Assessment of Acid Sulfate Soil materials in Ramsar wetlands of the Murray-Darling Basin: Banrock Station Wetland Complex

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Cover Photograph:

Main: View of dry section of the Banrock Station Wetland Complex taken during January 2008 when the entire wetland floodplain was dry. Inset: Regional location of Banrock Station Wetland Complex, south-eastern South Australia.

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EXECUTIVE SUMMARY

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. The Ramsar site is located in the lower Murray River 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.

The Murray-Darling Basin Authority (MDBA), in partnership with its Partner Governments and scientists, instigated the Murray-Darling Basin Acid Sulfate Soils Risk Assessment Project (MDB ASSRAP), which aims to assess the spatial occurrence of, and risks posed by, acid sulfate soil materials in the Murray-Darling Basin (MDB). The MDB ASSRAP project also aims to identify and assess broad management options.

Due to their ecological significance, a decision was made by the MDB Acid Sulfate Soils Risk Assessment Advisory Panel to prioritise the Ramsar-listed wetland complexes of the Murray-Darling Basin for immediate detailed acid sulfate soil assessment. This report provides the results of Phase 1 of a two-phased detailed acid sulfate soil assessment procedure for Banrock Station Wetland Complex. This Phase 1 report is aimed solely at determining whether or not acid sulfate soil materials are present in the Banrock Station Wetland Complex.

In this study, 30 soil layers and mineral samples were collected from eight 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) and **(v)** soil incubation (ageing). No surface water samples were collected from the floodplain wetlands due to a lack of water at the time of the survey.

The results indicate that sulfuric material was present and was identified at two of the eight sites assessed. Sulfidic material was also common, with seven of the eight sites containing measurable sulfide (>0.01% S_{CR}). The majority of sulfidic material identified classified as hypersulfidic. Only one site did not contain acid sulfate soil materials, but did contain soils with a field pH of less than 5.5.

While monosulfidic material was observed at only one site at the wetland, near surface soil material at all sites contained water soluble sulfate concentrations in excess of the 100 mg kg^{-1} trigger value suggesting that monosulfides have potential to form on re-flooding of the wetland.

The potential hazards at a wetland-scale posed by acid sulfate soil materials at the Banrock Station Wetland Complex are listed below:

- Acidification: The data indicate that the degree of acidification hazard is moderate as 50% of sites contained soil materials with a net acidity of >18 mole $H^+ t^{-1}$.
- Deoxygenation: The water soluble sulfate contents of all eight surface soil materials were over the trigger value for potential monosulfide formation and monosulfidic material was observed at one site indicating the possible development of an appreciable deoxygenation hazard after prolonged wet conditions.

- Metal mobilisation: The moderate acidification hazard indicates that soil acidification is likely to increase the solubility of metals. The potential for monosulfide formation identified in this wetland may also result in an appreciable metal release hazard depending on the metal loading in this wetland.

Using the priority ranking criteria adopted by the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soils Risk Assessment Project, there were two high priority sites based on the presence of sulfuric material and five high priority sites based on the presence of a hypersulfidic material. In addition, all eight sampling sites had a high priority ranking for Phase 2 detailed assessment of monosulfide formation potential.

1. INTRODUCTION

1.1. Wetland overview

Banrock Station Wetland Complex is located in the lower Murray River system, about 15 kilometres west of Barmera in South Australia (Figure 1-1) and is situated in a river red gum floodplain. The wetland is connected to the River by one meandering inlet creek, and one outlet creek. Flow control structures were installed at each creek in 1993.

The main 'Banrock Lagoon' became permanently flooded in 1925, when lock 3 was constructed, 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. The wetland was re-flooded in June 2008, with a drying cycle commencing again in January 2009 [e.g. see conceptual models in Fitzpatrick *et al.* (2009); Appendix 3].

