (i.e. approximately 5,500 BC to 1880s period), we have constructed the following series of predictive soil-regolith models across the Banrock wetland based on the previous monitoring and findings by Fitzpatrick et al. (2009b):

(i)   Before 1880s (approximately 5,500 BC to 1880s period) with partial drying and wetting/flushing cycles.

(ii)   During the 1880s to 1930s period when the river and wetland systems were first used for navigation and irrigation (mainly rewetting and partial drying).

(iii)   During the 1930s to 1993 period when the river and wetland systems were first managed using locks (mainly saturated).

(iv)   During the 1993 to 2006 period when sluice gates were installed allowing partial drying cycles and substantial rewetting cycles.

(v)   During the January 2007 to June 2008 period (18 months) when complete (or unprecedented) drying took place caused by the Millennium drought.

(vi)   During June 2008 to October 2008 period (5 months) when complete rewetting took place.

(vii)   During October 2008 to September 2013 period (~5 years) when approximately 4 wetting (rewetting) and partial drying took place.

(i) Before the 1880s (5,500 BC to 1880s). The Banrock Wetland Complex cycled between natural wetting and flushing, and partial drying conditions in response to seasonal (i.e. winter/summer) and climatic (e.g. drought/flood) cycles occurring in the upper MDB (Figure 6-3).
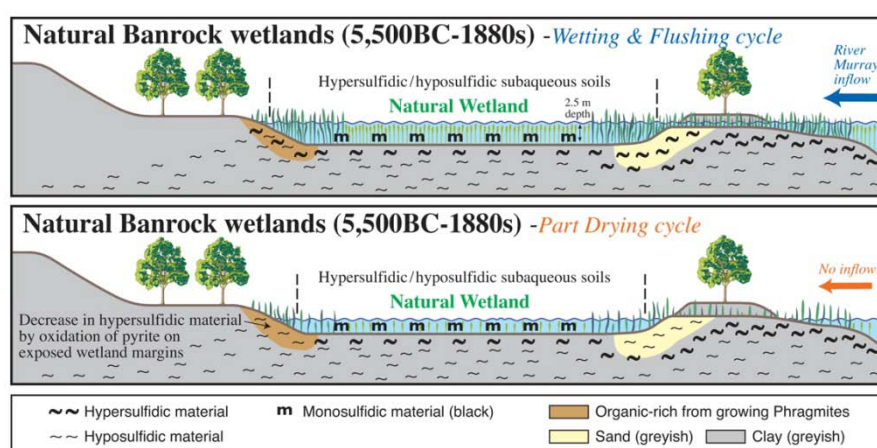
Figure 6-3: Explanatory soil-regolith models for Banrock wetland illustrating natural wetting and flushing (upper panel), and partial drying (lower panel) cycle conditions during pre-colonial times (5,500 BC - 1880s) (modified from Fitzpatrick et al. 2009b).

During wetter periods, the wetlands underwent regular partial drying and wetting/ flushing cycles (Figure 6-3- upper panel). Waters received by the wetlands were transferred via channels, via bank over flow, and by infiltration of rainfall. Wetlands

accumulated sulfidic materials from sulfate contained in surface waters and groundwaters. However, during dry periods such as droughts (Figure 6-3, lower panel) when river flows were lower, the wetland partially dried, causing oxidation of sulfidic materials, especially on the dry margins. Pyrite in the sulfidic material was oxidised with likely formation of sulfuric acid and potentially the formation of sulfuric materials. In wetter times and during floods, the acidic material was submerged in the water column, with dilution/neutralisation of acidity and the reformation of sulfidic material. The build-up of sulfidic materials in the Banrock wetland was regularly kept-in-check by oxidation (i.e. "burned-off") and removal from scouring floods.

(ii) During the 1880s to 1930s period. European settlers moderated the flows of the River Murray by the installation of various irrigation network systems (Figure 6-4). During this period, part of the wetland was "managed for flood irrigation" (e.g. citrus and dairy).
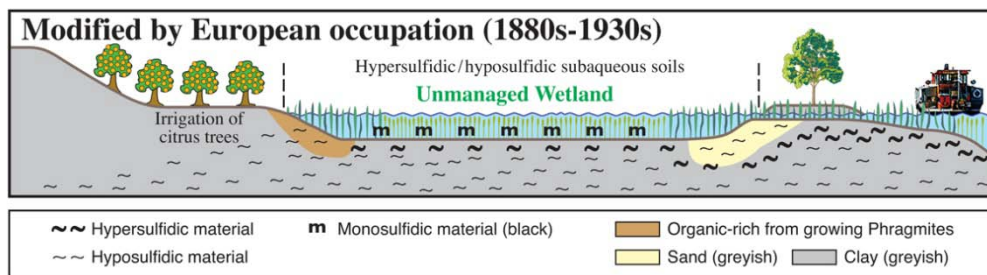
Figure 6-4: Explanatory soil-regolith model for Banrock wetlands, illustrating modification of water flows by European occupation (1880s- 1930s) (modified from Fitzpatrick et al. 2009b)

(iii) The 1925 to 1993 period. The river and wetland systems were managed using locks. The installation of locks enabled considerable build-up of sulfidic and monosulfide material in the wetland (Figure 6-5).
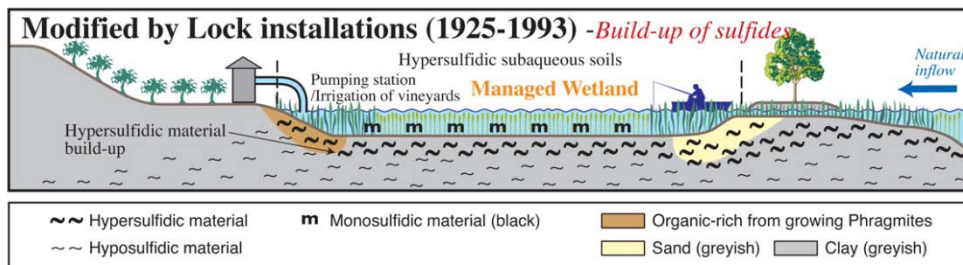
Figure 6-5: Explanatory soil-regolith model for the Banrock wetland illustrating modification of water flows by lock installations causing the build up of sulfides (i.e. hypersulfidic material) under continued subaqueous conditions from 1925-1993 (modified from Fitzpatrick et al. 2009b).

(**iv) The 1993 to 2006 period**. Partial drying cycles and rewetting cycles occurred due to the installation of flow control structures (sluice gates) (Figure 6-6). During dry periods (Figure 6-6 top panel) the wetland partly dried in places, likely causing oxidation of sulfidic materials, especially on the margins of the wetland.

The accumulated pyrite in the thick sulfidic material is likely to have partly oxidised with formation of sulfuric acid and the potential formation of sulfuric materials, similar to the natural system described in Figure 6-3. During the rewetting cycles, the acidic material was submerged in the water column, with dilution/neutralisation of acidity and the reformation of sulfidic material. Hence, the build-up of sulfidic material in the wetland was controlled by regular periods of oxidation. In 2006, the pump used for irrigation purposes was removed because of the Ramsar status of the wetland (in

Figure 6-6; the old irrigation pump has been removed and a new pump installed for
pumping river water into the wetland).
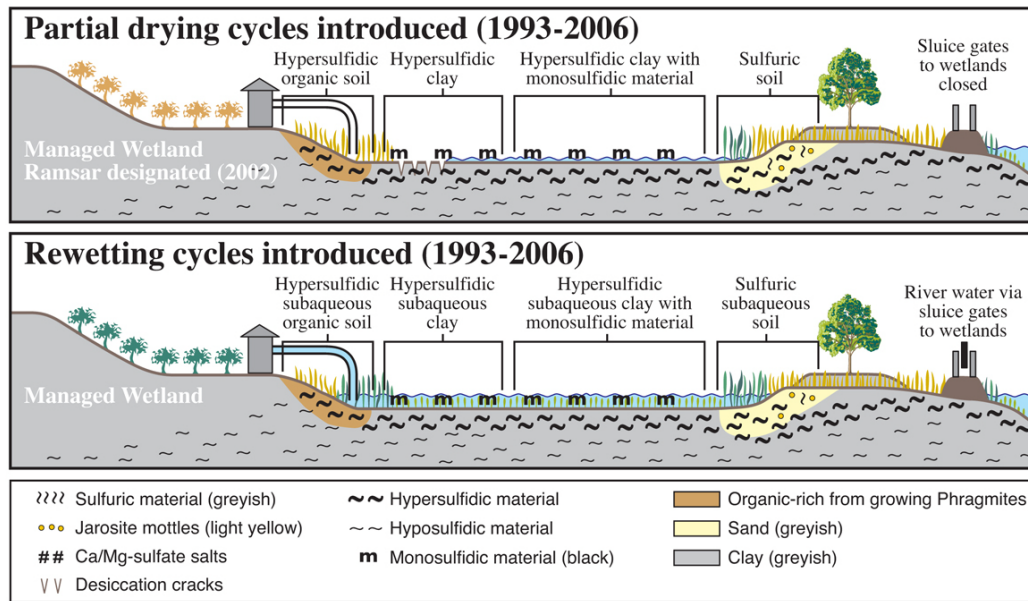
Figure 6-6: Explanatory soil-regolith model for the Banrock wetland illustrating the installation of sluice
gates to manage the partial drying cycle (upper panel) and the rewetting/ flushing cycle (lower panel)
during 1993 to 2006. The Banrock wetland was designated a Ramsar site in 2002. (modified from
Fitzpatrick et al. 2009b).

(v) **The 2007 to June 2008 period (18 months).** ##When drying of the upper soil in
whole wetland took place (Figure 6-7), the wetland effectively became hydraulically
disconnected from the river channel.
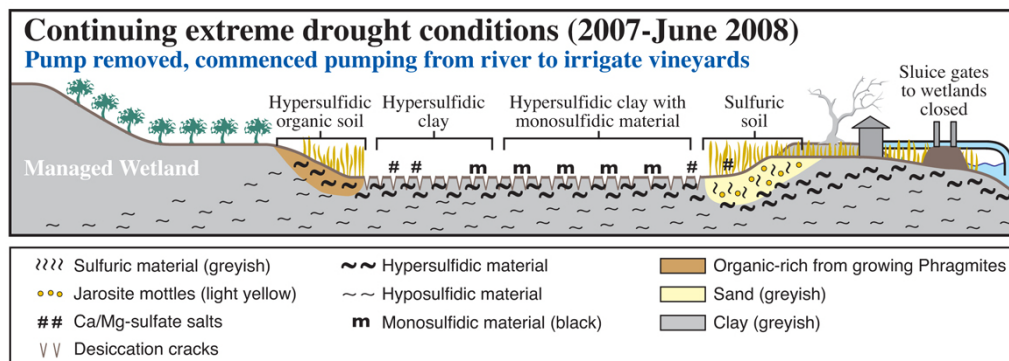
Figure 6-7: Explanatory soil-regolith model for the Banrock wetland illustrating the formation of: (i)
sulfuric material (pH < 4) by oxidation of sulfides in hypersulfidic material on the edges of the wetland,
(ii) sulfate-rich salt efflorescences and (iii) deep desiccation cracks; due to continued lowering of water
levels under persistent extreme drought conditions during 2007 – 2008 (modified from Fitzpatrick et al.
2009b).

During this period, subaqueous ASS transformed to waterlogged ASS and eventually
to dried ASS. This resulted in the formation of sulfuric material at the wetland
margins to depths up to 50 cm and deepening of desiccation cracks (> 50cm),
especially in areas that are organic-rich (>10 % organic carbon) and clayey (> 35 %
clay) (Thomas *et al.* 2011). Under such low pH conditions, acid dissolution of the
layer silicate soil minerals is likely to have caused the release of Fe, Al, Mg, Si (and
other elements) and the formation of sulfate-rich salt efflorescences in and near soil
surfaces (Figure 6-7). The continued drying of the wetlands caused further
desiccation, and the precipitation of sulfate-rich salt efflorescences in desiccation

cracks and on the sandy edges of the wetland. Areas with monosulfides continued to dry out, causing desiccation cracks to develop, especially in the fine textured material.

