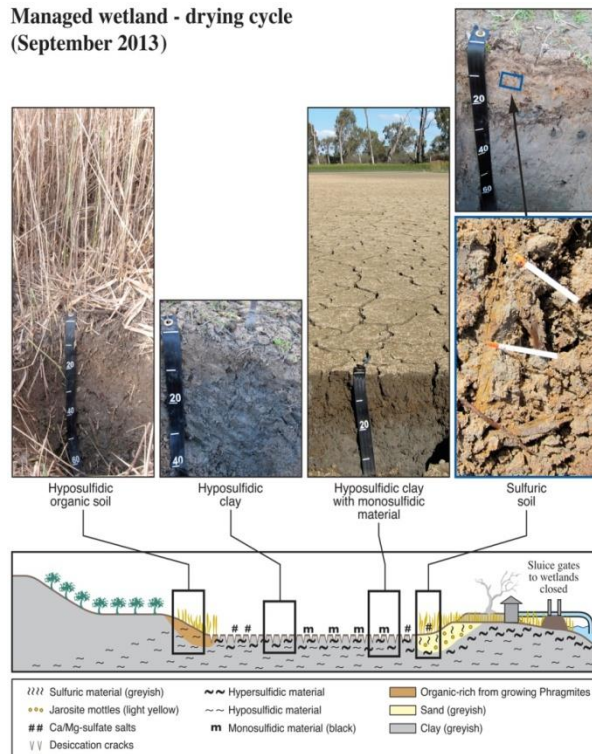


Acid Sulfate Soil Assessment and Monitoring of the Banrock Station wetland

Managed wetland - drying cycle
(September 2013)



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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

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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 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 October 2008 to September 2013 (~ 6 years). The monitoring data during the period from 2008 to 2013 has shown that successive wetting & drying cycles in the:

- **Lakebed regions** has caused **Hypersulfidic clayey soils** to transform to **Hyposulfidic clayey soils** (i.e. decrease and/or preservation of pyrite and/or increase in carbonates/neutralisation capacity)
- **Inner shoreline regions** caused **Sulfuric soils** to transform to **Hyposulfidic soils** (i.e. decrease and/or preservation of pyrite and/or increase in carbonates/neutralisation capacity)
- **Outer shoreline regions** has not caused Sulfuric soils to transform to other acid sulfate soil sub-types (i.e. they have remained in Static/Dynamic balance)

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.

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**.
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- (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 shoreline**. 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, NH₄, 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, for example 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.

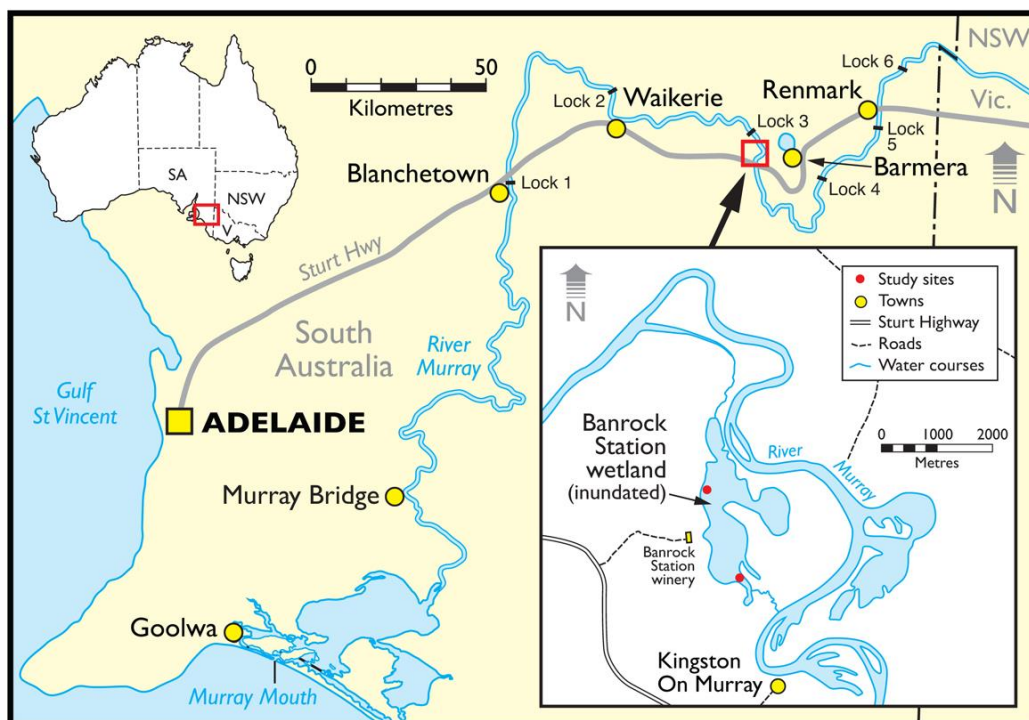


Figure 1-1 Locality map showing the Banrock Station Wetland Complex, the two groups of sites re-sampled on 2nd September, 2013 (sites RBAC-01 to RBAC-04 located in the southern section where the water enters the wetlands and sites RBAC-06 and RBAC-07, which is located in the northern section near the 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 (FeS₂). 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 and National Committee on Soils & Terrain 2016), 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 northern 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: (i) 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 and (ii) in the 2nd edition of the Australian Soil Classification (Isbell and National Committee on Soils & Terrain, 2016). This report follows these recommendations. Acid sulfate soils are essentially soils containing detectable sulfide minerals, principally pyrite (FeS₂) 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 in the 2nd edition of the Australian Soil Classification (Isbell and National Committee on Soils & Terrain, 2016).

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 – (Isbell and National Committee on Soils & Terrain 2016). 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 incubation.

Hyposulfidic material - (Isbell and National Committee on Soils & Terrain 2016): 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 a 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 (Isbell and National Committee on Soils & Terrain 2016). 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 pH_w 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 bypasses 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. H₂S – rotten egg gas and methyl thiols) as well as oxidising odours (SO₂) 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 <i>et al.</i> (2002) – for redoximorphic features

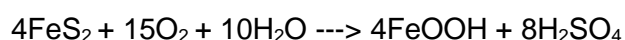
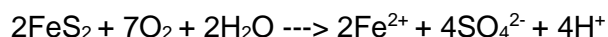
2.2 Laboratory soil analysis methods

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: FeS₂) may occur which produce acidity, including:



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} (pH _w)	Measures the current sampled status of the soil acidity or alkalinity	pH meter; 1:1 soil:water (Rayment and Higginson 1992)
pH _{peroxide} (pH _{ox})	Measures the potential end oxidized status of the soil pH	pH meter; Method 4E1 (Rayment and Higginson 1992)
pH _{incubation} (pH _{inc})	Represents a scenario for soil sample on exposure to air (oxygen) for a specified period of time	Fitzpatrick <i>et al.</i> 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 (pH _{KCL} >6.5) for deciding to test for acid neutralising capacity.	pH meter. Method 23A (Ahern <i>et al.</i> 2004)
Chromium reducible sulfur (S _{CR})	Identifies presence of sulfides. For acid base accounting	Method 23B (Ahern <i>et al.</i> 2004)
Titrateable actual acidity (TAA)	Identifies soil acidity. For acid base accounting.	Method 23F (Ahern <i>et al.</i> 2004)
Acid neutralising capacity (ANC) (where pH _{KCl} >6.5)	Identifies neutralising capacity of soil. For acid base accounting.	Method 19A2 (Ahern <i>et al.</i> 2004)
Retained acidity (RA)	Identifies stored soil acidity. For acid base accounting.	Method 20J (Ahern <i>et al.</i> 2004)
Net acidity (NA)	Identifies the soil acidity (or alkalinity)	Calculated (Ahern <i>et al.</i> 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

FIELD AND LABORATORY METHODS

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 cm³ polypropylene reactors. The evolved H₂S(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 $96 \pm 4\%$. 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 °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 PO₄ were analysed by colorimetric analysis using an Auto Analyser; Br, F and SO₄ 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) (Agilent 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 α 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 0.45µm 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±5°C.
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 to nitrogen ratios (C:N) are given in Table 3-3. The information gained from this data with 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 (Eastings and Northings; 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 brownish 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.

SOIL PROFILE ASSESSMENT

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

¹See Figure 1-2 for site locality

² See photographs in Figure 3-1

³See 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 3-6). This soil classifies as a Eutrophic, Sulfuric, Redoxic Hydrosol in accordance with the Australian Soil Classification 2nd ed. (Isbell and National Committee on Soils & Terrain, 2016; Table 3-5) and Hypothionic Gleysol (Drainic, Hypersulfidic) in accordance with the WRB (IUSS Working Group WRB, 2014; Table 3-6). 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: (i) “Sulfuric subaqueous soil” using the Australian ASS classification key (Fitzpatrick *et al.* 2008; Fitzpatrick 2013), (ii) Eutrophic, Sulfuric, Subaqueous Hydrosol using Isbell and National Committee on Soils & Terrain (2016; Table 3-5) and (iii) Subaquatic Hypothionic Gleysol (Hypersulfidic) using WRB (IUSS Working Group WRB, 2014; Table 3-6).

However, 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. In this report we have proposed the subgroups Typic Sulfowassept to describe the active subaqueous ASS in the Banrock station wetland complex (Table 3-4; Table 3-6). This involves the creation in the Inceptisol sub order, Wassepts with the new great group Sulfowassepts. These proposals are currently being drafted by Fitzpatrick *et al.* 2016 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 3-6).

All the other soils sampled on 2nd September, 2015 contained Hyposulfidic material and classified as Hyposulfidic 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). Similarly, The Australian Soil Classification 2nd edition (Isbell and National Committee on Soils & Terrain, 2016; Table 3-5) is also able to adequately classify these soils as Eutrophic, **Hyposulfidic**, Redoxic Hydrosols. The WRB (IUSS Working Group WRB, 2014; Table 3-6) also accommodates these soils by classifying them as Oxygleyic Gleysol (Drainic, **Hyposulfidic**).

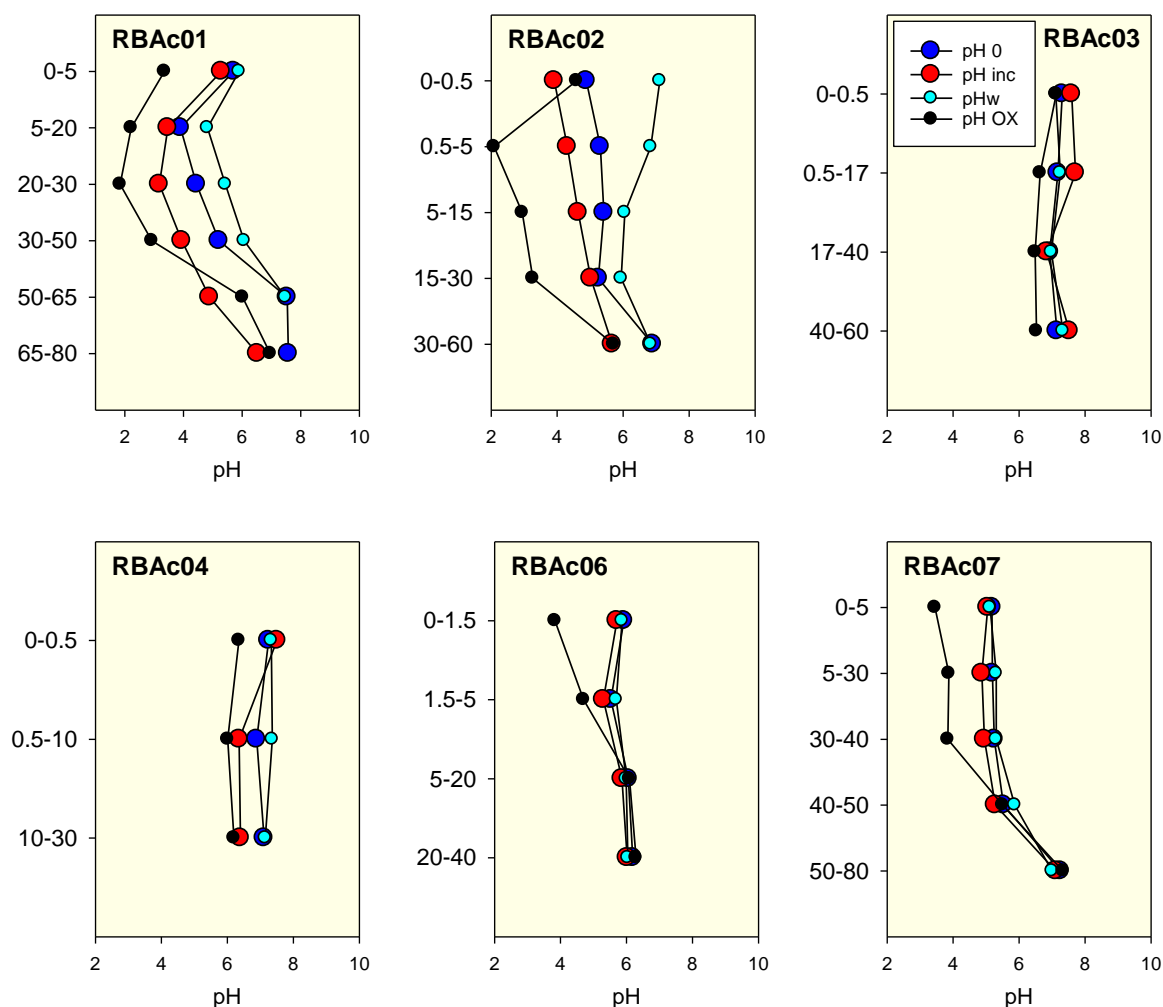


Figure 3-3: Initial incubation pH (pH_0 ; time zero), incubation pH after 16 weeks (pH_{inc}), pH after oxidation with hydrogen peroxide ($pH_{peroxide}$ or pH_{OX}), pH measured in 1:1 soil:water ratio (pH_w or pH_{water}) plotted against depth for each profile collected.

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, also 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^+ $tonne^{-1}$ (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 clays 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% organic carbon), with large negative net acidity, moderate levels of ANC, no TAA and minor RIS (S_{CR}) (Figure 3-4).

SOIL PROFILE ASSESSMENT

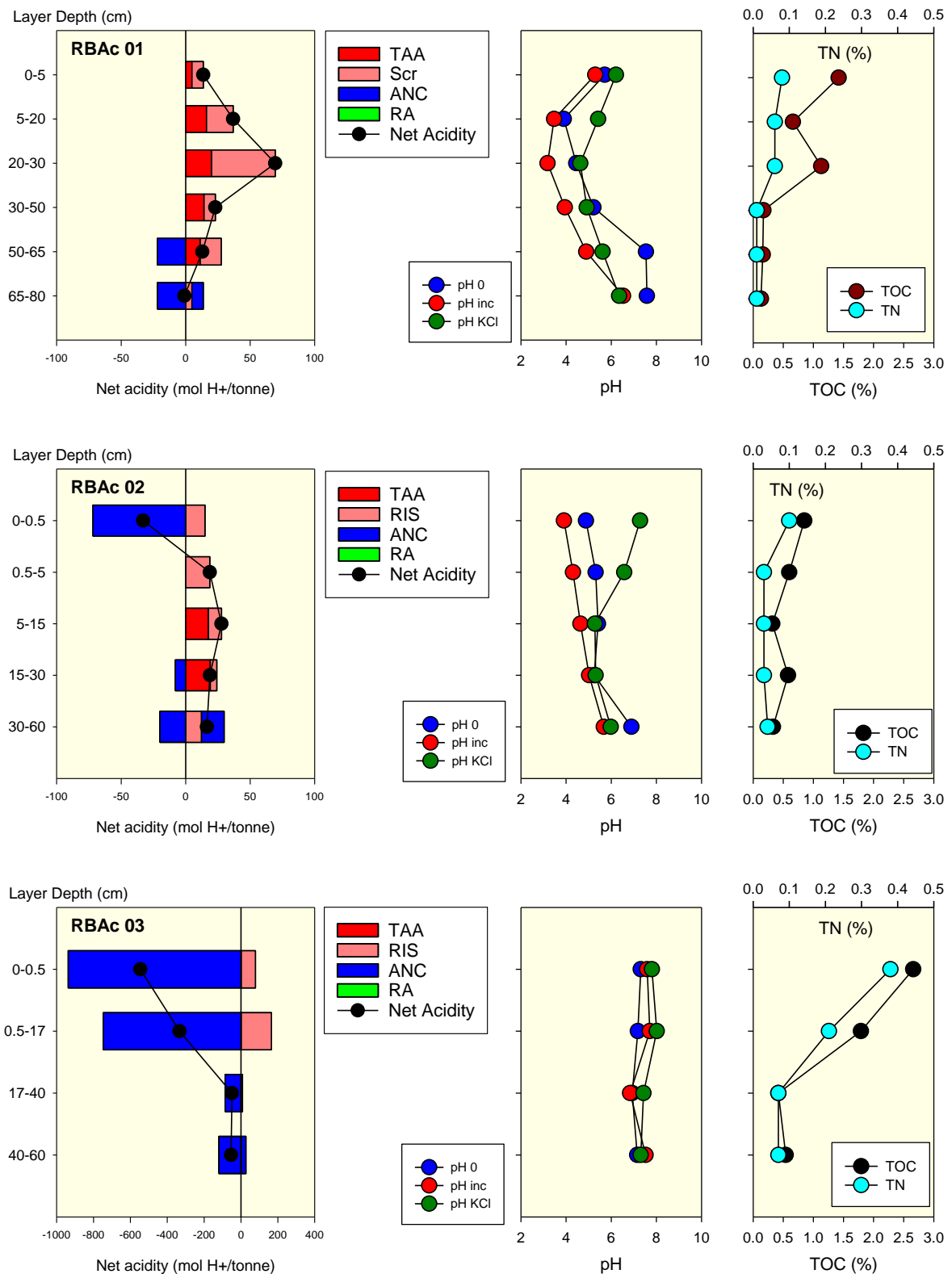


Figure 3-4 Acid base accounting [Titratable Actual Acidity (TAA), Reduced Inorganic Sulfur (RIS or sulfide-S or S_{CR} or Cr-reducible S), Acid Neutralising Capacity (ANC), Retained Acidity (RA) and Net Acidity (NA)], initial incubation pH (pH 0; time zero), incubation pH after 16 weeks (pH inc) and 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.