(vi) From June 2007 to October 2008 period (5 months). When complete rewetting took place by pumping water into the wetland (Figure 6-8), the dried Sulfuric soils on the edges of the wetland became inundated and transformed to Sulfuric subaqueous soils with clearly preserved jarosite mottles in sulfuric materials. As expected, during the re-wetting cycle, the sulfate-rich salt efflorescences dissolved and became mobilised in the water column. Once the wetland and anaerobic redox conditions resumed, the Hypersulfidic soils and clays were classified as Hypersulfidic subaqueous soils and clays with stable hypersulfidic materials, , while metals bioaccumulate, or accumulate. Under this management scenario, there is control of the distribution and eventual fate of sulfates, monosulfides and salts.
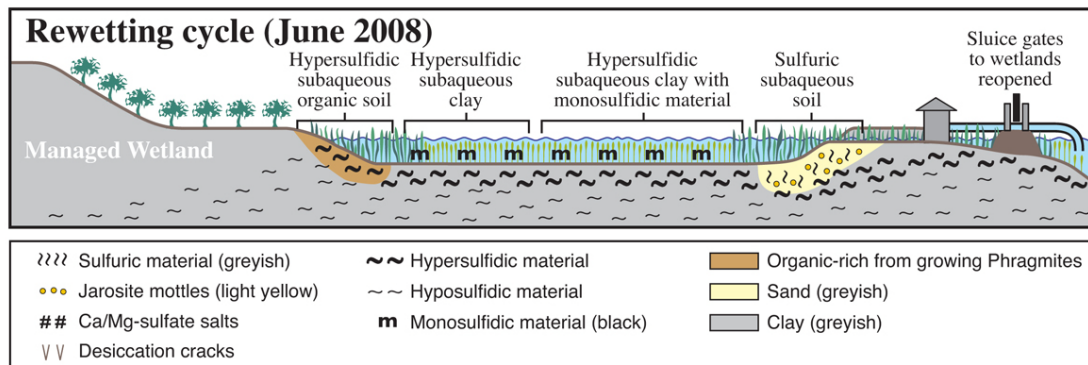
Figure 6-8: Explanatory soil-regolith model for the Banrock wetland showing complete re-wetting of the whole wetland in June 2008 with inundation and preservation of sulfuric material (Sulfuric subaqueous soils) and hypersulfidic material (Hypersulfidic subaqueous organic soils), which occurs on the edges of the wetland; and (ii) hypersulfidic subaqueous clays with MBO, which occur dominantly in the centre on the wetland (modified from Fitzpatrick et al. 2009b).

(vii) From October 2008 to September 2013 period (~5 years) Drying of the upper soil in the wetland took place in September 2013 (Figure 6-9), after at least 4 cycles of re-wetting and drying of the whole wetland over a 5 year period. During all 4 re-wetting cycles the Sulfuric subaqueous soils, continued to exhibit jarosite mottles in the sulfuric materials. As expected, during the drying period in September 2013, the Sulfuric subaqueous soils once again transformed to Sulfuric soils with preservation of jarosite mottles (Figure 6-9). This resulted in the formation of sulfuric material to depths up to 50 cm and deepening of desiccation cracks (> 50cm), especially in areas that are organic-rich (>10 % organic carbon) and clayey (> 35 % clay). Under such low pH conditions, acid dissolution of the layer silicate soil minerals is likely to have caused the release of Fe, Al, Mg, Si (and other elements) and the formation of sulfate-rich salt efflorescences on the soil surface.

Significantly, the 4 cycles of re-wetting and drying over the past 5 years has resulted in a decrease in pyrite content and/or increase in carbonate content (i.e. ANC) with the consequent transformation of hypersulfidic material [Hypersulfidic subaqueous organic and clay soils (Figure 6-8) and Hypersulfidic organic and clay soils (Figure 6-7)] to hyposulfidic material [i.e. Hyposulfidic organic and clay soils (Figure 6-9)].
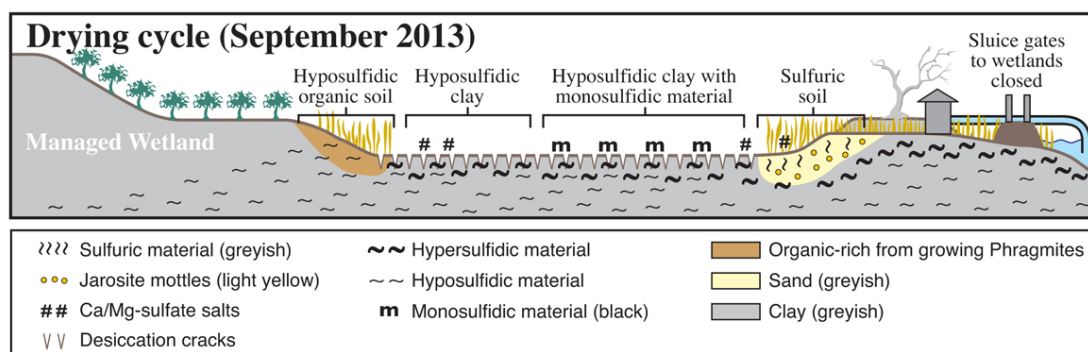
Figure 6-9: Explanatory soil-regolith model for the Banrock wetland after at least 4 cycles of re-wetting and drying of the whole wetland over a 5 year period with inundation of: (i) Sulfuric soils and Hyposulfidic organic soils, which occur on the edges of the wetland and (ii) hyposulfidic clays, which occur dominantly in the centre on the wetland.

6.4 Degree of external and internal factors controlling pedogenic processes in evolution and rehabilitation

The monitoring of the 6 to 8 representative sites between 2006 and 2013 has generated data to develop a conceptual model encompassing a series of 9 hydro-toposequence sections in a transect across the Banrock wetland complex (Figure 6-3 to Figure 6-9). This information was used to develop the following two synthesis evolutionary models in the form of summary tables:

- Soil-regolith evolutionary model (Table 6-1) illustrating temporal and spatial variations and changes in ASS subtypes at each site during two extrapolated historical periods [h_1 = managed locks 1925-1993; h_2 = managed sluice gates from 1993-2006) and three monitored periods (a = May 2008; b = June, 2008; c = September, 2013).
- Predictive soil-regolith evolutionary model (Table 6-2) illustrating the degree of external and internal factors that control the dominant pedogenic pathways and processes during the following 7 major periods:

    (i)   Before 1880s (approximately 5,500 BC to 1880s period).
    (ii)   During the 1880s to 1930s period when the river and wetland systems were first used for navigation and irrigation.
    (iii)   During the 1930s to 1993 period when the river and wetland systems were first managed using locks.
    (iv)   During the 1993 to 2006 period when partial drying cycles and substantial rewetting cycles occurred because of the installation of sluice gates.
    (v)   During the January 2007 to June 2008 period (18 months) when complete (or unprecedented) drying took place.
    (vi)   During the June 2008 to October 2008 period (5 months) when complete rewetting took place.
    (vii) During October 2008 to September 2013 period (~5 years) when approximately 4 wetting (rewetting) and drying/partial took place.

The Soil-regolith evolutionary (Table 6-1) and the Predictive soil-regolith evolutionary (Table 6-2) models both illustrate the key external drivers or thresholds that render the various ASS subtypes and features (e.g. cracks) relatively stable or susceptible to slow or rapid change (Fitzpatrick et al. 2012a). The dominant Acid Sulfate Soil pedogenic processes are assigned to each sequential model, which incorporates the following 3 pedogenic concepts:

(a) **Extrinsic and intrinsic pedogenic thresholds** (Muhs 1984). The pedogenic threshold is a value, unique to a particular soil system, beyond which the system adjusts or changes, not just in rate but also in soil type or subtype. In an extrinsic

pedogenic threshold, an external factor changes progressively, which triggers abrupt, fast or slow pedogenic changes. This is usually caused by climatic, geomorphic or human-induced changes (e.g. salt pond drainage). In contrast, intrinsic pedogenic thresholds occur when a system changes without a change in external variable.

(b) **Pedogenic rates** [e.g. dynamic balance of thickness (Johnson and Watson-Stegner 1987)].

(c) **Acid sulfate soil processes** [sulfidization & sulfuricization (Fanning and Fanning 1989)] where sulfidization describes the processes leading to the formation of sulfides (or Hypersulfidic materials) and sulfuricization describes those processes responsible for the formation of sulfuric acid (sulfuric materials).

The following terms and abbreviations are used in both Soil-regolith evolutionary models (Table 6-1; Table 6-2):

Ex- Extrinsic pedogenic threshold;
In - Intrinsic pedogenic threshold;
Dy - Dynamic balance of thickness;
Dp – deepening;
Rv – removals;
Up – upbuilding;
Pr(s) - Progressive pedogenesis (slow: relative to previous window);
Pr(f) - Progressive pedogenesis (fast relative to previous window);
Ab - Abrupt pedogenesis (relative to previous window);
Re - Regressive pedogenesis;
St - Static pedogenesis;
Sulfide – sulfidization;
Sulfuric - sulfuricization (Fitzpatrick et al. 2012a)

These conceptual hydro-toposequence and evolutionary models have provided a detailed understanding of 2D, 3D and 4D (predictive) ASS soil-landscape features in the wetland complex. They illustrate the complex sequential vertical and lateral changes in pedogenic processes as well as the mineralogical, hydrological and biogeochemical interactions that have occurred over recent geological time.

Following stabilisation of sea level to about its present position 5,500-6000 BC, the Banrock Wetland complex would have cycled between natural wetting and flushing, and partial drying conditions in response to seasonal and climatic cycles occurring in the upper Murray-Darling Basin and its own subcatchment (Figure 6-3). The build-up of hypersulfidic material in the Banrock Wetland complex was thus regularly kept in check by oxidation and removal during scouring floods (Fitzpatrick et al. 2009).

However, during the 1880s-1930s and 1930s-1993 periods the River Murray, adjacent creeks and wetland systems were managed using locks and bunds for irrigation network systems. These installations enabled considerable build-up of sulfidic and monosulfidic materials in the wetland (Figure 6-4, Figure 6-5, Table 6-1, Table 6-2). Prolonged inundation encouraged sulfate reduction and caused the formation of Hypersulfidic subaqueous clays.

Following the installation of flow control structures between 1993 to 2006 such as sluice gates (Figure 6-6) and during the extreme drought from 2007 to 2009 (Figure 6-7) the partial drying of the wetland complex caused the Hypersulfidic subaqueous soils to transform to Sulfuric soils. On rewetting, Sulfuric subaqueous clays were formed in June 2008.