SOIL PROFILE ASSESSMENT

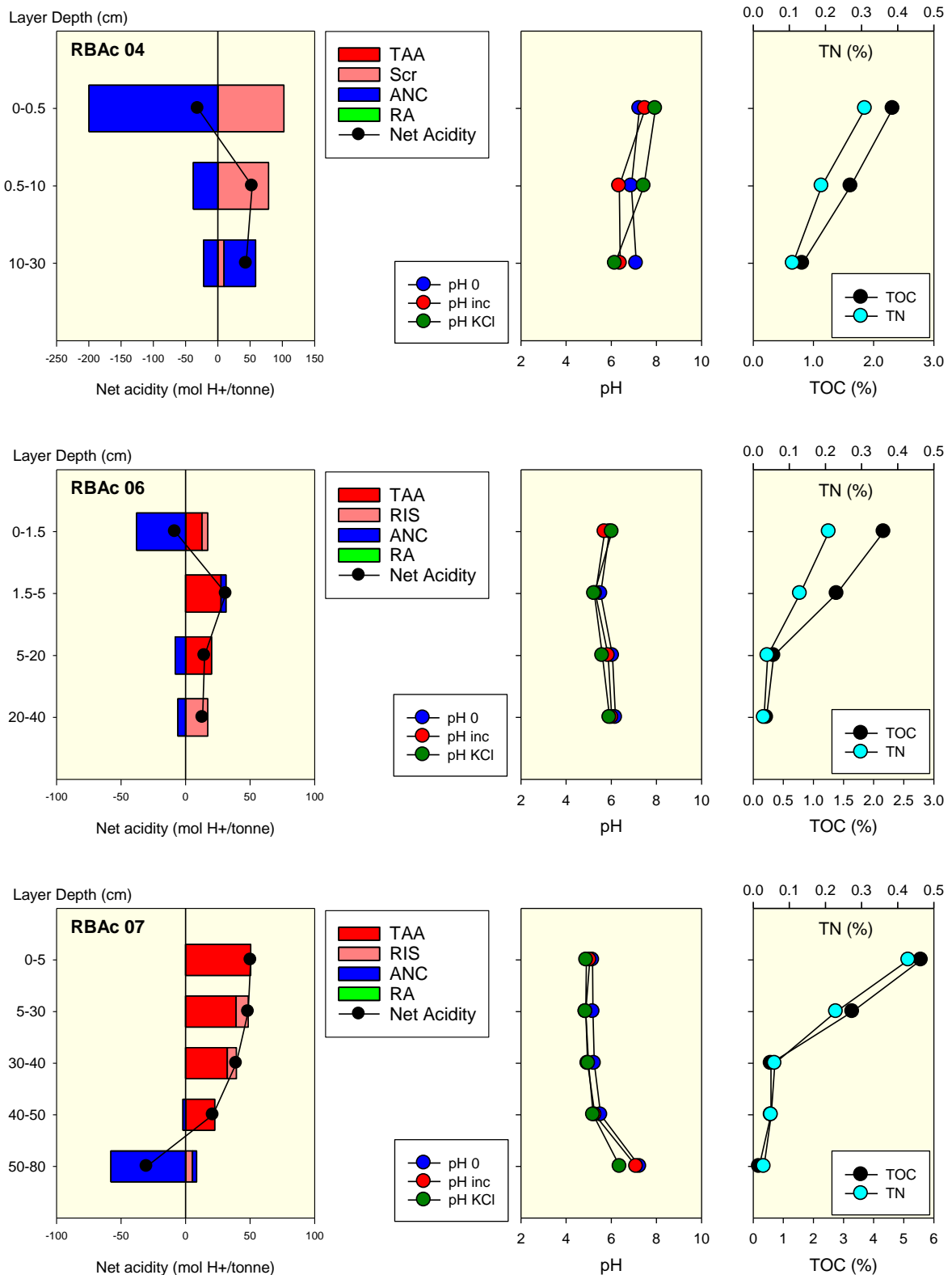


Figure 3-4 *continued*: Acid base accounting [Titratable Actual Acidity (TAA), Reduced Inorganic sulfur (RIS or sulfide-S or S_{CR} or Cr-reducible S), Acid Neutralising Capacity (ANC), Retained Acidity (RA) and Net Acidity (NA)], initial incubation pH (pH 0; time zero), incubation pH after 16 weeks (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' (RBA01) 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 conducted on 2nd September 2013, the soil profile on the outer edge of the wetland complex (RBA01) in the southern segment remained classified as a 'sulfuric soil' because the pH at 5-20 cm remained below 4 as measured during the previous investigations on 23rd May and 3rd October 2008. As well, in all the other horizons the pH before and after incubation for 16 weeks had not changed significantly indicating that the materials originally classified as hyposulfidic and hypersulfidic did not change (Table 3-3).

However, in the present survey a higher proportion of soils in the lower lying southern and northern segments of the wetland (e.g., dry lakebed) 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 in rainfall, 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 [$\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$] and hexahydrite ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) with subdominant epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and thenardite (Na_2SO_4), followed by minor amounts of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and trace amounts of bloedite ($\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$). 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) formed very loose and fluffy salts on the sides and base of the wooden posts and soft crusts on soil surfaces. They 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 lake bed, 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. The ratio also indicates 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 acid sulfate soil material is based on the definition in the 2nd edition of the Australian Soil Classification (Isbell and National Committee on Soils & Terrain, 2016)

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)

SOIL PROFILE ASSESSMENT

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 23 rd May 2008 (a)		² Reflooded 3 rd October 2008 (b)		³ Dry 2 nd September 2013 (c)	
Profile No	Identification key ⁴	Profile No	Identification key ⁴	Profile No	Identification key ⁴
BAa 1	Sulfuric soil	RBAb 1	Sulfuric subaqueous soil	RBAc 1	Sulfuric soil
RBAa 2	Sulfuric soil	RBAb 2	Sulfuric subaqueous soil	RBAc 2	Hyposulfidic soil
RBAa 3	Hypersulfidic clay	RBAb 3	Hypersulfidic subaqueous clay	RBAc 3	Hyposulfidic clay
RBAa 4	Hypersulfidic clay	RBAb 4	Hypersulfidic subaqueous clay	RBAc 4	Hyposulfidic clay
RBAa 5	Hypersulfidic clay	RBAb 5	Hypersulfidic subaqueous clay	RBAc 5	Hyposulfidic clay
RBAa 6	Hypersulfidic clay	RBAb 6	Hypersulfidic subaqueous clay	RBAc 6	Hyposulfidic clay
RBAa 7	Hypersulfidic clay	RBAb 7	Hypersulfidic subaqueous clay	RBAc 7	Hyposulfidic clay
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 report

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 the Australian Soil Classification for soils sampled previously (23rd May 2008 and 3rd October 2008) and in the current investigation (2nd September, 2013)

¹ Dry 23 rd May 2008 (a)		² Reflooded 3 rd October 2008 (b)		³ Dry 2 nd September 2013 (c)	
Profile No	Australian Soil Classification ⁴	Profile No	Australian Soil Classification ⁴	Profile No	Australian Soil Classification ⁴
BAa 1	Eutrophic, Sulfuric, Redoxic Hydrosol	RBAb 1	Eutrophic, Sulfuric, Subaqueous Hydrosol	RBAc 1	Eutrophic, Sulfuric, Redoxic Hydrosol
RBAa 2	Eutrophic, Sulfuric, Redoxic Hydrosol	RBAb 2	Eutrophic, Sulfuric, Subaqueous Hydrosol	RBAc 2	Eutrophic, Hyposulfidic, Redoxic Hydrosol
RBAa 3	Eutrophic, Hypersulfidic, Redoxic Hydrosol	RBAb 3	Eutrophic, Hypersulfidic, subaqueous clay	RBAc 3	Eutrophic, Hyposulfidic, Redoxic Hydrosol
RBAa 4	Eutrophic, Hypersulfidic, Redoxic Hydrosol	RBAb 4	Eutrophic, Hypersulfidic, Subaqueous Hydrosol	RBAc 4	Eutrophic, Hyposulfidic, Redoxic Hydrosol
RBAa 5	Eutrophic, Hypersulfidic, Redoxic Hydrosol	RBAb 5	Eutrophic, Hypersulfidic, Subaqueous Hydrosol	RBAc 5	Eutrophic, Hyposulfidic, Redoxic Hydrosol
RBAa 6	Eutrophic, Hypersulfidic, Redoxic Hydrosol	RBAb 6	Eutrophic, Hypersulfidic, Subaqueous Hydrosol	RBAc 6	Eutrophic, Hyposulfidic, Redoxic Hydrosol
RBAa 7	Eutrophic, Hypersulfidic, Redoxic Hydrosol	RBAb 7	Eutrophic, Hypersulfidic, Subaqueous Hydrosol	RBAc 7	Eutrophic, Hyposulfidic, Redoxic Hydrosol
RBAa 8	Humose-Acidic, Hypersulfidic, Redoxic Hydrosol	RBAb 8	Humose-Acidic, Hypersulfidic, Subaqueous Hydrosol	RBAc 8	Humose-Acidic, Hyposulfidic, Redoxic Hydrosol

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 report

⁴. Australian Soil Classification 2nd ed. (Isbell and National Committee on Soils & Terrain, 2016)

Table 3-6: Soil classification in accordance with Soil Taxonomy and WRB for soils sampled previously (23 May 2008 and 3 October 2008) and in the current investigation (2 September, 2013)

¹ Dry: 23 May 2008 (a)		² Reflooded: 3 October 2008 (b)		³ Dry: 2 September 2013 (c)	
Profile No	Soil Taxonomy ⁴ WRB ⁶	Profile No	Soil Taxonomy ⁴ WRB ⁶	Profile No	Soil Taxonomy ⁴ WRB ⁶
RBAa 1	Typic Sulfaquept Hypothionic Gleysol (Drainic, Hypersulfidic)	RBAb 1	⁵ Typic Sulfowassept Subaquatic Hypothionic Gleysol (Hypersulfidic)	RBAc 1	Typic Sulfaquept Hypothionic Gleysol (Drainic, Hypersulfidic)
RBAa 2	Typic Sulfaquept Oxygleyic Gleysol (Drainic, Hypersulfidic)	RBAb 2	Typic Sulfowassept Subaquatic Gleysol (Hypersulfidic)	RBAc 2	Typic Hydraquept Oxygleyic Gleysol (Drainic, Hyposulfidic)
RBAa 3	Typic Sulfaquept Oxygleyic Gleysol (Drainic, Hypersulfidic)	RBAb 3	Typic Sulfiwassept Subaquatic Gleysol (Hypersulfidic)	RBAc 3	Typic Hydraquept Oxygleyic Gleysol (Drainic, Hyposulfidic)
RBAa 4	Typic Sulfaquept Oxygleyic Gleysol (Drainic, Hypersulfidic)	RBAb 4	Typic Sulfiwassept Subaquatic Gleysol (Hypersulfidic)	RBAc 4	Typic Hydraquept Oxygleyic Gleysol (Drainic, Hyposulfidic)
RBAa 5	Typic Sulfaquept Oxygleyic Gleysol (Drainic, Hypersulfidic)	RBAb 5	Typic Sulfiwassept Subaquatic Gleysol (Hypersulfidic)	RBAc 5	Typic Hydraquept Oxygleyic Gleysol (Drainic, Hyposulfidic)
RBAa 6	Typic Sulfaquept Oxygleyic Gleysol (Drainic, Hypersulfidic)	RBAb 6	Aeric Sulfiwassepts Subaquatic Gleysol (Hypersulfidic)	RBAc 6	Typic Hydraquept Oxygleyic Gleysol (Drainic, Hyposulfidic)
RBAa 7	Typic Sulfaquept Oxygleyic Gleysol (Drainic, Hypersulfidic)	RBAb 7	Aeric Sulfiwassepts Subaquatic Gleysol (Hypersulfidic)	RBAc 7	Typic Hydraquept Oxygleyic Gleysol (Drainic, Hyposulfidic)
RBAa 8	Typic Sulfihemists Murshic Histosol (Hypersulfidic)	RBAb 8	Fibric Sulfiwassepts Fibric Histosol (Hypersulfidic)	RBAc 8	Hydric Haplofibrist Murshic Histosol (Hyposulfidic)

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 in Soil Taxonomy (Soil Survey Staff, 2014)

⁵ Typic Sulfowassept is a new subgroup proposal to Soil Taxonomy. A new proposal is currently being prepared by Fitzpatrick *et al.* (2016 – in preparation) to USDA-NRCS to consider for inclusion in revised versions of the US Keys to Soil Taxonomy the following: (i) a new suborder, which would be Wassepts, (ii) with the existence of Wassepts suborder, a great group of Sulfowassepts will need to be proposed within the suborder and (iii) with the existence of Sulfowassepts great group, a subgroup of Typic Sulfowassept will need to be proposed within the great group.