Table 6-1 Summary of temporal and spatial variations and changes in ASS subtypes at each key RBA site (01, 02, 03, 06 and 07). Note: (i) Cells shaded orange summarise data presented within this report, (ii) all other cells are based on/extrapolated from data presented in and (iii) cells bordered in blue indicate subaqueous conditions

Banrock Sites		Managed Locks 1925-1993 (h₁)	Managed Sluice gates 1993-2006 (h₂)	Managed Drought/ Drying May 2008 (a)	Managed Reflooding June 2008 (b)	Managed Drying Sept 2013 (c)	Summary
RBA-01	[1]Classification & [2]Acid hazard	Hypersulfidic subaqueous (H)	Sulfuric soil (H)	Sulfuric soil (H)	Sulfuric subaqueous soil (H)	Sulfuric soil (H)	During the extreme drought period (2007 to 2009) this site was identified as a Sulfuric soil and remained a Sulfuric subaqueous soil when reflooded in June 2008. After at least 4 wetting and drying cycles between 2008 and 2013 a Sulfuric soil remained.
	Dominant water and ASS process	UW & Sulfide	RW & Sulfuric	LW & Sulfuric	RW & Sulfuric	RW & Sulfuric	
	[3]Threshold Pedogenic Rate	Ex, Up, Pr(f)	Ex, Rv, Pr(f)	Ex, Up, Pr(f)	Ex, Up, Pr(f)	Ex, St, Dy	
RBA-02	[1]Classification & [2]Acid hazard	Hypersulfidic subaqueous (H)	Sulfuric soil (H)	Sulfuric soil (H)	Sulfuric subaqueous soil (H)	Hyposulfidic soil (L)	During the extreme drought period (2007 to 2009) this site was identified as a Sulfuric soil and remained a Sulfuric subaqueous soil when reflooded in June 2008. However, after prolonged inundation for at least 4 wetting and drying cycles between 2008 and 2013 (~5 years) resulted in the formation of an "acidic" **Hyposulfidic soil.**
	Dominant water and ASS process	RW & Sulfide	RW & Sulfuric	RW & Sulfuric	RW & Sulfuric	RW & Sulfide loss	
	[3]Threshold Pedogenic Rate	Ex, Up, Pr(f)	Ex, Rv, Pr(f)	Ex, Up, Pr(f)	Ex, Up, Pr(f)	Ex, Rv, Pr(f)	
RBA-03	[1]Classification & [2]Acid hazard	Hypersulfidic subaqueous clay (H)	Hypersulfidic clay (H)	Hypersulfidic clay (H)	Hypersulfidic subaqueous clay (M)	Hyposulfidic Clay (L)	During the extreme drought period (2007 to 2009) this site was identified as a **Hypersulfidic clay** and remained as a **Hypersulfidic subaqueous clay** when reflooded in June 2008. However, after prolonged inundation, for at least 4 wetting and drying cycles between 2008 and 2013 (~5 years), it transformed to a *Hyposulfidic* **clay** (this could be due to Spatial variability caused mainly by calcium carbonates or sulfide loss).
	Dominant water and ASS process	RW & Sulfide	RW & Sulfide	RW & Sulfide	RW & Sulfide	RW & Sulfide loss	
	[3]Threshold Pedogenic Rate	Ex, Up, Pr(f)	Ex, Dp, Pr(s)	Ex, Dp, Pr(s)	Ex, Dp, Pr(s)	Ex, Rv, Pr(f)	
RBA-06	[1]Classification & [2]Acid hazard	Hypersulfidic subaqueous clay (H))	Hypersulfidic clay (H)	Hypersulfidic clay (H))	Hypersulfidic subaqueous clay (M)	Hyposulfidic clay (L)	During the extreme drought period (2007 to 2009) this site was identified as a **Hypersulfidic clay** and remained as a **Hypersulfidic subaqueous clay soil** when reflooded in June 2008. However, after prolonged inundation, for at least 4 wetting and drying cycles between 2008 and 2013 (~5 years), it transformed to a *Hyposulfidic* **clay** (this could be due to Spatial variability caused mainly by calcium carbonates or sulfide loss).
	Dominant water and ASS process	RW & Sulfide	RW & Sulfide	RW & Sulfide	RW & Sulfide	RW & Sulfide loss	
	[3]Threshold Pedogenic Rate	Ex, Up, Pr(f)	Ex, Dp, Pr(s)	Ex, Dp, Pr(s)	Ex, Dp, Pr(s)	Ex, Rv, Pr(f)	
RBA-07	[1]Classification & [2]Acid hazard	Hypersulfidic subaqueous organic soil (H)	2 m high live Phragmites Hypersulfidic organic soil (H)	2 m high live Phragmites Hypersulfidic organic soil (M)	2 m high live Phragmites Hypersulfidic subaqueous organic soil (M)	2 m high live Phragmites Hyposulfidic organic soil (L)	During the extreme drought period (2007 to 2009) this site was identified as a **Hypersulfidic organic soil** and remained as a **Hypersulfidic subaqueous organic soil** when reflooded in June 2008. However, after prolonged inundation, for at least 4 wetting and drying cycles between 2008 and 2013 (~5 years), it transformed to a *Hyposulfidic* **organic soil** (this could be due to Spatial variability caused mainly by calcium carbonates or sulfide loss).
	Dominant water and ASS process	RW & Sulfide 2 m high live Phragmites	RW & Sulfide	RW & Sulfide	RW & Sulfide	RW & Sulfide loss	
	[3]Threshold Pedogenic Rate	Ex, Up, Pr(f)	Ex, Dp, Pr(s)	Ex, Dp, Pr(s)	Ex, Dp, Pr(s)	Ex, Rv, Pr(f)	

[1] **Classification – Acid Sulfate Soil subtype classification**
[2] **Acid hazard – Acidification hazard: H = High; M = medium; L = Low; VL = Very Low**
Dominant Water process
LW – Lowering water level regime to expose soil to air due to drought conditions and water evaporation
UW – Unchanged water regime, which had not yet evaporated to expose soil to air
RW – Rising water level regime to inundate and saturate soils by reflooding (e.g. due to pumping, regulator installation, river flow and groundwater)
RF – Rain fall rewetting and natural reflooding to inundate and saturate soils
[3]**Ex**- Extrinsic pedogenic threshold
[3]**In** - Intrinsic pedogenic threshold
[3]**Dy** - Dynamic balance of thickness
[3]**Dp** - deepening
[3]**Rv** - removals
[3]**Up** - upbuilding

Dominant ASS – process
Sulfuric – Sulfuricization - oxidation of pyrite in hypersulfidic material due to onset of aerobic conditions to form sulfuric material
Sulfuric* – As above with acidic minerals and/or salt efflorescences noted (i.e. measurable RA)
Sulfide – Sulfidization due to sulfide accumulation to form hypersulfidic material
Monosulfide – Monosulfidization due to monosulfide accumulation to form monosulfidic material
Leach – Leaching of acid from soil by winter rain fall
Sulfuric **subaqueous** with **overlying circa neutral water** pH >4: = font coloured blue or default
Sulfuric **subaqueous** soil with **overlying acid water** pH <4: = font coloured red
Where h₁ to h₃ = historical sampling; (a) – (b) sampling conducted in this project

[3]**Pr(s)** - Progressive pedogenesis (slow: relative to previous window)
[3]**Pr(f)** - Progressive pedogenesis (fast relative to previous window)
[3]**Ab** - Abrupt pedogenesis (relative to previous window)
[3]**Re** - Regressive pedogenesis
[3]**St** - Static pedogenesis

Table 6-2 Predictive soil-regolith evolutionary model illustrating the dominant pedogenic pathways and processes

Period or Activity ASS subtypes	Dominant pedogenic processes
(i) Before 1880s Natural wetting & flushing, and partial drying cycle conditions during pre-colonial times	**St** - Static pedogenesis; **Dy** - Dynamic balance of the thickness and amount of sulfide formation - caused by cyclic climatic & geomorphic changes
(ii) 1880s to 1930s period Subaqueous ASS formation with wetlands, illustrating modification of water flows by European occupation (1880s-1930s)	Extrinsic pedogenic threshold (**Ex**) caused by human-made changes (bund wall construction of bunds in streams with rapid flooding of water for irrigation. Slow transformation *Hyposulfidic* clayey soils to *Hypersulfidic* subaqueous clayey soils – with monosulfidic material Progressive **slow** pedogenesis [**Pr(s)**] in <50cm layers in upbuilding sulfides **(Up) / (Sulfide)**
(iii) 1930 to 1993 period (h₁) Hypersulfidic subaqueous soil formation in wetlands due to modification of water flows by lock installations causing the build up of sulfides	Extrinsic pedogenic threshold (**Ex**) caused by human-made changes (lock 3 construction with rapid long-term flooding of water. Rapid transformation *Hyposulfidic* clayey soils to *Hypersulfidic* subaqueous clayey soils – with monosulfidic material Progressive **fast** pedogenesis [**Pr(f)**] in <50cm layers in upbuilding sulfides **(Up) / (Sulfide)**
(iv) The 1993 to 2006 period (h₂) Substantial rewetting cycles and partial drying cycles occurred due to the installation of flow control structures (sluice gates).	Extrinsic pedogenic threshold (**Ex**) caused by human-made changes (mostly re-wetting with sporadic draining of wetlands). *Shoreline*: Abrupt pedogenesis (**Ab**) with fast transformation *Hypersulfidic* subaqueous soils to Sulfuric soils and Sulfuric subaqueous soils (RBA-01 RBA-02). Progressive **fast** pedogenesis [**Pr(f)**] in removal of sulfides (**Rv**) and upbuilding of soluble sulfate salts**, Mg-sulfates and jarosite (Up)** *Lakebed*: Slow formation of shallow cracks to 20cm and profile deepening (**Dp**). Increased formation of pyrite in *Hypersulfidic* subaqueous clayey soils to *Hypersulfidic* & subaqueous clayey soils (RBAc-03 - RBAc-06). Progressive **slow** pedogenesis [**Pr(s)**] in formation of sulfides (**Up**)
(v): 2007 to June 2008 period (18 months) (a) Extreme drought caused drying of the upper soil in whole wetland to became hydraulically disconnected from the river channel	Extrinsic pedogenic threshold (**Ex**) caused by climatic and human-made changes (draining of wetlands) *Shoreline*: Fast transformation *Hypersulfidic* subaqueous soils to Sulfuric soils (RBAc-01 RBAc-02) Progressive **fast** pedogenesis [**Pr(f)**] in removals of water & sulfides (**Rv**) & upbuilding of **Mg-sulfates and jarosite (Up)** *Lakebed*: Abrupt pedogenesis (**Ab**) in fast formation of deep cracks to >50cm and profile deepening (**Dp**). Transformation *Hypersulfidic* subaqueous clayey soils to *Hypersulfidic* clayey soils (RBAc-03 - RBAc-06) Progressive **fast** pedogenesis [**Pr(f)**] in removals of water & sulfides (**Rv**) & upbuilding of soluble sulfate salts, **Mg-sulfates & jarosite (Up))**
(vi) June 2007 to October 2008 period (5 months) (b) Complete re-wetting of wetland with inundation and preservation of sulfuric materials, which occurs on the edges of the	Extrinsic pedogenic threshold (**Ex**) caused by human-made changes (flooding of wetland) *Shoreline*: Abrupt pedogenesis (**Ab**) in rapid formation of *Sulfuric* subaqueous soils. Upbuilding of **Mg-sulfates & jarosite (Up))** Progressive **fast** pedogenesis [**Pr(f)**] in submergence of water and removal of soluble sulfate salts, **Mg- and** gypsum (**Rv))** *Lakebed*: Increased oxidation of pyrite during the transformation of *Hypersulfidic* subaqueous clayey soils to *Hypersulfidic* clayey soils
(vii): October 2008 to September 2013 period (c) Drying of the upper soil in September 2013, after at least 4 cycles of re-wetting and drying over a 5 year period.	Extrinsic pedogenic threshold (**Ex**) caused by human-made changes (flooding and drying of wetland) *Shoreline*: **St** - Static pedogenesis; **Dy** - Dynamic balance of thickness resulting in stability of *Sulfuric* soil at site RBAc-01; However, at site RBAc-02 pronged wetting & drying cycles (~5 years) resulted in the transformation of *Sulfuric* soils to an "acidic" *Hyposulfidic* soil. Progressive **fast** pedogenesis [**Pr(f)**] in submergence of water and removal of soluble sulfate salts, **Mg- and** gypsum (**Rv))** *Lakebed*: Fast pedogenesis / transformation of *Hypersulfidic* subaqueous clayey soils to *Hyposulfidic* clayey soils (RBA-03 - RBA-06)

7. ACID SULFATE SOIL CLASSIFICATION MAPS AND HAZARD RATING MAPS

7.1 Construction of acid sulfate soil classification maps

Each soil profile was allocated an acid sulfate soil subtype according to the Acid Sulfate Soil Identification Key (Appendix 1; Fitzpatrick et al., 2010). The key is designed for people who are not experts in soil classification systems, assisting them to identify five acid sulfate soil types (subaqueous, organic, cracking clay, sulfuric and hypersulfidic soils) and 18 sub-types based on the occurrence of sulfuric, hypersulfidic, hyposulfidic, or monosulfidic material, and clayey or sandy layers.