⁶ IUSS Working Group WRB (2014): World Reference Base for Soil Resources 2014. World Soil Res. Report 106, FAO, Rome. <http://www.fao.org/3/a-i3794e.pdf>

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 SO₄ dominating as the major anion. High SO₄/Cl ratios suggest an additional source of SO₄ 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, NH₄, 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 °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.

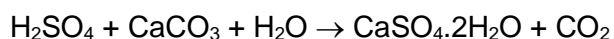
Nitrogen species, Cl and PO₄ were analysed by colorimetric analysis using an Auto Analyser; Br, F and SO₄ by ion chromatography; and NPOC by a TOC Analyser in the Adelaide Waite laboratories at CSIRO. For cation analyses, water samples were transported to the CSIRO laboratory at Lucas Heights, Sydney 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) (Varian 730 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) (Agilent 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 positively with alkalinity ($r^2=0.97$; $n = 4$; 2 d.f.) and negatively with Eh ($r^2=0.91$; $n = 4$; 2 d.f.). 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 SO₄ for all samples, with the waters varying from Ca-SO₄ type to Na-SO₄-type. The Ca-SO₄ type waters comprised the highest and lowest pH samples, but all had very high SO₄/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:



Nitrogen species and phosphate are shown on Figure 4-3 **Error! Reference source not found.** 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.

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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 ($\mu\text{S cm}^{-1}$)	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 ($\mu\text{g l}^{-1}$)	33100	398	8.9	36400
Co ($\mu\text{g l}^{-1}$)	40	153	26	14
Cu ($\mu\text{g l}^{-1}$)	52	29	8.0	13
Fe ($\mu\text{g l}^{-1}$)	19300	250	18	20500
Mn ($\mu\text{g l}^{-1}$)	252	1630	31	152
Ni ($\mu\text{g l}^{-1}$)	21	38	8.3	19
W ($\mu\text{g l}^{-1}$)	128	76	65	29
Zn ($\mu\text{g l}^{-1}$)	89	193	22	62
SO ₄ /Cl	8.9	24	28	3.3

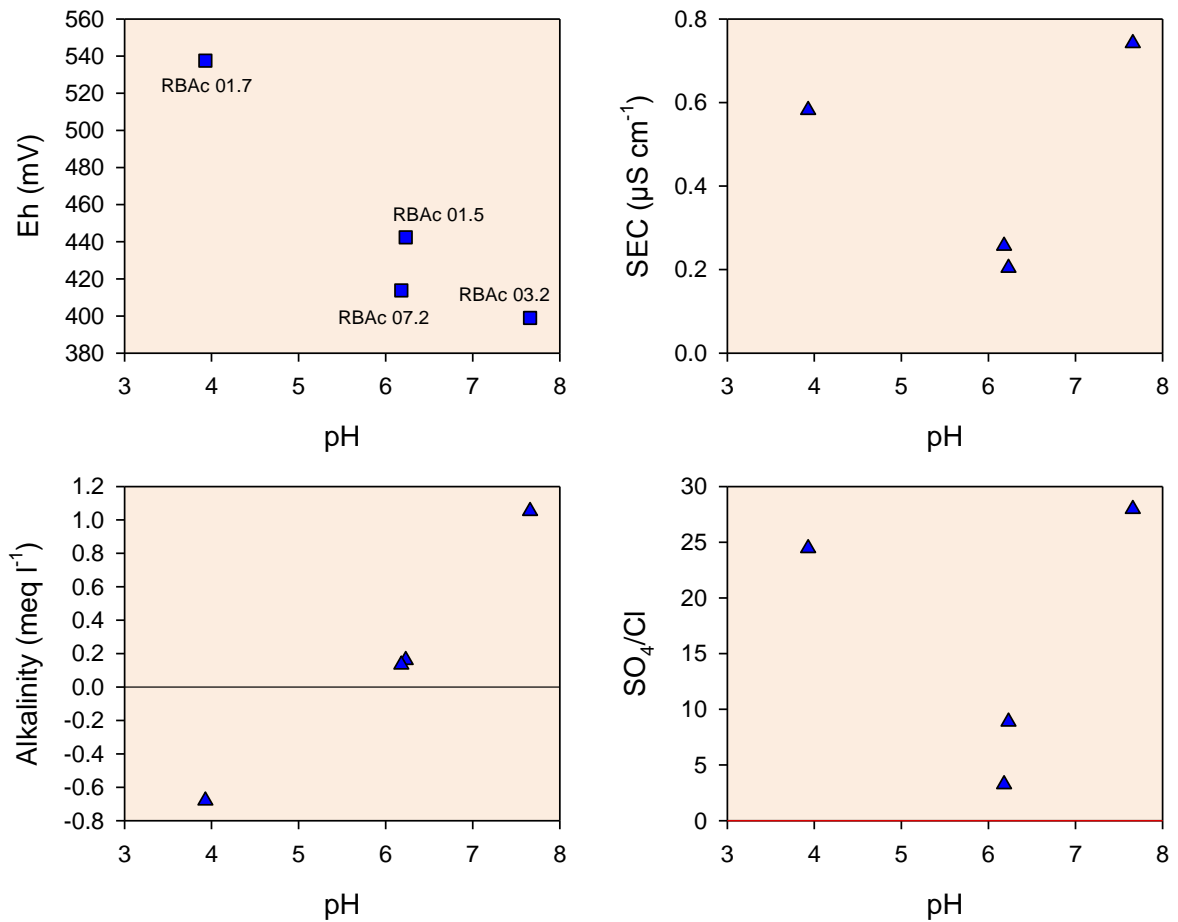


Figure 4-1 Plots of Eh, SEC and SO₄/Cl ratio plotted as a function of pH. Acidity is plotted as negative alkalinity on the alkalinity plot. The SO₄/Cl ratio for seawater (red line) is 0.142.

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 have 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 these pH values. 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 $\mu\text{g l}^{-1}$): 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).

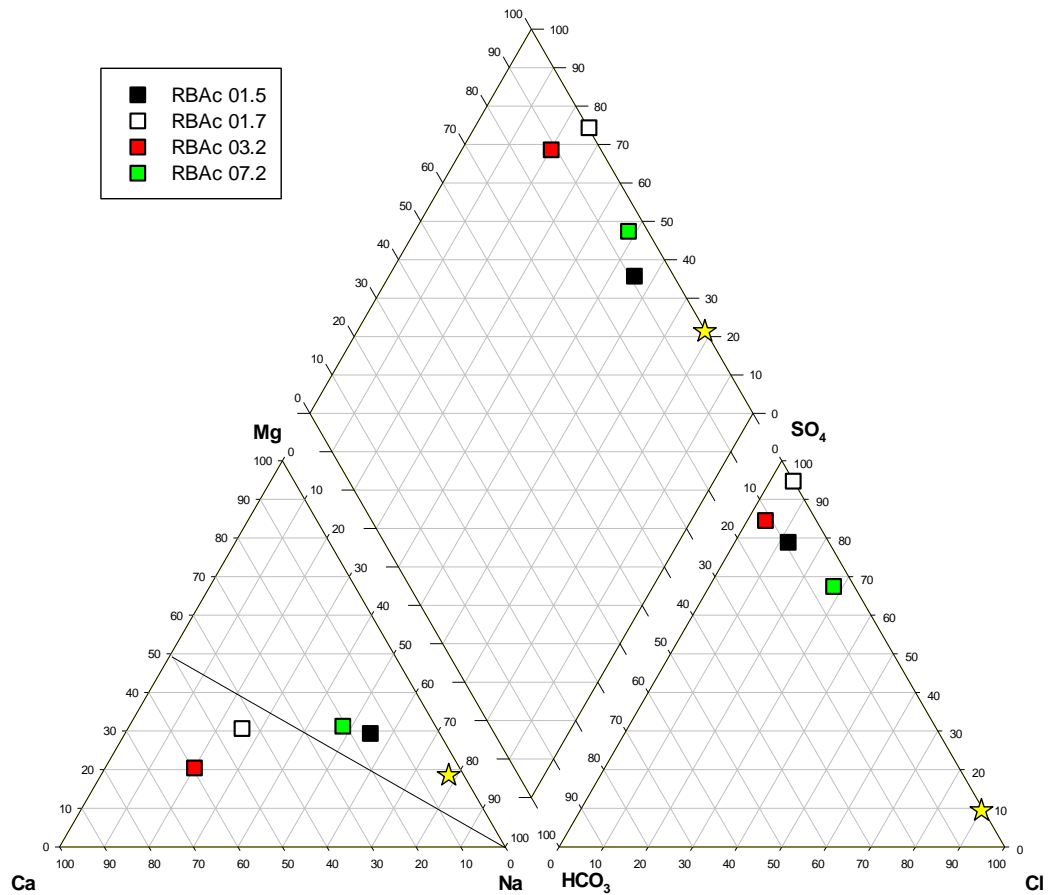


Figure 4-2 Piper plot showing the relative proportions of major elements in soil extractions. Seawater is shown for comparison (yellow star).

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 $[4.11 * \text{Mg}] + [2.47 * \text{Ca}]$) 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.