Acid sulfate soil subtypes were identified for soil profiles at all sites following the field investigation on 2nd September 2013 (Table 3-3). Soil layers and horizons that did not satisfy the acid sulfate "soil material" classification were listed in Table 3-3 as "other soil materials".

Based on the information presented in Table 3-3 when sampled on 2nd September 2013, which is representative of current dry and predicted dry conditions, legends for "Acid Sulfate Soil classification maps" were constructed that could be used to identify areas defined by "polygon boundaries" where an acid sulfate soil class is likely to occur. The "ASS classification map" for dry conditions will classify a number of soil properties throughout the depth of the soil profile and allocates it to a soil class. To construct acid sulfate soil classification maps, the following six (6) input steps were used:

Step1: Each profile (or sampling site) was classified in accordance with the following procedure, as applied to soil classification keys, which is based on the presence or absence of ASS materials with the highest hazard ASS material keying out first, as follows: (i) sulfuric material keys out first, (ii) hypersulfidic material keys out second, (iii) hyposulfidic material keys out third and (iv) lastly all other non-acid sulfate soil types. The classification of ASS materials (i.e. sulfuric, hypersulfidic, hyposulfidic or monosulfidic) is based mainly on the initial pH (pH at time zero) and after incubation for at least 16 weeks as shown in Table 3-3.

A soil profile that classifies as a "Sulfuric soil", requires sulfuric material (i.e. pH <4 at time zero incubation) to be identified in a layer or horizon, which is at least 10 cm thick within 150 cm of the soil surface. A soil profile that classifies as a "Hypersulfidic soil", requires hypersulfidic material (i.e. decrease in pH to pH 4 or less after incubation for at least 16 weeks) to be identified in a layer or horizon, which is at least 10 cm thick within 150 cm of the soil surface. Finally, a soil profile that classifies as a "Hyposulfidic soil", requires hyposulfidic material (i.e. decrease in pH to >pH 4 after incubation for at least 16 weeks) to be identified in a layer or horizon, which is at least 10 cm thick within 150 cm of the soil surface.

Step2: Visual identification of additional "**key soil / water features**" such as:

- Surface water levels, 2.5 m below the surface water level to estimate areas with "subaqueous soils" = W
- Surface water levels, 0.50 m above the surface water level to estimate areas with "hydrosols" = Hyd
- Drained soils with water level below 50 cm: Unsaturated = Uns
- Salt efflorescences = Ef,
- Gypsum / Halite crusts = Gyp

- Monosulfidic material that is wet (Mow) or dry (Mod)
- Organic = O
- Clays = Cy
- Sands = Sa
- Loams = Lo
- Shell grit gravel = Sh
- Sulfuric material = Su
- Hypersulfidic material = He
- Hyposulfidic material = Ho
- Non-acid clays = Non

Examples of these features are displayed in "Map Key Legends" for: (i) southern section of the wetland (profiles: RBAc 01; RBAc 02; RBAc 03 and RBAc 04).

Step 3: Each sampling site was classified (e.g. Sulfuric loam for RBAc 01 as shown in Table 7-1) in accordance to the dominant acid sulfate soil material present (i.e. Soil subtype in accordance to the soil identification key outlined in Appendix 1) and texture (i.e. Soil Subtype in accordance to the soil identification key in Appendix 1).

Table 7-1. Map Legend showing potential soil map units ordered by landscape (ponded water level) and then acid sulfate soil class and texture.

Landscape	Acid Sulfate Soil Class	Soil Texture Class	Soil Map Unit Name
Subaqueous (0 to 2 water depth)			
	Sulfuric	Loamy	Sulfuric subaqueous loams
	Hypersulfidic	Heavy Clay	Hypersulfidic subaqueous clays
	Hyposulfidic	Heavy Clay	Hyposulfidic subaqueous clays
Hydrosols (saturated within 50cm below soil surface)			
	Sulfuric	Loamy	Sulfuric hydrosol loams
	Hypersulfidic	Heavy Clay	Hypersulfidic hydrosol clays
	Hyposulfidic	Heavy Clay	Hyposulfidic hydrosol clays
Unsaturated (unsaturated within 50cm below soil surface)			
	Sulfuric	Loamy	Sulfuric loams
	Hypersulfidic	Heavy Clay	Hypersulfidic clays
	Hyposulfidic	Heavy Clays	Hyposulfidic clays

Step 4: Based on information from steps 1 to 3 together with soil surveyor and local knowledge, allocate dominant Acid Sulfate Soil Subtypes [e.g. Hyposulfidic (~80 %) & hypersulfidic (~20 %) hydrosol clays] and related soil features to map polygons on the digital NearMap (http://www.nearmap.com/) aerial image taken in September, 2013.

Soils in the **Southern** *segment of* the wetland comprise: (i) Sulfuric loams along the shorelines of the wetland with **high** acidification hazard ratings (Table 7-2) and **low** deoxygenation/malodour hazard ratings (Table 7-3) and (ii) hyposulfidic clays in the lakebed of the wetland with **low** acidification hazard ratings (Table 7-2) and **medium** deoxygenation/malodour hazard ratings (Table 7-3).

Soils in the **Northern** *segment of* the wetland comprise: (i) Hyposulfidic hydrosol clays with organic-rich material along the shorelines of the wetland with **low** acidification hazard ratings (Table 7-2) and **medium** deoxygenation/malodour hazard ratings (Table 7-3) and (ii) Hyposulfidic hydrosol loams over clays with monosulfidic material in the lakebed of the wetland with **low** acidification hazard ratings and **medium** deoxygenation/malodour hazard ratings.

Table 7-2. Dominant and subdominant soil subtypes and other features (e.g. texture) and map symbols with *acidification* hazard ratings

Map Symbol	Map Unit Name
Southern segment	
Su1 UnsLo Ef	Sulfuric loams with Salt efflorescences
Ho 1 HydCyEfMod	Hyposulfidic hydrosol clays with monosulfidic material (dry)
Northern segment	
Ho2 HydCyO	Hyposulfidic hydrosol clays with organic-rich material
Ho3 HydLo/CyMow	Hyposulfidic hydrosol loams over clays with monosulfidic material (dry)

Acidification hazard categories used in maps and tables in this report are: high (Yellow), medium (Brown) and low (Blue).

Table 7-3. Dominant and subdominant soil subtypes and other features (e.g. texture) and map symbols with *Deoxygenation/malodour* hazard ratings

Map Symbol	Map Unit Name
Southern segment	
Su1 UnsLo Ef	Sulfuric loams with Salt efflorescences
Ho1 HydCyEfMod	Hyposulfidic hydrosol clays with monosulfidic material (dry)
Northern segment	
Ho 2 HydCyO	Hyposulfidic hydrosol clays with organic-rich material
Ho 3 HydLo/CyMow	Hyposulfidic hydrosol loams over clays with monosulfidic material (dry)

Deoxygenation/malodour hazard categories used in maps and tables in this report are: high (Yellow), medium (Brown) and low (Blue).

Step 5: Based on steps 1 to 4, identify lists of "potential or preliminary" soil map units and symbols as shown in the map legends displayed for the wetland in Table 7-2 and Table 7-3.

Step 6: Allocate final Soil Map Symbols (e.g. Su1) and Soil Unit code (e.g. UnsLo Ef) for each polygon after creating final map overlay boundaries on a digital NearMap (http://www.nearmap.com/) aerial image taken in September, 2013 (i.e. electronic/digital and hardcopy formats).

A back check is then conducted to identify how well the map units 'honoured' the sites that occurred in each map unit and agreed with the map unit description, and a further iteration of the map will be conducted to update and refine.

Confidence level of soil classification mapping

It is often not possible to fully classify soils in specific areas because of lack of access to properties (e.g. deep water, areas with a low ability to support a load or with low bearing capacity i.e. has an n-Values (Appendix 2) > 1, no road or track access). For this reason, the following levels of confidence are used to classify soil-landscapes:

(i) *high confidence* when a high quantity of detailed soil profile observations are made of areas or map units via soil pit, auger or road cutting investigations,

(ii) *moderate confidence* when only reconnaissance observations are made of areas or map units through few detailed soil profile observations via pits, auger or road cutting investigations – but mostly via visual observations through either walking across landscapes (e.g. selected transects) or windows of a moving vehicle with satisfactory road access and road cuttings;

(iii) *fair to provisional confidence* because soil-landscape classification is based on a knowledge of *similar* soils in similar environments (e.g. knowledge extrapolation based on soil or geological maps documented during the office assessment) especially where no road or property access was available during field investigations.

Acid sulfate soils and their classification are strongly dependant on water conditions as a change in water level will typically influence soil redox conditions and its acid status. Hence, it should be noted that the acid sulfate soil map is not an end in itself and to be a useful aid to any form of land management, it has to be interpreted, often with supplementary information for the user. The user may find it difficult to read a soil map, despite the kind of guidance given in this report, and may not realise the potential value of soil maps to their land management interest. It may be necessary for a professional expert to produce "interpretative maps", based on soil maps, but adding other information relevant to the specific application of the map (e.g. different water levels in parts of the ponds will likely alter or reverse the occurrences of certain soil Subtypes).

7.2 Acid sulfate soil classification map

It is strongly recommended that a follow-up field investigation be conducted to produce an Acid sulfate soil map of the wetland using the map legends outlined in Table 7-2 and Table 7-3.

7.3 Acid sulfate soil hazard ratings for acidity and **deoxygenation/smell**

7.3.1 Hazard or risk evaluation

This section comprises investigations and interpretations that are primarily focussed on determining the relative hazards associated with the presence of ASS materials and more importantly with the various ASS subtypes.

Defining and Assessing Hazards

Acid sulfate soil materials when disturbed can lead to the following hazards:

   a. Acidification;

   b. Deoxygenation/malodours (i.e. presence of monosulfidic material)

   c. Contaminant mobilisation.

It is acknowledged that there are other hazards associated with acid sulfate soil materials such as the production of odours, noxious gases and dust. These hazards may be identified and acknowledged in reports dealing with the detailed assessment of acid sulfate soil materials.

The field and laboratory analyses carried out using current standard Acid Sulfate Soil protocols for sampling, field characterisation, laboratory analysis and data presentation (see Chapter 2) help determine whether ASS materials present a potential hazard to ponds and whether further investigation is required to elucidate risk. Information emanating from the data and interpretations in Chapters 1 to 5 will therefore:

   a. Report on the presence, nature and extent of observed ASS materials;

   b. Advise on potential **hazards** posed by ASS soil materials where possible;

   c. Make recommendations on the requirement for further analyses including the number of samples to be analysed.

Defining and Assessing Risk

Risk is a measure of both the consequences of a hazard occurring, and the likelihood of its occurrence (MDBA 2010). Consequence is the impact of the acid sulfate soil materials being expressed, and primarily takes into account environmental and water quality impacts. Level of consequence will be determined in consultation with environmental managers at Banrock station for each identified hazard in a specific salt pond using a standardised Table 7-4.

Table 7-4: Standardised table used to determine the consequence of a hazard occurring.

Descriptor	Definition
Extreme	Irreversible damage to wetland values and/or adjacent waters; localised species extinction; permanent loss of water supplies
Major	Long-term damage to wetland values and/or adjacent waters; significant impacts on listed species; significant impacts on water supplies
Moderate	Short-term damage to wetland values and/or adjacent waters; short-term impacts on species
Minor	Localised short-term damage to wetland values and/or adjacent waters; temporary loss of water supplies
Insignificant	Negligible impact on wetland values and/or adjacent waters; no detectable impacts on species

Likelihood is the probability of disturbance of the acid sulfate soil material and requires understanding of both the nature and severity of the acid sulfate soil materials (e.g. extent, net acid generating potential, etc) as well as contributing factors influencing the risk (e.g. disturbance of acid sulfate soil materials, wetland management regime).

Level of likelihood will be determined separately for each hazard type. This is due to the variability of contributing factors for each hazard. Likelihood should be determined by assessing the probability of disturbance of the acid sulfate soil materials (Table 7-4). Examples of disturbance include:

- re-wetting of acid sulfate soil materials after they have oxidised;
- acid sulfate soil materials that are currently inundated and that may be oxidised; or
- acid sulfate soil materials that are currently inundated and that may be dispersed by flushing (e.g. scouring flows).

Table 7-5: Likelihood ratings for the disturbance scenario (from MDB 2010).

Descriptor	Definition
Almost certain	Disturbance is expected to occur in most circumstances
Likely	Disturbance will probably occur in most circumstances
Possible	Disturbance might occur at some time
Unlikely	Disturbance could occur at some time
Rare	Disturbance may occur only in exceptional circumstances

Risks are ranked using a standardised risk assessment matrix in Table 7-4. Table 7-5 is used as the product to estimate the likelihood of disturbance of the acid sulfate soil materials and the consequences to wetland values and/or adjacent waters. This must also take into account the scientific assessment of the nature and extent of the acid sulfate soil materials present at the site as confirmed through the field and laboratory analyses through detailed ASS analyses.

According to MDBA (2010), acid sulfate soil scientists conducting detailed assessments cannot alone determine the level of consequence or likelihood at a given wetland – input of relevant managers of the salt fields and adjacent tidal coastline (mangroves) areas will be critical. As such, assessment of risk must be made in consultation with the Banrock environmental managers. This is to ensure that acid sulfate soil scientists have an understanding of the wetland values and context of wetland management for the site.

Table 7-6: Risk assessment matrix (Standards Australia/Standards New Zealand, 2004).

Likelihood category	Consequences category				
	Extreme	Major	Moderate	Minor	Insignificant
Almost Certain	Very High	Very High	High	High	Medium
Likely	Very High	High	High	Medium	Medium
Possible	High	High	High	Medium	Low
Unlikely	High	Medium	Medium	Low	Low
Rare	High	Medium	Medium	Low	Low

Legend: It is suggested that, sites with

Very High: Very High Risk - immediate action recommended;

High: High Risk - senior management attention needed;

Medium: Moderate Risk - management action may be recommended. Agency responsible must be specified;

Low: Low Risk - manage by routine procedures (should be monitored regularly to determine whether the hazard is increasing).

Reporting on Risk

Reports of assessments will establish the level of risk associated with each identified hazard at a wetland using the framework outlined here and in consultation with relevant wetland managers. In order to assist wetland managers in decision-making, the level of risk outlined in final reports should be accompanied by an explanation of the major contributing factors to the risk level (e.g. water management regimes, water chemistry, wetland values etc).

7.4 Acidification hazard

The wetland acidification hazard ratings for the southern and northern sections are presented in Table 7-2. These ratings should be assigned to maps based on the sub-

type of acid sulfate soil material, the depth of occurrence, proportion, and distribution in the polygon.

Acid sulfate soil hazard ratings should then be assigned, with polygons rated as high (yellow), medium (brown) and low (blue). This assessment was based on data obtained during the September 2013 field survey of the wetland. It is important to realise that the pond acidification and deoxygenation/malodour hazard ratings status could change with time, e.g. acid sulfate soil materials can change from hypersulfidic (or even hyposulfidic) to sulfuric as the soil dries and/or is re-flooded. These changes can occur relatively rapidly (Fitzpatrick et al., 2009), and if net acidities are high the change from sulfuric to sulfidic can be months to years (Shand et al., 2010; Baker et al., 2013).

Generally, acidification categories used in this report are:

• High acidification rating (yellow map unit colour) indicated that sulfuric (dominant) or hypersulfidic soil materials were present near the surface throughout the polygon.

• Medium acidification rating (brown map unit colour) indicated that hypersulfidic or hyposulfidic soil materials were present, usually in the subsoil and in about 50% of the polygon.

• Low rating (blue map unit colour) indicated that hyposulfidic materials (dominant) were present near the surface throughout the polygon.

Wetland sections with high (i.e. yellow) acidification rating should be monitored regularly, and have management plans in place to activate if triggers are reached, as they are more likely to increase in acidification hazard. Wetlands with lower ratings are less likely to be of concern and would require less monitoring.

7.5 Soil **deoxygenation/malodour** hazard

The wetland deoxygenation/malodour hazard ratings for the southern and northern sections are presented in Table 7-3. These ratings should be assigned to maps based on the subtype of acid sulfate soil material, the depth of occurrence, proportion, and distribution in the polygon.

Generally, deoxygenation/malodour hazard categories used in this report are:

• High rating (yellow map unit colour) indicated that high amounts of monosulfidic materials (wet) were present at or near the surface (i.e. is exposed and not covered by a crust or topsoil) throughout the polygon.

• Medium rating (brown map unit colour) indicated that monosulfidic materials (wet) were present, and in about 50% of the polygon.

• Low rating (blue map unit colour) indicated that no monosulfidic materials (wet) materials (dominant) were present near the surface throughout the polygon.

7.6 Sodicity hazard

Sodic soils are characterized by low permeability and thus restricted water flow because the clay and organic fractions of these soils are dispersed.

All the ASS soils described classify as "moderately saline soils" (Table 7-7) and comprise "flocculated clays" (i.e. fluffy or loosely aggregated clay particles). Consequently, these saline topsoils and surface layers with salt efflorescences are prone to wind erosion. However, if these saline soils with relatively freely draining topsoils are not treated with "calcium-based soil amendments" they will likely transform to "sodic soils" over time due to leaching with rain water (i.e. low levels of salinity). This will occur because of the leaching of the high levels of soluble salts and the formation of sodic soils with resultant low levels of total salt and high levels of exchangeable sodium (Na).

Sodic soils develop very poor structure and drainage over time because sodium ions on clay particles cause the soil particles to deflocculate, or disperse. Sodic soils are hard and cloddy when dry and tend to crust. Water intake is usually poor with sodic soils, especially those high in silt and clay. Poor plant growth and germination are also common.

Applying especially gypsum (highly soluble salt) and lime to clayey sodic soils with poor drainage will likely be most beneficial.

Table 7-7: Salinity hazard as defined by the electrical conductance of a saturation extract (ECse) and 1:5 soil:water extract (i.e. soil is extracted with distilled water)[1]

Salinity hazard	EC_{se} dS/m	Effects on plant yield	1:5 Soil/Water Extract (dS/m)				
			Loamy sand	Loam	Sandy clay loam	Light clay	Heavy clay
Non-saline	<2	Negligible effect	<0.15	<0.17	<0.25	<0.30	<0.4
Slightly saline	2-4	Very sensitive plants effected	0.16-0.30	0.18-0.35	0.26-0.45	0.31-0.60	0.41-0.80
Moderately saline	4-8	Many plants effected	0.31-0.60	0.36-0.75	0.46-0.90	0.61-1.15	0.81-1.60
Very saline	8-16	Salt tolerant plants uneffected	0.61-1.20	0.76-1.45	0.91-1.75	1.16-2.30	1.60-3.20
Highly saline	>16	Salt tolerant plants effected	>1.20	>1.45	>1.75	>2.30	>3.20

[1] EC 1:5 - the electrical conductance of a 1:5 soil:water extract (i.e. soil is extracted with distilled water), normally expressed in units of Siemens (S) or deciSiemens (dS) per meter at 25°C. While the EC1:5 method is quick and simple it does not take into account the effects of soil texture. It is therefore inappropriate to compare the EC1:5 readings from two soil types with different textures. It is possible to approximately relate the conductivity of a 1:5 soil-water extract (EC1:5) to that of the saturation extract (ECse) and predict likely effects on plant growth. The above criteria are used for assessing soil salinity hazard and yield reductions for plants of varying salt tolerance, ECse is saturated paste electrical conductivity (after Richards, 1954) and EC1:5 is the corresponding calculated electrical conductivity of a 1:5 soil:water extract for various soil textures.

8. SUMMARY AND FUTURE WORK

1.1 Brief summary

Spatial and temporal changes in acid sulfate soil environments

This investigation was carried out to assess and to develop further understanding of the temporal and spatial changes in a wide range of representative ASS caused by inundation and drying cycles in the Banrock wetland complex. The current investigation involved field sampling on 2nd September 2013 (dry-sampling-c) at 6 (six) previously sampled study areas, which were sampled on 23rd May 2008 (dry-sampling-a) and October 2008 (wet-Sampling-b). The overall assessment, which includes a series of predictive conceptual models involved interpreting all the field and laboratory investigations from 2008 to 2013.

The following four independent standard methods were applied to assess ASS acidification deoxygenation/malodour in the wetland complex: (i) soil morphology descriptions, (ii) incubation experiments (tests), (iii) acid-base accounting and (iii) peroxide pH testing on selected samples. These highlighted considerable variability among sites in the wetlands with regard to acid generation, acid neutralisation capacity and deoxygenation/malodour development.

Acidification and deoxygenation/malodour hazard assessment ratings were undertaken based on: (i) soil morphology features, (ii) ASS material and subtype classification, (iii) pH data, (iv) acid base accounting and AVS and (v) landscape position. Acidification and deoxygenation/smell hazard categories were classified as: (i) high, (ii) medium or (iii) low.

In summary, we have established that soil acidification and deoxygenation/smell hazards in the wetlands were variable and ranged from low to high as shown in the acidification and deoxygenation/malodour rating map legends.

In general, soil profiles along the wetland shoreline in the southern segment are mainly Sulfuric soils (dry periods) and Sulfuric *subaqueous* soils (wet/flooded periods) with **high** acidification hazard ratings and **low** malodour hazard ratings.

In general, soil profiles in the lakebeds of the southern and northern *segments* are mainly hyposulfidic clays (dry periods) and hyposulfidic *subaqueous* clays (wet/flooded periods) with **low** acidification hazard ratings and **moderate** malodour hazard ratings.

Soil-regolith models and Acid sulfate Soil Maps
To aid in understanding the spatial heterogeneity of acid sulfate soil properties eight (8) representative soil landscape cross-sections in the form of a conceptual soil-regolith toposequence models has been developed.

The predictive conceptual models illustrate the complexities and importance of understanding specific sites to assess: (i) time-related changes and soil evolution, (ii) detailed behaviour (changes and/or stability) and implications of various ASS materials (e.g. sulfuric, hypersulfidic, hyposulfidic and monosulfidic), (iii) features in layers and horizons (e.g. cracks, salt efflorescences), (iv) shallow regolith materials (e.g. clay and sandy layers), (v) degree of external and internal factors controlling pedogenic pathways and processes of soil evolution (i.e. extrinsic and intrinsic pedogenic thresholds, pedogenic rates and acid sulfate soil processes, such as sulfidization and

sulfuricization) and (vi) different management options (e.g. pumping from Murray River).

In summary, the legend developed to produce acid sulfate soil maps in combination with the generalised conceptual toposequence models presents an understanding of acid sulfate soil distribution in three dimensions.

1.2 Suggestions for further monitoring and research

It is recommended that a follow-up field investigation be conducted during a future dry period and reflooded period to produce Acid sulfate soil maps of the wetland using the map legends outlined in Table 7-2 and Table 7-3. This spatial information will be used to assist in future land management planning options for the wetland complex.

9. REFERENCES

Ahern CR, McElnea AE, Sullivan LA (2004). Acid sulfate soils laboratory methods guidelines. In 'Queensland Acid Sulfate Soils Manual 2004'. Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia.

ANZECC and ARMCANZ (2000). Australian and New Zealand guidelines for fresh and marine water quality: Volume 1 - The guidelines.
http://www.environment.gov.au/water/publications/quality/nwqms-guidelines-4-vol1.html

Bronswijk, J., Nugroho, K., Aribawa, I., Groenenberg, J., Ritsema, C., (1993). Modeling of oxygen transport and pyrite oxidation in acid sulphate soils. Journal of environmental quality 22, 544-554.

Burton ED, Bush RT, Sullivan LA (2006). Acid-volatile sulfide oxidation in coastal flood plain drains: Iron-sulfur cycling and effects on water quality. Environmental Science and Technology 40: 1217-1222.

Burton, E.D., Bush, R.T. Sullivan, L.A. and Mitchell, D.R.G. (2007). Reductive transformation of iron and sulfur in schwertmannite-rich accumulations associated with acidified coastal lowlands, Geochimica et Cosmochimica Acta 71:4457-4473.