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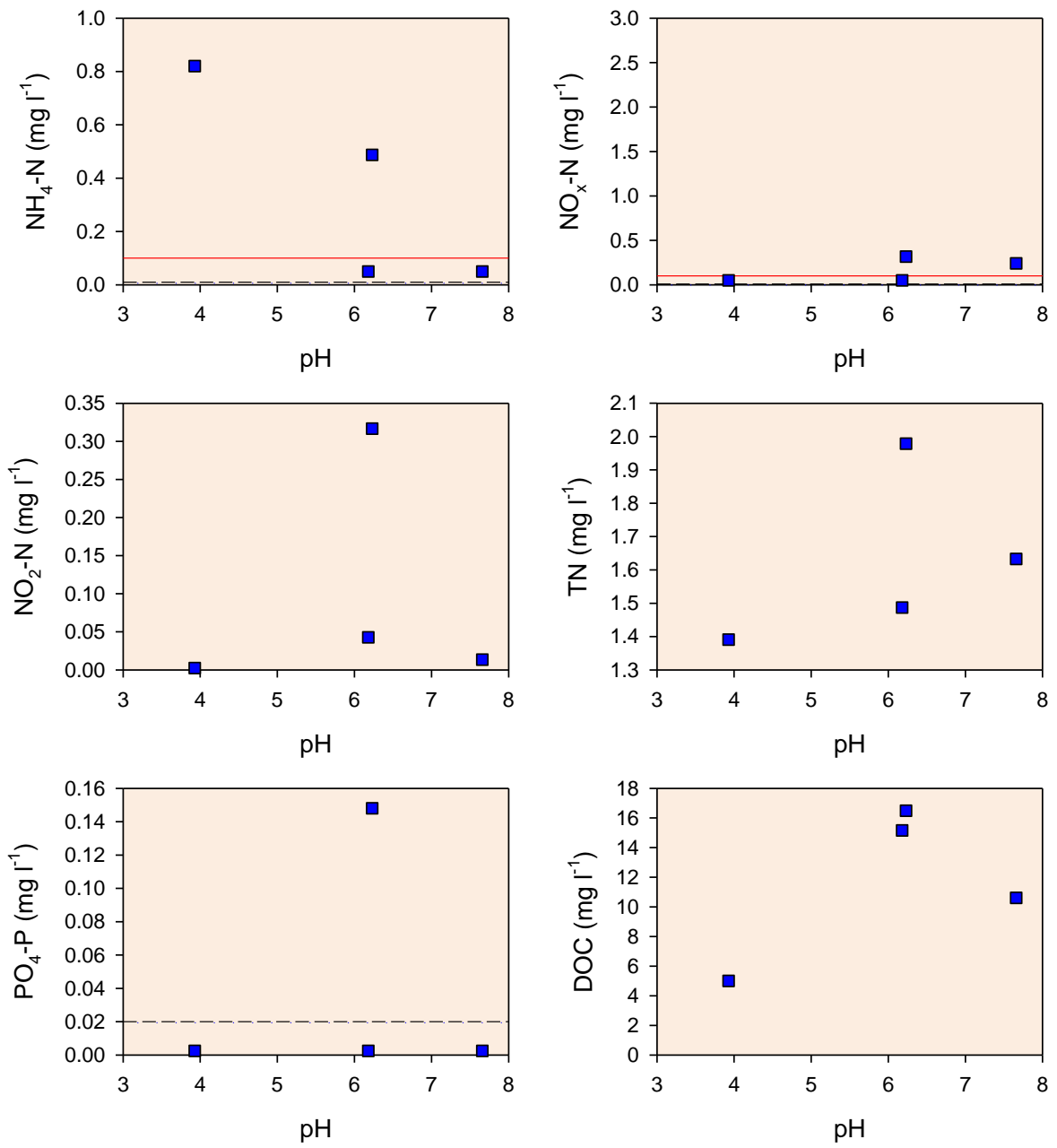


Figure 4-3 Plots of nutrient concentrations plotted as a function of sample pH. ANZECC Guideline values shown as dashed line and detection limits highlighted by red line

RAPID METAL RELEASE

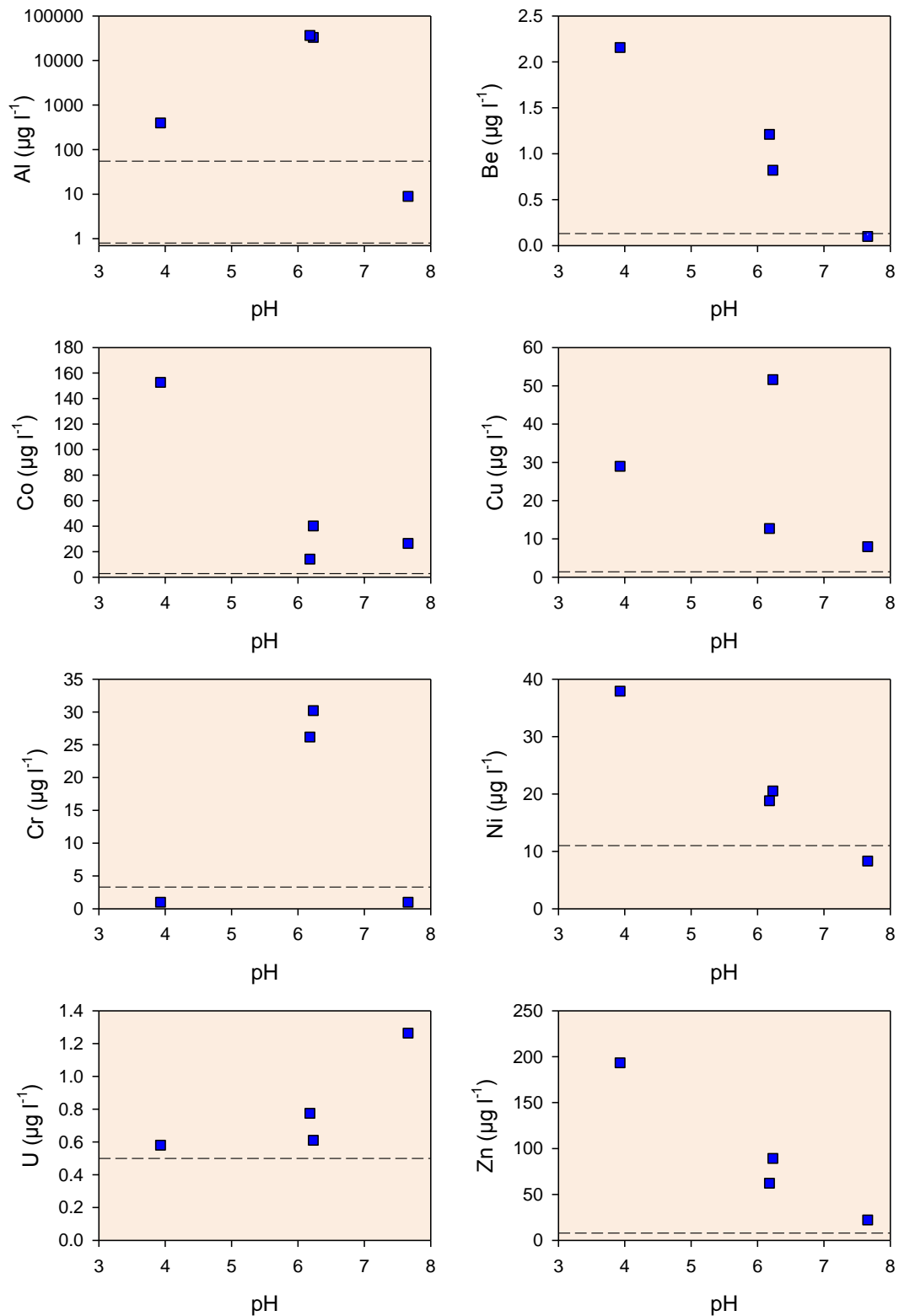


Figure 4-4 Plots of nutrient concentrations plotted as a function of sample pH. ANZECC Guideline trigger values shown as dashed line (for Al, upper line pH >6.5; lower line pH >6.5). Note log scale for Al plot.

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

Summary

The aim of this chapter is to summarise a series of four journal papers by Jayalath *et al.* (2016 a, b, c, d) to determine the effect of type of organic matter (OM) on pH and redox potential of three types of Acid Sulfate Soils (referred to as a sulfuric soil, hypersulfidic soil and hyposulfidic soil) during wet and dry periods.

The specific objectives of this work was to conduct a series of incubation experiments to:

1. Determine the influence of addition of different forms of OM on pH and Eh under submerged/reduced and the following dry/oxidised period in three wetland ASS soils. The outcomes of these experiments are given in Jayalath *et al.* (2016a) with a brief summary presented in section 5.1 below.
2. Investigate the impact of addition of OM to three wetland ASS on pH changes during wet-dry-wet regime and determine the effect of water content during the dry phase on pH dynamics. The outcomes of these experiments are given in Jayalath *et al.* (2016b) with a brief summary presented in section 5.2 below.
3. Determine the effect of mixing sulfidic clayey soils with sulfuric sandy soil on pH changes during a submerged/reduced and a following dry/oxidised period and investigate how the pH effect is related to clay soil properties such as clay content, RIS concentration and pHBC. The outcomes of these experiments are given in Jayalath *et al.* (2016c) with a brief summary presented in section 5.3 below.
4. Determine the effect of OM addition over two successive wet-dry cycles in four ASS. The outcomes of these experiments are given in Jayalath *et al.* (2016d) with a brief summary presented in section 5.4 below.

5.1 Addition of organic matter influences pH changes in reduced and oxidized acid sulfate soils

Purpose:

Organic matter plays an important role in acid sulfate soils, as an energy source for sulfate reducing bacteria during submergence and by stimulating competition for oxygen between oxidation of iron sulfide and utilisation by decomposers during dry periods. The aim of this first experiment was to assess the effect of organic matter addition, as a potential management strategy, on pH changes in ASS in submerged and dry periods. For more details of the methods, results and discussion see Jayalath *et al.* (2016a).

Materials and Methods:

The following three acid sulfate soil materials were collected at different depths from one profile at site RBAc01 during the dry period in 2013: sulfuric material from sample RBAc01.4; hypersulfidic material from RBAc01.5 and hyposulfidic material from RBAc01.7 (see Table 3-3, Table 3-4, Table 3-5). These three ASS materials are representative of typical soils in Banrock wetland and adjacent wetlands (Fitzpatrick *et al.*, 2009). These three materials were air-dried and sieved to <2 mm and in this experiment the three soils are referred to as: soil 1 (sulfuric soil), soil 2 (hypersulfidic soil) and soil 3 (hyposulfidic soil) and were used unamended or amended with 10 g C kg⁻¹ as finely ground wheat straw.

The soils were exposed to a submerged (wet) period, a dry period, followed by another wet period.

Results and Discussion:

In the first wet period (10 weeks), the pH increased only in the amended soils, which was accompanied by a strong decrease in redox potential. To investigate the effect of water content during the dry period on pH, the soils were rapidly dried to 40, 60, 80 or 100% of water holding capacity (WHC) at the start of the dry period. This water content was maintained during the dry period. The pH decrease during the 10 week dry period was greater in amended than in unamended soils and greater at 60, 80 or 100% than at 40% of WHC. At the end of the dry period, the pH was higher in amended than in unamended soils and greater at 40% of WHC than at the higher water contents.

In the second wet period (16 weeks), the pH increased only in the amended soils. The pH increase was accompanied by a decrease in redox potential in the amended soils. The water content in the previous dry period did not influence pH in the second wet period in the unamended soils, but in the amended soils, the pH was higher in soils previously maintained at 40% of WHC than that maintained at higher water contents. At the end of the second wet period, the pH was higher in amended than in unamended soils. This study shows the ameliorative effect of organic matter addition in ASS.