Burton ED, Bush RT, Sullivan LA, Johnston SG, Hocking RK (2008a). Mobility of arsenic and selected metals during re-flooding of iron- and organic-rich acid-sulfate soil. Chemical Geology 253: 64-73.

Burton ED, Sullivan LA, Bush RT, Johnston SG, Keene AF (2008b). A simple and inexpensive chromium-reducible sulfur method for acid-sulfate soils. Applied Geochemistry 23: 2759-2766.

Bush RT (2000). Iron sulfide micromorphology and mineralogy in acid sulfate soils: Their formation and behaviour. Unpublished. School of Biological, Earth and Environmental Sciences. Sydney, University of NSW. Ph.D.

Bush, R.T., Sullivan, L.A., (1999). Pyrite micromorphology in three Australian Holocene sediments. Soil Research 37, 637-654.

Bush RT, Sullivan LA, Lin C (2000). Iron monosulfide distribution in three coastal floodplain acid sulfate soils, eastern Australia. Pedosphere 10: 237- 245.

Butcher R, Hale J, Muller K, Kobryn H (2009) Ecological character description for the Banrock Station Wetland Complex. Prepared for Department for the Environment, Water, Heritage and the Arts.

Creeper Nathan N, Paul Shand, Warren Hicks and Rob W Fitzpatrick (2015). Porewater geochemistry of Inland Acid Sulfate Soils with sulfuric horizons following post-drought reflooding with freshwater. Journal of Environmental Quality.
http://dx.doi.org/10.2134/jeq2014.09.0372

Crosbie R, McEwan K, Jolly I, Holland K, Lamontagne S (2007) Surface water - groundwater interactions in three River Murray floodplain wetlands: Results from field studies. CSIRO, Adelaide.

Dear SE, Moore NG, Dobos SK, Watling KM, Ahern CR (2002). Soil management guidelines. In 'Queensland Acid Sulfate Soil Technical Manual.' Department of Natural Resources and Mines, Indooroopilly, Queensland, Australia.

Dent, D (1986). Acid sulfate soils: a baseline for research and development. ILRI Publication No. 39, pp 31-32. Wageningen, The Netherlands, International Institute for Land Reclamation and Improvement.

Fanning, D.S. (2002). Acid sulfate soils. In 'Encyclopedia of Soil Science' (Ed. R. Lal) Pp 11-13. (Marcel Dekker, New York).

Fanning, D.S. and Fanning M.(1989). Soil: Morphology, Genesis, and Classification (John Wiley & Sons, New York).

Ferguson A, Eyre B (1999). Behaviour of aluminium and iron in acid runoff from acid sulphate soils in the lower Richmond River catchment. Journal of Australian Geology and Geophysics 17: 193-201.

Fitzpatrick R.W. 2008. Soils and Natural Resource Management (Chapter 12) In: Regolith Science. (Eds. KM Scott and CF Pain). pp. 307-339 (colour plates: pp 172-174). CSIRO Publishing (Australia) and Springer.

Fitzpatrick, R.W. & Self, P.G. (1997) Iron oxyhydroxides, sulfides and oxyhydroxysulfates as indicators of acid sulfate weathering environments. *Advances in GeoEcology* 30, 227-240.

Fitzpatrick R.W. (2013). Demands on Soil Classification and Soil Survey Strategies: Special-purpose soil classification systems for local practical use. In. S.A Shahid, F.K. Taha and M.A. Abdelfattah (eds.), Developments in Soil Classification, Land Use Planning and Policy Implications: Innovative Thinking of Soil Inventory for Land Use Planning and Management of Land Resources, Springer Science+Business Media Dordrecht. pp. 51-83. DOI 10.1007/978-94-007-5332-7_2

Fitzpatrick, R.W, Baker, A.K.M, Shand, P., Merry, R.H, Grealish, G and Mosley, L.M (2012). A modern soil-landscape characterization approach to reconstructing and predicting pedogenic pathways of inland Acid Sulfate Soils. In: P. Osterholm, M Yli-Halla and P. Eden (Editors). Proceedings of 7th International Acid Sulfate Soil Conference, 26-30 August 2012, Vaasa, Finland. Geological Survey of Finland, Guide 56. pp 47-50. http://arkisto.gtk.fi/op/op56/op_056.pdf [8MB]

Fitzpatrick, R.; Marvanek, S; Powell, B Grealish, G.(2010) Atlas of Australian Acid Sulfate Soils: Recent developments and future priorities. In: RJ Gilkes and N Prakongkep (Editors). Proceedings of the 19th World Congress of Soil Science; Soil Solutions for a Changing World; ISBN 987-0-646-53783-2; Published on DVD; http//www.iuss.org; Symposium WG 3.1 Processes in acid sulfate soil materials; 2010 Aug 1–6, Brisbane, Australia; IUSS; 2010, pp 24-27.

Fitzpatrick RW, Marvanek S, Shand P, Merry RH, Thomas M & Raven M (2008a) Acid Sulfate Soil Maps of the River Murray below Blanchetown (Lock 1) and Lakes Alexandrina and Albert when water levels were at pre- drought and current drought conditions. CSIRO Land and Water Science Report 12/08. CSIRO, Adelaide. 16 pp. http://www.clw.csiro.au/publications/science/2008/sr12-08_withmaps.pdf.

Fitzpatrick R.W. and R.H. Merry (1999). Pedogenic Carbonate Pools and Climate Change in Australia p.105-119. In: R. Lal, J.M. Kimble, H. Eswaran and B.A. Stewart (eds.). "Global Climate Change and Pedogenic Carbonates". CRC Press Lewis Publishers. Boco Raton. FL Proceedings of the International Workshop on Global Climate Change and Pedogenic Carbonates. Tunis, Tunisia. 13-17 October, 1997.

Fitzpatrick R.W., R., Powell, B. and Marvanek, S. (2008b). Atlas of Australian Acid Sulfate Soils. In Inland Acid Sulfate Soil Systems Across Australia (Eds. R.W. Fitzpatrick and P Shand). pp 75-89. CRC LEME Open File Report No. 249. (Thematic Volume) CRC LEME, Perth, Australia.

Fitzpatrick RW, Merry RH, Raven MD & Shand P (2008c) Acid Sulfate Soil Materials and Salt Efflorescences in Subaqueous and Wetland Soil Environments at Tareena Billabong and Salt Creek, NSW: Properties, Risks and Management. In Inland Acid Sulfate Soil Systems Across Australia (Eds Rob Fitzpatrick and Paul Shand. pp 281–293. CRC LEME Open File Report No. 249. (Thematic Volume) CRC LEME, Perth, Australia.

Fitzpatrick, RW, Shand, P. and Hicks, W. (2011). Technical Guidelines for Assessment and Management of Inland Freshwater Areas impacted by Acid Sulfate Soils. CSIRO Land and Water Science Report, 05/11. 171 pp. Published Version (pdf) (17.56MB)

Fitzpatrick RW, Shand P, Merry RH (2009). Acid Sulfate Soils. In 'Natural History of the Riverland and Murraylands'. (Ed. JT Jennings) pp. 65-111. (Royal Society of South Australia (Inc.) Adelaide, South Australia).

Fitzpatrick RW, Shand P, Marvanek S, Merry RH, Thomas M, Simpson SL, Raven MD, McClure S (2008d) Acid sulfate soils in subaqueous, waterlogged and drained soil environments in Lake Albert, Lake Alexandrina and River Murray below Blanchetown (Lock 1): properties, distribution, genesis, risks and management. Prepared for Department of Environment and Heritage, SA. CSIRO Land and Water Science Report 46/08. CSIRO, Adelaide.

Fitzpatrick Rob and Paul Shand (2008). Inland Acid Sulfate Soils: Overview and conceptual models. In Inland Acid Sulfate Soil Systems Across Australia (Eds. Rob Fitzpatrick and Paul Shand). pp 6-74. CRC LEME Open File Report No. 249 (Thematic Volume) CRC LEME, Perth, Australia.

Fitzpatrick RW, Thomas, BP, Simpson, S Shand, P and R.H Merry (2012) "Assessment of Acid Sulfate Soil materials (Phase 2): Banrock Station Wetland Complex. CSIRO Water for a Healthy Country Flagship Client Report, 48 pp (Appendix 3: 21 pages).

Fitzpatrick R.W. and M.J. Wright (1994). Climate change and its implications for South Australian soils. Transactions of the Royal Society of S. Aust. 118, 27–34. Same paper also published in book entitled: Climate Change and its Implications for South Australia. In M. Davies (ed.). Royal Society of South Australia Inc. Adelaide, South Australia. p. 27–34.

Grealish GJ, Fitzpatrick RW and P Shand (2014). Regional distribution trends and properties of acid sulfate soils during severe drought in wetlands along the lower River Murray, South Australia: Supporting hazard assessment. Geoderma Regional. 2–3, 60–71. http://dx.doi.org/10.1016/j.geodrs.2014.10.003

Hsieh Y, Chung S, Tsau Y, Sue C (2002). Analysis of sulfides in the presence of ferric minerals by diffusion methods. Chemical Geology 182, 195-201.

Isbell RF (1996). 'The Australian soil classification.' (CSIRO Australia: Collingwood, VIC, Australia).

Isbell RF (2002). 'The Australian soil classification.' (CSIRO Australia: Collingwood, VIC, Australia).

Isbell RF (2015). 'The Australian soil classification.' revised 2nd edition (CSIRO Australia: Collingwood, VIC, Australia).

Johnson DL, Watson-Stegner D (1987) Evolution model of pedogenesis. Soil Science 143, 349-366.

Lamontagne S, Hicks WS, Fitzpatrick RW, Rogers S (2004) Survey and description of sulfidic materials in wetlands of the Lower River Murray floodplains: Implications for floodplain salinity management. Technical Report 28/04. CSIRO Land and Water. Adelaide, Australia.

Lamontagne S, Hicks WS, Fitzpatrick RW, Rogers S (2006) Sulfidic materials in dryland river wetlands. Marine and Freshwater Research 57, 775–788.

McDonald RC, Isbell RF, Speight JG, Walker J, Hopkins MS 1998. 'Australian soil and land survey field handbook.' Second edition. Canberra, Australian Collaborative Land Evaluation Program.

McDonald RC, Isbell RF, Speight JG, Walker J, Hopkins MS (1990). 'Australian soil and land survey field handbook.' (Inkata Press, Melbourne).

MDBA (2010). Detailed Assessment of Acid Sulfate Soils in the Murray-Darling Basin: Protocols for sampling, field characterisation, laboratory analysis and data presentation. Murray–Darling Basin Authority Publication 57/10. ISBN 978-1-921557-67-5. 58 pp.

Mosley, L.M., Palmer, D., Leyden, E., Cook, F., Zammit, B., Shand, P., Baker, A., Fitzpatrick, R.W., (2014). Acidification of floodplains due to river level decline during drought. Journal of Contaminant Hydrology 161, 10-23.

National Working Party on Acid Sulfate Soils (2000). National strategy for the management of coastal acid sulfate soils. NSW Agriculture, Wollongbar. http://www.mincos.gov.au/pdf/natass.pdf (Accessed March 2007.)

Muhs DR (1984) Intrinsic thresholds in soil systems. Physical Geography 5, 99-110.

Murray-Darling Basin Authority (2010). Detailed Assessment of Acid Sulfate Soils in the Murray-Darling Basin: Protocols for sampling, field characterisation, laboratory analysis and data presentation. Murray–Darling Basin Authority Publication 57/10.

Murray-Darling Basin Commission (2006a) The Barmah-Millewa Forest Icon Site Environmental Management Plan 2006-2007. MDBC Publication No. 30/06.

Murray-Darling Basin Commission (2006b) The Gunbower-Koondrook-Perricoota Forest Icon Site Environmental Management Plan 2006-2007. MDBC Publication No. 32/06.

Murray-Darling Basin Commission (2006c) The Hattah Lakes Icon Site Environmental Management Plan 2006-2007. MDBC Publication No. 31/06.

Murray-Darling Basin Commission (2006d) The River Murray Channel icon site environmental management plan 2006-2007. MDBC Publication No. 35/06.

Pons, L.J. (1973). Outline of the genesis, characteristics, classification and improvement of acid sulphate soils. In 'Proceedings of the 1972 (Wageningen, Netherlands) International Acid

Sulphate Soils Symposium, Volume 1.' (Ed. H. Dost) Pp 3-27. International Land Reclamation Institute Publication 18. (Wageningen, Netherlands).

Preda M, Cox ME (2001). Trace metals in acid sediments and waters, Pimpama catchment, southeast Queensland, Australia. Environmental Geology 40: 755-768.

Rayment GE, Higginson FR (1992). 'Australian laboratory handbook of soil and water chemical methods.' Melbourne, Inkata Press.

Rayment G.E., Lyons D.J.(2010). Soil chemical methods - Australasia CSIRO Publishing: Collingwood.

Rigby, P.A., Dobos, S., Cook, F.J., Goonetilleke, A., (2006). Role of organic matter in framboidal pyrite oxidation. Science of the Total Environment 367, 847-854.

Sammut J, Callinan RB, Fraser GC (1993). The impact of acidified water on freshwater and estuarine fish populations in acid sulphate soil environments. Proceedings National Conference on Acid Sulphate Soils, Coolangatta, NSW. 24-25 June 1993, CSIRO, NSW Agriculture, Tweed Shire Council.

Shand P, Edmunds WM (2008) The baseline inorganic chemistry of European groundwaters. In 'Natural Groundwater Quality'. (Eds WM Edmunds, P Shand) pp. 21-58. (Blackwell Publishing: Oxford).

Shand P, Grocke S, Kirby J & Baker AK (2012) The characterisation of metal and metalloid contaminants in re-flooded Acid Sulfate Soils of Lake Alexandrina, South Australia. Water for a Healthy Country Flagship Report series ISSN: 1835-095X 58pp.

Shand P, Fitzpatrick RW, Thomas M, Merry RH, Grocke S, Thomas B, Creeper N, Hollis B, Marsland K, Fogg M, Turner R & Goode J (2010a) Mobilisation of metals and acidity during reflooding of a wetland containing acid sulfate soils. In, P. Birkle & I.S. Torres-Alvarado (eds.), Water-Rock Interaction 13, CRC Press Balkema, London, 303-306.

Shand P, Merry R, Grocke S, Thomas M, Fitzpatrick RW, Thomas B, Baker A & Creeper N (2010b) Water and soil quality impacts during reflooding of Nelwart Lagoon, South Australia. CSIRO: Water for a Healthy Country National Research Flagship.

Shand P, Merry RH, and Fitzpatrick, RW (2008a) Acid sulfate soil assessment of wetlands associated with Lock 8 and Lock 9 weir pools. Prepared for Murray-Darling Basin Board. CSIRO Land and Water Science Report 40/08. CSIRO, Adelaide, 88 pp.
http://www.clw.csiro.au/publications/science/2008/sr40-08.pdf

Shand P, Merry RH & Fitzpatrick RW (2008b) Acid sulfate soil assessment of Noora Basin, South Australia Prepared for Murray-Darling Basin Board. CSIRO Land and Water Science Report 41/08. CSIRO, Adelaide, 69 pp.
http://www.clw.csiro.au/publications/science/2008/sr41-08.pdf

Shand P, Merry RH, Fitzpatrick RW & Thomas M (2009) Acid sulfate soil assessment of disconnected wetlands between Lock 1 and Lock 5, River Murray, South Australia. Client Report. CSIRO: Water for a Healthy Country National Research Flagship. 197 pp
http://www.clw.csiro.au/publications/waterforahealthycountry/2009/wfhc-Murray-acid-sulfate-assessment.pdf

Simpson, S.L., Fitzpatrick, R.W., Shand, P., Angel, B., Sparado, D.A. & Mosley, L. (2010) Climate-driven mobilisation of acid and metals from acid sulfate soils. Marine and Freshwater Research, 61, 129-138.

Simpson SL, Fitzpatrick RW, Shand P, Angel BM, Spadaro D, Merry RH, Thomas M (2008) Acid, metal and nutrient mobilisation following rewetting of acid sulfate soils in the Lower Murray. Prepared for the South Australian Environmental Protection Agency. CSIRO Land and Water Science Report 27/08, Bangor, NSW.

Soil Survey Staff (2014) Keys to soil taxonomy, 12th edn. USDA-Natural Resources Conservation Service, Washington, DC

Sullivan LA, Burton ED, Bush RT, Watling K, Bush M (2008). Acid, metal and nutrient mobilisation dynamics in response to suspension of MBOs in freshwater and to freshwater inundation of dried MBO and sulfuric soil materials. Lismore, NSW, Southern Cross GeoScience, Report Number 108.

Sullivan LA, Bush RT (1997). Quantitative elemental microanalysis of roughsurfaced soil specimens in the scanning electron microscope using a peak-to background method. Soil Science 162: 749-757.

Sullivan LA, Bush RT, Fyfe D (2002). Acid sulfate soil drain ooze: Distribution, behaviour and implications for acidification and deoxygenation of waterways. Acid sulfate soils in Australia and China. C. Lin, M. D. Melville and L. A. Sullivan. Bejing, China, Science Press: 91-99.

Sullivan LA, Bush RT, McConchie DM (2000). A modified chromium-reducible sulfur method for reduced inorganic sulfur: optimum reaction time for acid sulfate soil. Australian Journal of Soil Research 38: 729-734.

Sullivan LA, Fitzpatrick RW, Bush RT, Burton ED, Shand P, Ward NJ (2010). The classification of acid sulfate soil materials: further modifications. Southern Cross GeoScience Technical Report No. 310. April, 2010

Sullivan LA, Ward NJ, Bush RT (2001). Chemical analysis for acid sulfate soil management. Proceedings of the 2nd Australia and New Zealand Conference on Environmental Geotechnics - Geoenvironment 2001, Newcastle, Australian Geomechanics Society Inc.

Sullivan LA, Ward NJ, Bush RT, Burton ED (2009). Improved identification of sulfidic soil materials by a modified incubation method. Geoderma 149: 33-38.

Sullivan LA, Ward NJ, Bush RT, Lin C (2002). 'Evaluation of approaches to the chemical analysis of acid sulfate soil.' Acid sulfate soils in Australia and China, Beijing, Science Press.

Sundstrom R, Aström M, Osterholm P (2002). Comparison of the metal content in acid sulfate soil runoff and industrial effluents in Finland. Environmental Science & Technology 36: 4269-4272.

Thomas, BP., Fitzpatrick RW, Shand, P., Simpson S and Jayalath, N. (2011) Assessment of Acid Sulfate Soil materials in Ramsar wetlands of the Murray Darling Basin: Banrock Station Wetland Complex. Prepared for Murray-Darling Basin Authority (MDBA) by CSIRO Water for a Healthy Country Flagship. [PDF 3.9 MB] http://www.mdba.gov.au/kid/files/911-AASSM-Banrock.pdf

Ward NJ, Sullivan LA, Bush RT (2002) Sulfide oxidation and acidification of acid sulfate soil materials treated with CaCO3 and seawater-neutralised bauxite refinery residue. Australian Journal of Soil Research 40, 1057-1067.

Ward, N.J., Bush, R.T., Burton, E.D., Appleyard, S., Wong, S., Sullivan, L.A., Cheeseman, P.J., (2010). Monosulfidic black ooze accumulations in sediments of the Geographe Bay area, Western Australia. Marine Pollution Bulletin 60, 2130-2136.

10. Appendix 1 – Australian acid sulfate soil identification key

Australia's current national soil classification (Isbell 1996) and other internationally recognised classification systems such as Soil Taxonomy (Soil Survey Staff 2003) require considerable expertise and experience to be used effectively. More importantly, these classification systems do not yet incorporate new acid sulfate soil terminologies such as: (i) monosulfidic, hypersulfidic and hyposulfidic material (Sullivan *et al.* 2008) and (ii) subaqueous soils, which is used in the nationally consistent legend of "The Atlas of Australian Acid Sulfate Soils" (Fitzpatrick et al. 2010; available on the Australian Soil Resource Information System: www.asris.gov.au). To assist users to identify types and subtypes of soils a user-friendly Soil Identification Key was developed to more readily define and identify the various types and subtypes of acid sulfate soil and non-acid sulfate soil (see Fitzpatrick et al. 2010, Fitzpatrick 2012). The key is designed for people who are not experts in soil classification systems such as the Australian Soil Classification (Isbell 1996). Hence it has been used to deliver soil-specific land development and soil management packages to advisors, planners and engineers working in the Murray-Darling Basin.

The soil identification key uses non-technical terms to categorise acid sulfate soils and other soils in terms of attributes that can be assessed in the field by people with limited soil classification experience. Attributes include water inundation (subaqueous soils), soil cracks, structure, texture, colour, features indicating water logging and 'acid' status – already acidified, i.e. sulfuric material, or with the potential to acidify, i.e. sulfidic material– and the depths at which they occur or change in the soil profile.

The key consists of a systematic arrangement of soils into 5 broad acid sulfate soil types, each of which can be divided into up to 6 soil subtypes. The key layout is bifurcating, being based on the presence or absence of particular soil profile features (i.e. using a series of questions set out in a key). A soil is allocated to the first type whose diagnostic features it matches, even though it may also match diagnostic features further down the key. The key uses a collection of plain language names for types and subtypes of ASS in accordance with the legend for the Atlas of Australian Acid Sulfate Soils (Fitzpatrick et al. 2010; Fitzpatrick 2012). It recognises the following five acid sulfate soil types: (i) Subaqueous Soils, (ii) Organic Soils, (iii) Cracking Clay Soils, (iv) Sulfuric Soils and (v) Hypersulfidic Soils (Table A1-1). These are further sub-divided into 18 soil subtypes based on occurrence of sulfuric material, hypersulfidic material, clayey or sandy layers; monosulfidic material and firmness.

Table A1-1: Summary soil identification key for acid sulfate soils. After finding the soil type, use Table A2.2 to find the soil subtype.
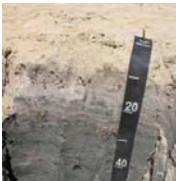
Diagnostic features for Soil Type	Soil Type
Does the soil occur in shallow permanent flooded environments (typically not greater than 2.5 m)? No ↓ Yes →	**Subaqueous soil**
Does the upper 80cm of soil consist of more than 40 cm of organic material (peat)? No ↓ Yes →	 **Organic soil**
Does the soil develop cracks at the surface OR in a clay layer within 150 cm of the soil surface OR have slickensides (polished and grooved surfaces between soil aggregates), **AND** is the subsoil uniformly grey coloured (poorly drained or very poorly drained)? No ↓ Yes →	**Cracking clay soil**
Does a sulfuric layer (pH<4) occur within 150 cm of the soil surface, **AND** is the subsoil uniformly grey coloured (poorly drained)? No ↓ Yes →	**Sulfuric soil**
Does sulfidic material (pH>4 which changes on ageing to pH<4) occur within 150 cm of the soil surface, **AND** is the subsoil uniformly grey coloured (poorly drained)? No ↓ Yes →	**Hypersulfidic soil**
Does sulfidic material (pH>4 which does not change on ageing to pH<4) occur within 150 cm of the soil surface, **AND** is the subsoil uniformly grey coloured (poorly drained)? No ↓ Yes →	**Hyposulfidic soil**
Other soils	**Other soils**

Table A1-2: Soil identification key for acid sulfate soil subtypes in this report