Conclusions:

Organic matter addition can improve energy supply for sulfate reducers which results in an increase in pH during the wet period and lead to a higher pH in the oxidation period. The smaller pH increase and redox potential decrease in amended soils in the second compared to the first wet period suggest that OM decomposition was lower in the second wet period likely because rapidly decomposable compounds had been utilised in the previous wet and dry periods and only recalcitrant OM remained. Therefore OM may have to be added repeatedly for sustained amelioration of ASS.

Reference:

Jayalath N, Mosley LM, Fitzpatrick, RW, Marschner P. (2016a). Addition of organic matter influences pH changes in reduced and oxidized acid sulfate soils. *Geoderma*. **262**, 125-132.
<http://dx.doi.org/10.1016/j.geoderma.2015.08.012>

5.2 Type of organic carbon amendment influences pH changes in acid sulfate soils in flooded and dry conditions

Purpose:

Acid sulfate soils (ASS) are common in wetlands and can pose an environmental threat when they dry because oxidation of pyrite may cause strong acidification. Addition of organic matter can stimulate sulfate reduction during wet periods and minimize acidification during dry periods. However, the effect of the organic amendment may depend on its composition.

The second experiment was carried out to assess the effect of OM addition on pH in a wet-dry cycle followed by a second wet period. A further aim was to investigate the influence of water content during the dry period on acidification.

For more details of the methods, results and discussion see Jayalath et al. (2016b).

Materials and Methods:

The following three acid sulfate soil materials were collected at different depths from one profile at site RBAc01 during the dry period in 2013: sulfuric material from sample RBAc01.4; hypersulfidic material from RBAc01.5 and hyposulfidic material from RBAc01.7 (see Table 3-3, Table 3-4, Table 3-5). These three materials were air-dried and sieved to <2 mm and in these experiments the three soils are referred

to as: sulfuric soil, hypersulfidic soil and hyposulfidic soil. These three soils were used unamended or amended with 10 g C kg⁻¹ 10 g C kg⁻¹ as glucose, wheat straw, pea straw, or Phragmites litter and were incubated for 18 weeks under flooded conditions ("wet period") followed by 10 weeks during which the soils were maintained at 100 % of maximum water-holding capacity ("dry period"). The soils were exposed to a submerged (wet) period, a dry period, followed by another wet period.

Results and Discussion:

During the wet period, the pH decreased in the control and with glucose to pH 3–4, but increased or was maintained in residue-amended soils (pH at the end of the wet period about 7). In the dry period, the pH of the control and glucose-amended soils remained low, whereas the pH in residue-amended soils decreased. However, at end of the dry period, the pH was higher in residue-amended soils than in the control or glucose amended soils, particularly with pea straw (C/N 50).

Conclusions:

Amendment of acid sulfate soils with plant residues (particularly those with low to moderate C/N ratio) can stimulate pH increase during flooding and reduce acidification under oxidizing conditions.

Reference

Jayalath Nilmini, Fitzpatrick, Rob W, Mosley Luke, Marschner Petra. (2016b) Type of organic carbon amendment influences pH changes in acid sulfate soils in flooded and dry conditions. *J Soils Sediments*. **16(2)**, 518-526 <http://dx.doi.org/10.1007/s11368-015-1240-1>

5.3 Addition of clayey soils with high net negative acidity to sulfuric sandy soil can minimize pH changes during wet and dry periods

Purpose:

Wetland environments may have hypersulfidic soils, that contain pyrite, which can generate extreme acidity and form sulfuric soils (pH b 4), when exposed to oxygen which poses a threat to the environment. Management of sulfuric soils by addition of neutralising agents such as lime or inundation with seawater may be uneconomical or ineffective in inland environments.

The aim of this third experiment was to test the effects of the addition of three clayey soils with different net negative acidities to a sulfuric sandy soil as an amelioration option.

The aim was to investigate the effect of addition of hyposulfidic clay soils to a sulfuric sandy soil on pH changes in reduced and oxidised conditions.

For more details of the methods, results and discussion see Jayalath et al. (2016c).

Materials and Methods:

A sulfuric sandy soil (pH 4.1) was mixed with three hyposulfidic clay soils (with clay contents ranging between 38 and 72%) to give clay soil proportions of 0, 25, 50, 75 and 100 (%dry soil).

According to their net negative acidity, the three clay soils are referred to as: NA-334, NA-54 and NA-8 (values in mol H⁺ tonne⁻¹). All soils were collected in the Banrock Ramsar wetland. The soils were amended with wheat straw at 10 g of C kg⁻¹ and then incubated for 14 weeks under reducing conditions (wet period) followed by 11 weeks incubation under oxidising conditions (dry period) during which they were maintained at 100% of maximum water holding capacity.

Results and Discussion:

The pH of the sulfuric soil alone increased during the wet period by about two pH units (to pH 6) and decreased by more than two pH units (to pH 4) during the dry period. In the clay soils alone and treatments with sulfuric soil, the pH during the wet period decreased by 0.5 to 1 unit with NA-334 and NA-54 and increased by one unit with NA-8. The pH was 6 in all clay treatments at the end of the wet period. During the dry period, the pH remained above pH 7 with NA-334 and decreased by about one unit (to pH 5.5) with NA-8. In treatments with NA-54, the pH decrease during the dry period depended on the proportion of clay soil, ranging from 0.5 pH unit with 75% clay soil to two pH units with 25% clay soil.

Conclusions:

The capacity of the clay soil treatments to maintain stable pH during wet and dry periods depended mainly on the negative net acidity of the added clay soils, but was not related to their concentration of reduced inorganic sulfur or clay content. It can be concluded that addition of clay soils with high negative net acidity could be used to ameliorate acidity in acid sulfate soils with sulfuric materials.

However, field experiments will be required to test how long mixing with clay soils is effective in reducing acidity. The pH stabilisation by clay soil addition to sulfuric soil in this experiment may also be due to the fine grinding of both the sulfuric and clay soils and the thorough mixing of the two soils. This will have maximised the effect of the clay soils in binding protons and buffering the pH. The effect may be smaller in the field where after mixing the clay and sulfuric soils, the clay soil may be in clods of varying size and unevenly distributed.

Reference

Jayalath N, Mosley LM, Fitzpatrick, RW, Marschner P. (2016c) Addition of clayey soils with high net negative acidity to sulfuric sandy soil can minimize pH changes during wet and dry periods. *Geoderma*. **269**: 153-159 <http://dx.doi.org/10.1016/j.geoderma.2016.01.040>

5.4 Addition of wheat straw to acid sulfate soils with different clay contents reduces acidification in two consecutive wet-dry cycles

Purpose:

Acid sulfate soils (ASS) are wide-spread in wetlands and experience distinct biogeochemical changes in wet and dry periods. During wet periods, under reducing conditions, sulfate reduction can result in an increase in pH whereas dry periods induce sulfide and ferrous iron oxidation, which may result in acidification, which may pose a threat to environments.

This fourth experiment was conducted to determine the effect of OM addition over two successive wet-dry cycles in four ASS with differing in clay contents (10, 15, 23 and 38%).

Materials and Methods:

The four soils were collected from two different soil profiles during a dry period in 2013 in the Banrock Station wetland complex. From soil profile 1 (RBAc-01), which is at the edge of the wetland adjacent to Phragmites stands the following three materials were sampled: sulfuric material from sample RBAc01.4 (5-20cm with 10% clay); hypersulfidic material from RBAc01.5 (20-30cm with 15% clay) and hyposulfidic material from RBAc01.7 (50-65cm with 23% clay) (see Table 3-3, Table 3-4, Table 3-5). From soil profile 2 (RBAc-06), which is located closer to the lower lying lakebed the following material were sampled: hyposulfidic material from RBAc06.1 (0-1.5cm, with 38% clay) (see Table 3-3, Table 3-4, Table 3-5).

The four soils differing in clay content (10, 15, 23, 38% referred to as C10, C15, C23 and C38) were unamended or amended with 10 g C kg⁻¹ finely ground wheat straw and incubated over 24 weeks with each wet and each dry period lasting 6 weeks.

During the wet periods, the soils were maintained under a layer of water, in the dry periods they were kept at 100% of water holding capacity.

Results and Discussion:

The soil pH increased in both wet periods, particularly in amended soils with low clay content (C10 and C15). The redox potential (Eh) decreased more strongly in amended soils than in unamended soils and became negative from week 2 onwards whereas the Eh stayed positive in unamended soils except C38.

In the dry periods, the pH decreased more strongly in amended soils than in unamended soils, particularly in C10 and C15. Changes in pH during wet and dry periods were greater in soils with low clay content (C10, C15) than those with high clay content (C23, C38).

The effect of wheat straw addition on pH at the end of wet and dry periods did not differ between the two wet-dry periods, with a higher pH in amended than unamended soils.

Conclusions:

This study showed that wheat straw addition maintains its ameliorative effect on soil pH for at least two wet-dry cycles, but the pH effect depends on clay content, being greater in soils with low clay content. The effectiveness of this method would have to be tested under field conditions, particularly where wet and dry periods continue for longer periods.

Reference:

Jayalath N, Fitzpatrick, RW, Mosley LM, Marschner P. (2016d) Addition of wheat straw to acid sulfate soils with different clay contents reduces acidification in two consecutive wet-dry cycles. *Journal of Soils and Sediments (In Press)*.

5.5 Implications for wetlands

The results of the series of experiments conducted by Jayalath *et al.* (2016 a, b, d) 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.

It can be concluded that large changes in pH during wet and dry periods in sulfuric soils can be minimised by mixing with clay soils (2016 c). In agreement with previous studies (Jayalath *et al.*, 2015a; Yuan *et al.*, 2015), organic matter addition stimulated sulfate reduction and lead to a pH increase in treatments where the pH at the start of the wet period is low. However, organic matter addition at the start of the experiment did not prevent acidification of the sulfuric sandy soil in the dry period in this study. Reduction of acidity in acid sulfate soils by organic matter addition relies on decomposition of the added organic matter to stimulate sulfate reduction during the wet period and proton consumption during the dry period. Therefore a sustained effect may require repeated addition of organic matter. In contrast, addition of clay soil could be a once-off amelioration strategy for pH stabilisation of sulfuric soils, especially in wetlands where clay soils occur immediately adjacent to sulfuric soils.

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 and wet/dry monosulfidic material),
- surface water ponding, and
- 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/drainage 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 acidity 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 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).

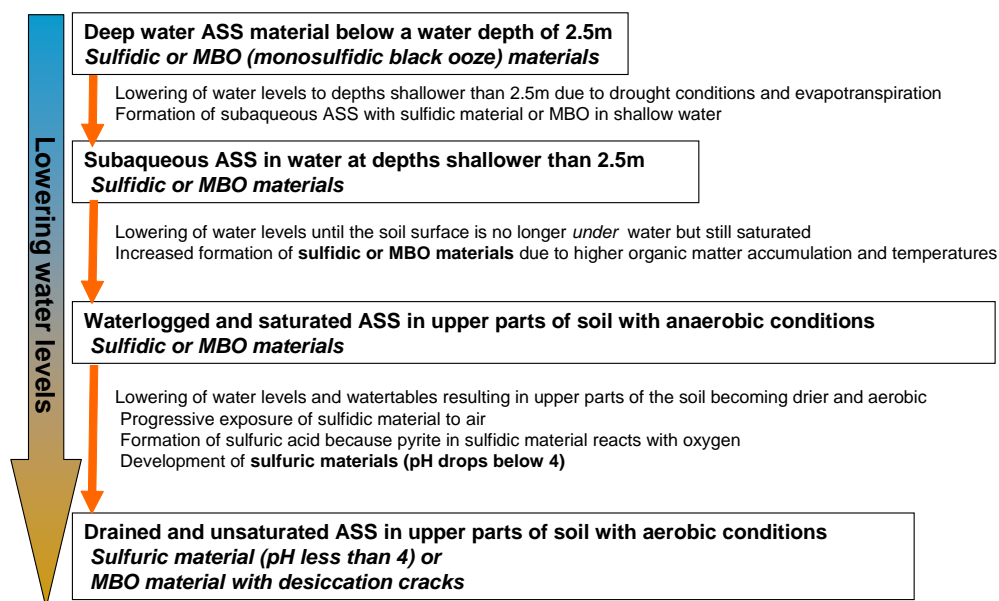


Figure 6-1 Generalised conceptual model showing the sequential transformation of four classes of ASS due to lowering of water levels from: “Deep-water ASS” to → “Subaqueous ASS” to → “Waterlogged and saturated ASS” (all containing sulfidic / hypersulfidic material with high sulfide concentrations and 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-sulfate salts.
- Acid sulfate soil materials (monosulfidic, hypersulfidic and hyposulfidic materials), which integrates the incubation data (16 weeks) and Acid Base Accounting data.

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- 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 capillarity and 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).

Managed wetland - drying cycle
(September 2013)

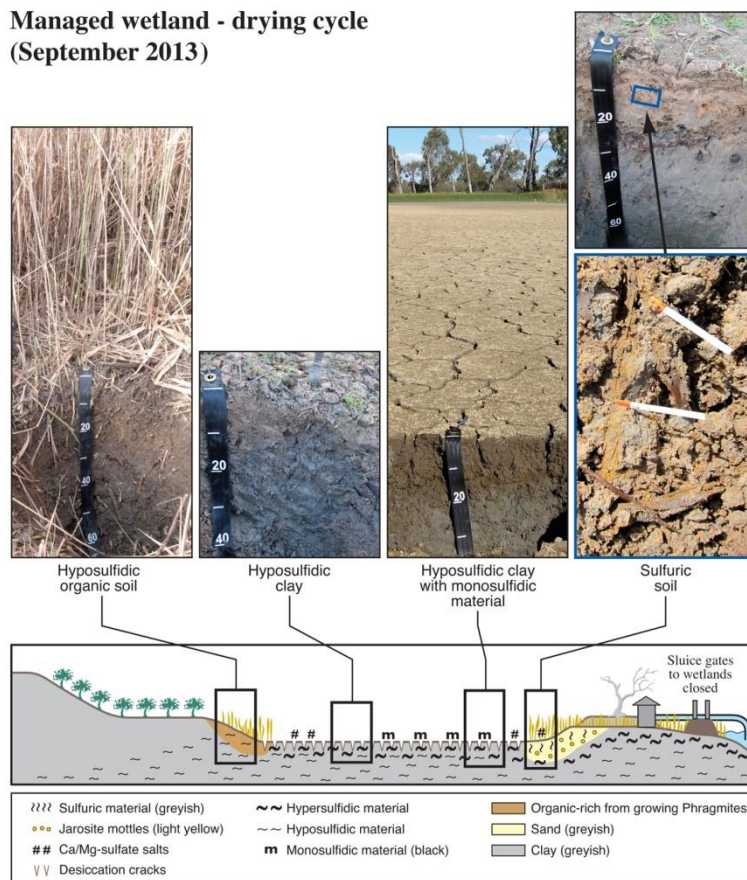


Figure 6-2: Explanatory soil-regolith model for the Banrock wetland with soil profile photographs and cross-section diagram of Acid Sulfate Soil subtypes (i.e. Sulfuric soil, Hyposulfidic organic soil, Hyposulfidic clay with monosulfidic material) sampled on 2nd September 2013 after at least 4 cycles 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

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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 [at Banrock](#) 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).

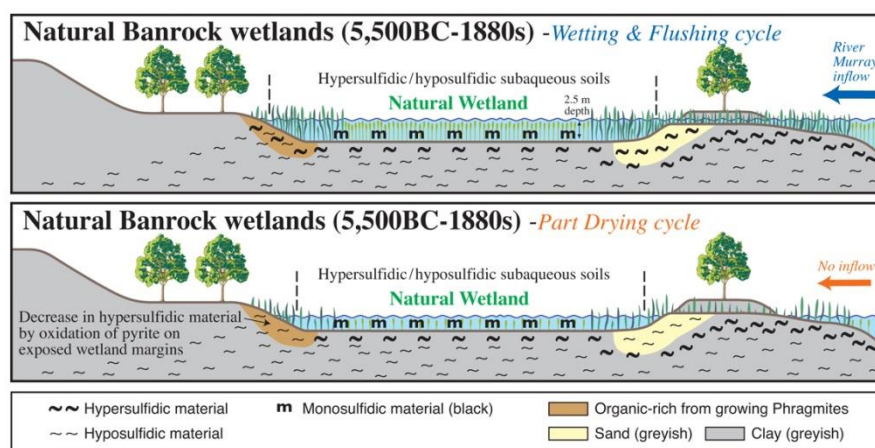


Figure 6-3: Explanatory soil-regolith models for Banrock wetland illustrating natural wetting and flushing (upper panel), and partial drying (lower panel) cycle conditions during pre-colonial times (5,500 BC - 1880s) (modified from Fitzpatrick *et al.* 2009b).

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 by 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).

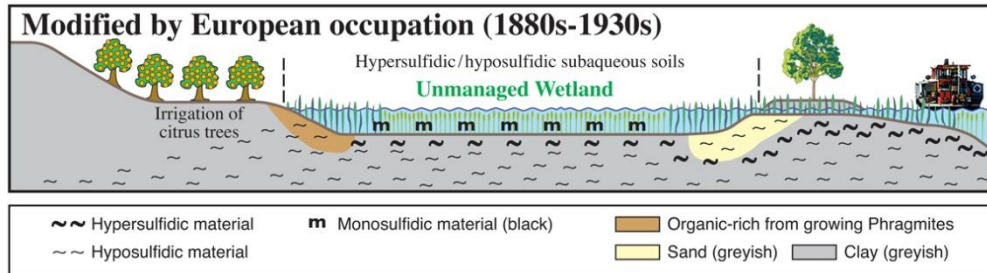


Figure 6-4: Explanatory soil-regolith model for Banrock wetlands, illustrating modification of water flows by European occupation (1880s- 1930s) (modified from Fitzpatrick *et al.* 2009b)

(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).

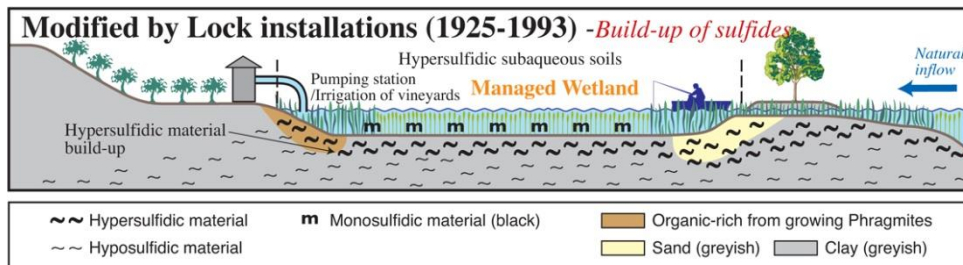


Figure 6-5: Explanatory soil-regolith model for the Banrock wetland illustrating modification of water flows by lock installations causing the build up of sulfides (i.e. hypersulfidic material) under continued subaqueous conditions from 1925-1993 (modified from Fitzpatrick *et al.* 2009b).

(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).

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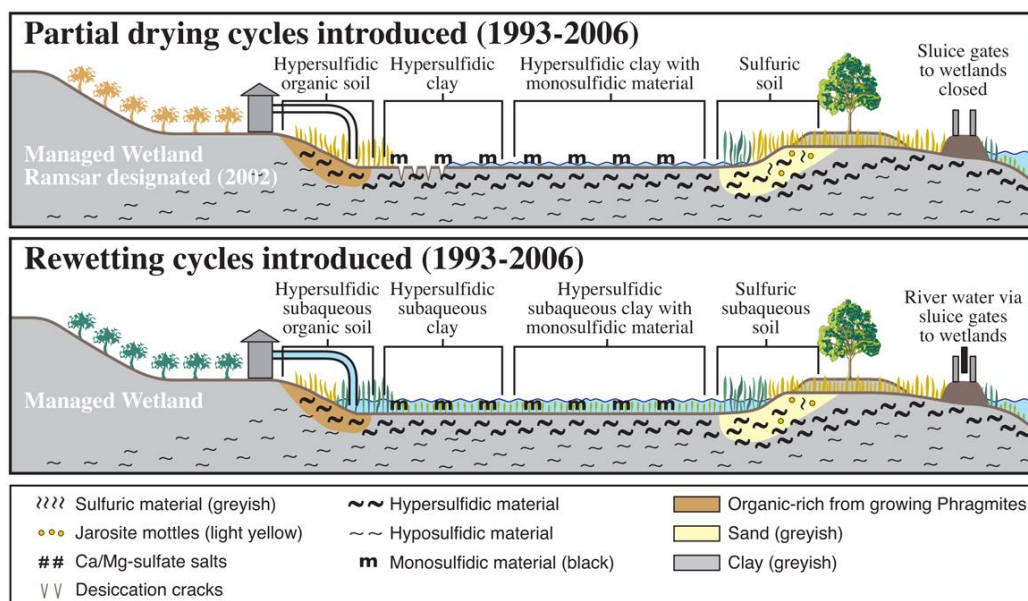


Figure 6-6: Explanatory soil-regolith model for the Banrock wetland illustrating the installation of sluice gates to manage the partial drying cycle (upper panel) and the rewetting/ flushing cycle (lower panel) during 1993 to 2006. The Banrock wetland was designated a Ramsar site in 2002 (modified from 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.