Soil Type	Diagnostic features for Soil Subtype		Soil Subtype
Subaqueous soil No ↓ Yes →	Does **sulfuric** material occur within 150 cm of the soil surface? No ↓ Yes →	Does the upper 80cm of soil consist of more than 40 cm of organic material (peat)? No ↓ Yes →	**Sulfuric subaqueous organic soil**
	↓	Does a clayey layer with slickensides occur within 150 cm of the soil surface? No ↓ Yes →	**Sulfuric subaqueous clay soil**
		→	**Sulfuric subaqueous soil**
	Does **hypersulfidic** material (pH>4 which changes on ageing to pH<4) occur within 150 cm of the soil surface? No ↓ Yes →	Does the upper 80cm of soil consist of more than 40 cm of organic material (peat)? No ↓ Yes →	**Hypersulfidic subaqueous organic soil**
	↓	Does a clayey layer with slickensides occur within 150 cm of the soil surface? No ↓ Yes →	**Hypersulfidic subaqueous clayey soil**
		→	**Hypersulfidic subaqueous soil**
	Does **hyposulfidic** material (pH>4 which does not change on ageing to pH<4) occur within 150 cm of the soil surface? No ↓ Yes →	Does the upper 80cm of soil consist of more than 40 cm of organic material (peat)? No ↓ Yes →	**Hyposulfidic subaqueous organic soil**
	↓	Does a clayey layer with slickensides occur within 150 cm of the soil surface? No ↓ Yes →	**Hyposulfidic subaqueous clayey soil**

Soil Type	Diagnostic features for Soil Subtype		Soil Subtype
		→	**Hyposulfidic subaqueous soil**
		→	**Subaqueous soil**
Not subaqueous soil No ↓ Yes →	Does **sulfuric** material occur within 150 cm of the soil surface? No ↓ Yes →	Does the upper 80cm of soil consist of more than 40 cm of organic material (peat)? No ↓ Yes →	**Sulfuric organic soil**
	↓	Does a clayey layer with slickensides occur within 150 cm of the soil surface? No ↓ Yes →	**Sulfuric clayey soil**
	→	→	**Sulfuric soil**
	Does **hypersulfidic** material (pH>4 which changes on ageing to pH<4) occur within 150 cm of the soil surface? No ↓ Yes →	Does the upper 80cm of soil consist of more than 40 cm of organic material (peat)? No ↓ Yes →	**Hypersulfidic organic soil**
	↓	Does a clayey layer with slickensides occur within 150 cm of the soil surface? No ↓ Yes →	**Hypersulfidic clayey soil**
	→	→	**Hypersulfidic soil**
	Does **hyposulfidic** material (pH>4 which does not change on ageing to pH<4) occur within 100 cm of the soil surface? No ↓ Yes →	Does the upper 80cm of soil consist of more than 40 cm of organic material (peat)? No ↓ Yes →	**Hyposulfidic organic soil**
	↓	Does a clayey layer with slickensides occur within 150 cm of the soil surface? No ↓ Yes →	**Hyposulfidic clayey soil**

Soil Type	Diagnostic features for Soil Subtype		Soil Subtype
		→	Hyposulfidic soil
	→	→	Soil
Other soils			Hydrosol - sandy or loamy

n-Value or Index of Squishiness

The n-Value via the index of squishiness is a field estimate of mechanical properties that describes the ability of a saturated soil to support a load. The n-value (sometimes referred to as ``index of squishiness") concept was developed by Pons and Zonneveld (1965) to define the degree of physical ripening of soft sediments (i.e. "**pelagic ooze**" materials) as they dewater. It is a measure of the physical bearing capacity of a soil material. The following definition has been modified from Fanning and Fanning (1989) and Soil Survey Staff (1992). It is mathematically defined for Soil Taxonomy for soil materials that are not thixotropic as follows:

n=(A-0.2R)/(L+3H)
A=% water in soil in field condition,
(calculated on a dry-soil basis);

R=% silt + sand

L=% clay (<2 μm);

H=% organic matter (organic carbon x 1.724).

Photograph of Professor J. L Pons undertaking the "index of squishiness" or n-value test. The photograph was taken by Rob Fitzpatrick in the Mekong Delta, Vietnam in 1992 during the 4th International Acid Sulfate Soil Conference.

This simple field test involves squeezing a fist-full of soil. If the soil flows between the fingers but with difficulty (i.e., slightly fluid), the n value is likely between 0.7 and 1.0. If the soil flows easily (i.e., moderately fluid or very fluid), it is greater than 1.0. If no soil flows between the fingers (non-fluid), it is less than 0.7. An n-value of 0.7 of more is used in Soil Taxonomy (Soil Survey, 1992) to define certain classes considered to have *a low bearing capacity.* Sandy materials are considered to be physically ripe regardless of their water content.

n= <0.7: Ripe material is firm, not particularly sticky, and cannot be squeezed between fingers.

n= 0.7 to 1.0: Nearly Ripe Material is fairly firm; it tends to stick to the hands, and can be kneaded but not squeezed between fingers. Its water content is between 55 and 65%. It is not churned up, it will support by weight of stock and ordinary vehicles;

n= 1.0 - 1.4: Half Ripe Mud is fairly soft; sticky; and can be squeezed between fingers. Its water content is between 65 and 75% and its mechanical strength when disturbed is low. A man will sink ankle to knee deep unless supported by vegetation.

n= 1.4 - 2.0: Practically Unripe Mud is very soft; sticks fast to everything, and can be squeezed between fingers by very gentle pressure. Its water content is between 70 and 80%. A man will sink to his thighs unless supported by vegetation.

n= > 2.0: Totally Unripe Mud is fluid; it flows between fingers. In predominantly mineral sediments the water content is >80% by mass.

Fanning, D.S. and Fanning, M.C.B. (1989). Soil: Morphology, genesis, and classification. John Wiley and Sons, New York.

Pons J.L. and Zonneveld, I.S. (1965). Soil ripening and soil classification. Initial soil formation in alluvial deposits and classification of the resulting soils. Inst. Land Reclam. and Impr. Pub. 13. Wageningen, The Netherlands. 128pp.

11. Appendix 2 –Field photographs (electronic file)

12. Appendix 3 – Mineralogy: X-ray diffraction

The samples were ground in an agate mortar and pestle and gently back pressed into stainless steel sample holders for X-ray diffraction analysis. XRD patterns were recorded with a PANalytical X'Pert Pro Multi-purpose Diffractometer using Fe filtered Co K alpha radiation, automatic divergence slit, 2° anti-scatter slit and fast X'Celerator Si strip detector. The diffraction patterns were recorded in steps of 0.017° 2 theta with a 0.5 second counting time per step.

Sample ID	Sample type	Konyaite	Gypsum	Bloedite	Thenardite	Hexahydrite	Epsomite
RBA 1.1a	**White salt**	CD	M	T	SD	CD	SD

RBA1.1 White efflorescence
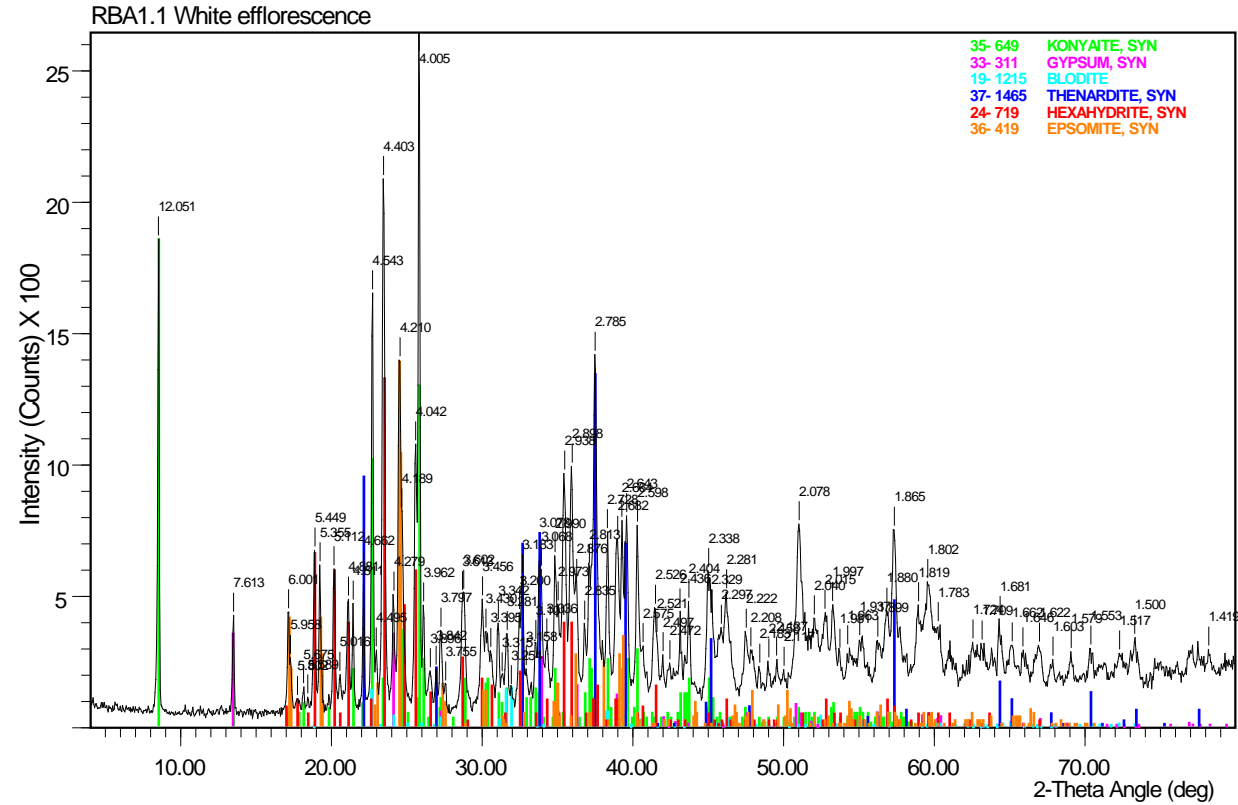
File Name: c:\...\x'pert~1\25538.xpt

13. Appendix 4 – pH incubation data

pH incubation data (electronic file).

14. Appendix 5 – Acid Base Accounting, AVS, Total Organic carbon and Nitrogen data

Acid Base Accounting data (electronic file)

* NOTE:

1 - All analysis is Dry Weight (DW) - samples dried and ground immediately upon arrival (unless supplied dried and ground)

2 - Samples analysed by SPOCAS method 23 (i.e. Suspension Peroxide Oxidation Combined Acidity & sulfate) and 'Chromium Reducible Sulfur' technique (S_{CR} - Method 22B)

3 - Methods from Ahern, CR, McElnea AE , Sullivan LA (2004). *Acid Sulfate Soils Laboratory Methods Guidelines.* QLD DNRME.

4 - Bulk Density is required for liming rate calculations per soil volume. Lab. Bulk Density is no longer applicable - field bulk density rings can be used and dried/ weighed in the laboratory.

5 - **ABA Equation**: **Net Acidity = Potential Sulfidic Acidity (i.e. Scrs or Sox) + Actual Acidity + Retained Acidity - measured ANC/FF   (with FF currently defaulted to 1.5)**

6 - The neutralising requirement, lime calculation, includes a 1.5 safety margin for acid neutralisation (an increased safety factor may be required in some cases)

7 - For Texture: coarse = sands to loamy sands: medium = sandy loams to light clays: fine = medium to heavy clays and silty clays

8 - .. denotes not requested or required

9 - SCREENING, CRS, TAA and ANC are NATA accredited but other SPOCAS segments are currently not NATA accredited

10- Results at or below detection limits are replaced with '0' for calculation purposes.

11 - Projects that disturb >1000 tonnes of soil, the ≥0.03% S classification guideline would apply (refer to acid sulfate management guidelines).

(Classification of potential acid sulfate material if: coarse Sc≥0.03%S or 19mole H $^{+}$/t: medium Scr≥0.06%S or 37mole H^{+}/t: fine Scr≥0.1%S or 62mole H^{+}/t)
- as per QUASSIT Guidelines

15. Appendix 6 – Metal Extraction Data

Metal Extraction data (electronic file)

This page can be removed if you are using pre-printed report covers. If you are not using pre-printed covers this page is to remain for all electronic and other printing types.

Specific contact details are to be included at the front of this report above the Distribution list, Copyright and Disclaimers.