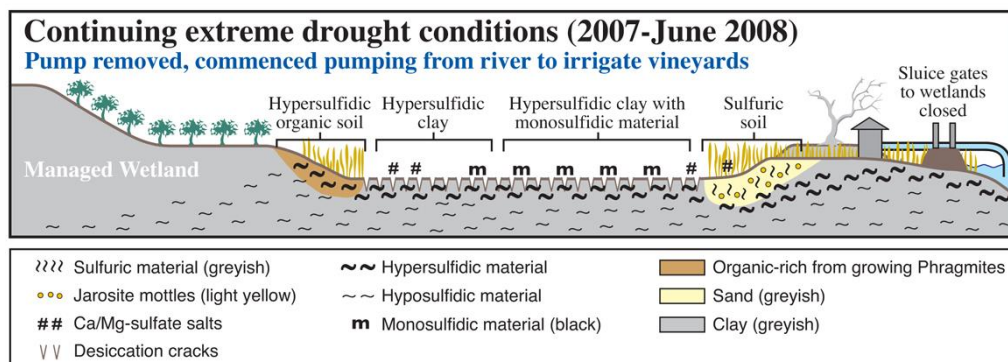


Figure 6-7: Explanatory soil-regolith model for the Banrock wetland illustrating the formation of: (i) sulfuric material ($\text{pH} < 4$) by oxidation of sulfides in hypersulfidic material on the edges of the wetland, (ii) sulfate-rich salt efflorescences and (iii) deep desiccation cracks; due to continued 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 ($> 50\text{cm}$), 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.

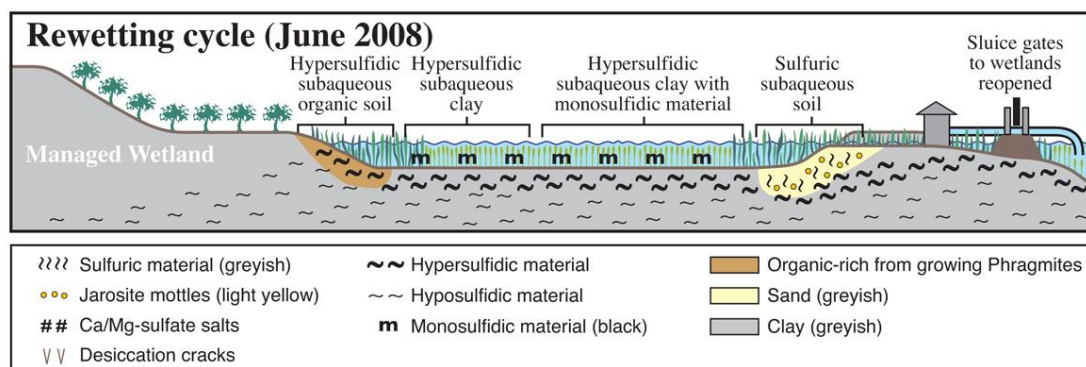


Figure 6-8: Explanatory soil-regolith model for the Banrock wetland showing complete re-wetting of the whole wetland in June 2008 with inundation and preservation of sulfuric material (Sulfuric subaqueous soils) and hypersulfidic material (Hypersulfidic subaqueous organic soils), which occurs on the 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 and 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)].

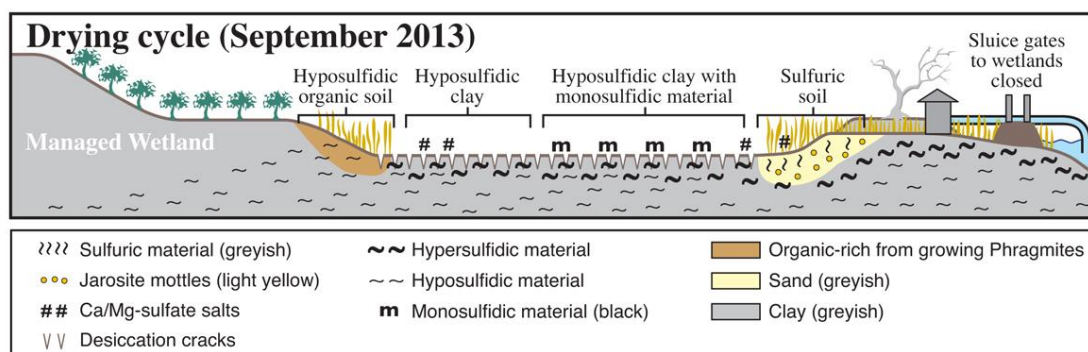


Figure 6-9: Explanatory soil-regolith model for the Banrock wetland after at least 4 cycles of re-wetting and drying of the whole wetland over a 5 year period with inundation of: (i) Sulfuric soils and Hyposulfidic organic soils, which occur on the edges of the wetland and (ii) hyposulfidic clays, which 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 (h ₁)	Managed Sluice gates 1993-2006 (h ₂)	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)	Hypersulfidic 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" Hypersulfidic 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)	Hypersulfidic 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 Hypersulfidic 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)	Hypersulfidic 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 Hypersulfidic 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 Hypersulfidic 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 Hypersulfidic 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

³Ex- Extrinsic pedogenic threshold

³In - Intrinsic pedogenic threshold

³Dy - Dynamic balance of thickness

³Dp - deepening

³Rv - removals

³Up - upbuilding

Dominant ASS – process

Sulfuric – Sulfurization - 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

³Pr(s) - Progressive pedogenesis (slow: relative to previous window)

³Pr(f) - Progressive pedogenesis (fast relative to previous window)

³Ab - Abrupt pedogenesis (relative to previous window)

³Re - Regressive pedogenesis

³St - Static pedogenesis

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

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 <i>Hyposulfidic</i> clayey soils to <i>Hypersulfidic</i> 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 <i>Hyposulfidic</i> clayey soils to <i>Hypersulfidic</i> 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 <i>Hypersulfidic</i> 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 <i>Hypersulfidic</i> subaqueous clayey soils to <i>Hypersulfidic</i> & 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 become hydraulically disconnected from the river channel	Extrinsic pedogenic threshold (Ex) caused by climatic and human-made changes (draining of wetlands) Shoreline: Fast transformation <i>Hypersulfidic</i> 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 <i>Hypersulfidic</i> subaqueous clayey soils to <i>Hypersulfidic</i> 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 wetland	Extrinsic pedogenic threshold (Ex) caused by human-made changes (flooding of wetland) Shoreline: Abrupt pedogenesis (Ab) in rapid formation of <i>Sulfuric</i> 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: Preservation of pyrite during the transformation of <i>Hypersulfidic</i> clayey soils to <i>Hypersulfidic</i> subaqueous 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 <i>Sulfuric</i> soil at site RBAC-01; However, at site RBAC-02 pronged wetting & drying cycles (~5 years) resulted in the transformation of a <i>Sulfuric</i> soil to a <i>Hyposulfidic</i> soil. Progressive fast pedogenesis [Pr(f)] in submergence of water and removal of soluble sulfate salts, Mg- and gypsum (Rv) Lakebed: Fast pyrite oxidation/sulfate removal during transformation of <i>Hypersulfidic</i> subaqueous clayey soils to <i>Hyposulfidic</i> clayey soils.

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 0.50 m: Unsaturated = Uns
- Salt efflorescences = Ef,
- Gypsum / Halite crusts = Gyp
- Monosulfidic material that is wet (Mo_w) or dry (Mo_d)

ACID SULFATE SOIL CLASSIFICATION MAPS AND HAZARD RATING MAPS

- 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 HydCyEfMo _d	Hyposulfidic hydrosol clays with monosulfidic material (dry)
Northern segment	
Ho2 HydCyO	Hyposulfidic hydrosol clays with organic-rich material
Ho3 HydLo/CyMo _w	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 HydCyEfMo _d	Hyposulfidic hydrosol clays with monosulfidic material (dry)
Northern segment	
Ho 2 HydCyO	Hyposulfidic hydrosol clays with organic-rich material
Ho 3 HydLo/CyMo _w	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 (EC_{se}) 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 affected	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 affected	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 unaffected	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 affected	>1.20	>1.45	>1.75	>2.30	>3.20

¹EC 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 (EC_{se}) 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, EC_{se} 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 sulfurization) 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.

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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 subdivided 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.




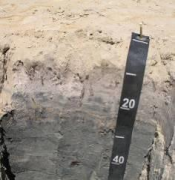


Diagnostic features for Soil Type	Soil Type
<p>Does the soil occur in shallow permanent flooded environments (typically not greater than 2.5 m)?</p> <p>No ↓ Yes →</p>	<p>Subaqueous soil</p> 
<p>Does the upper 80cm of soil consist of more than 40 cm of organic material (peat)?</p> <p>No ↓ Yes →</p>	<p>Organic soil</p> 
<p>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)?</p> <p>No ↓ Yes →</p>	<p>Cracking clay soil</p> 
<p>Does a sulfuric layer (pH<4) occur within 150 cm of the soil surface, AND is the subsoil uniformly grey coloured (poorly drained)?</p> <p>No ↓ Yes →</p>	<p>Sulfuric soil</p> 
<p>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)?</p> <p>No ↓ Yes →</p>	<p>Hypersulfidic soil</p> 
<p>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)?</p> <p>No ↓ Yes →</p>	<p>Hyposulfidic soil</p> 
<p>Other soils</p>	<p>Other soils</p>

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

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 or 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

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. S_{CR} or S_{ox}) + 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 $\geq 0.03\%$ S classification guideline would apply (refer to acid sulfate management guidelines).**

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

15. Appendix 6 – Metal Extraction Data

Metal Extraction data (electronic file)

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