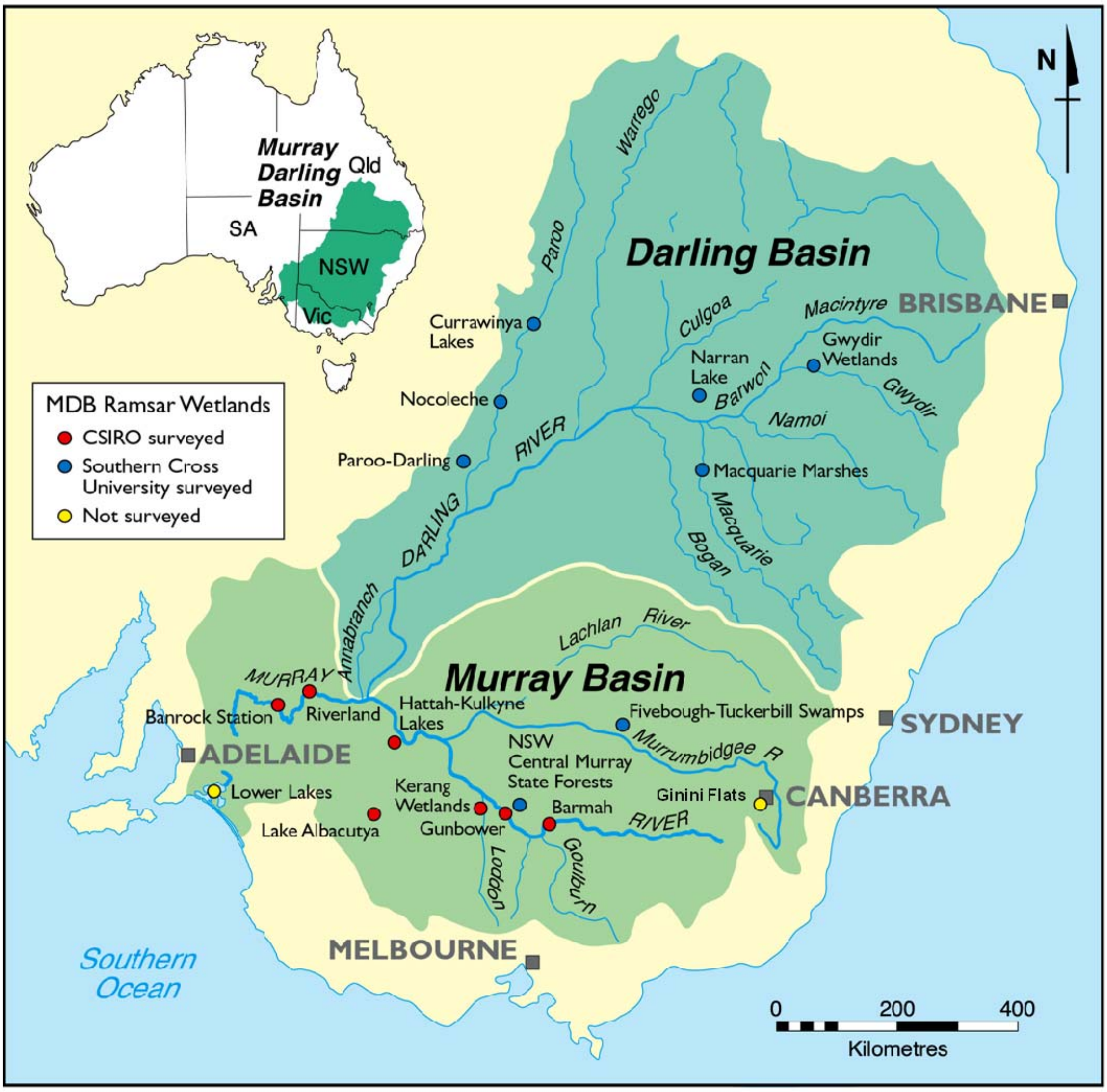

Figure 1-1 The Murray-Darling Basin contains 16 Ramsar-listed wetlands. The Banrock Station Wetland Complex is located in south-eastern South Australia.

1.2. Acid sulfate soils in the Murray-Darling Basin

Acid sulfate soil is the term commonly given to soil and sediment that contain iron sulfides, or the products of sulfide oxidation. Pyrite (FeS_2) is the dominant sulfide in acid sulfate soil, although other sulfides including the iron disulfide marcasite (Bush 2000; Sullivan and Bush 1997) and iron monosulfides (Bush *et al.* 2000; Sullivan and Bush 1997) can also be found.

Sulfidic sediments accumulate under waterlogged conditions where there is a supply of sulfate, the presence of metabolisable organic matter and iron containing minerals (Dent 1986). Under reducing conditions, sulfate is bacterially reduced to sulfide, which reacts with reduced iron to form iron sulfide minerals. These 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).

Acid sulfate soils form naturally when sulfate in the water is converted to sulfide by bacteria. 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). 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.

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.

Record low inflows and river levels in recent years have led to the drying of many wetlands in the MDB, resulting in the exposure of sulfidic material in acid sulfate soil, and soil acidification in many wetlands. The extent and potential threat posed by acid sulfate soil requires urgent assessment.

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, we have only recently advanced far enough to appreciate the wide spectrum of acid sulfate soil subtypes and processes that are operating in these contemporary environmental settings - especially from continued lowering of water levels (e.g. Fitzpatrick *et al.* 2008a; Fitzpatrick *et al.* 2008b; Fitzpatrick *et al.* 2008c; Fitzpatrick *et al.* 2008d; Lamontagne *et al.* 2006; Shand and Edmunds 2008; Shand *et al.* 2008b; Simpson *et al.* 2008; 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 at key wetlands in the MDB.

The MDBA, in partnership with its Partner Governments and scientists, designed the MDB ASS Risk Assessment Project, which aims to assess the spatial occurrence of, and risks posed by, acid sulfate soil in the Murray-Darling Basin. The project also aims to identify and assess broad management options.

The project established a list of more than 10,000 wetlands that were then assessed against a number of criteria aimed at identifying those that had potential for acid sulfate soil occurrence. Due to their ecological significance, the decision was made to prioritise Ramsar-listed wetland complexes of the Murray-Darling Basin (Figure 1-1) for immediate detailed acid sulfate soil assessment. Wetlands within these complexes were then identified and selected for further assessment. CSIRO Land and Water carried out a detailed assessment at eight representative sites within the Banrock Station Wetland Complex (Figure 2-1) in May 2008 to determine whether acid sulfate soils were present, or if there was a potential for acid sulfate soil to form within these wetlands. This assessment included the determination of sulfide content within the soil profile at each site. Water soluble sulfate was used as an indicator of the potential of monosulfide black ooze (MBO) formation in these wetland sites.

1.3. Detailed acid sulfate soil assessments using two phases

The detailed assessment stage of the MDB ASS Risk Assessment Project involves comprehensive analysis using a set of established and tested field and laboratory methods to determine the presence and extent of acid sulfate soil and associated hazards, including potential for acidification, metal mobilisation and deoxygenation.

In summary, the protocol developed by the MDB ASS Risk Assessment Project Scientific Reference Panel (MDBA 2010) requires a two-phase procedure.

Phase 1 aims to determine whether or not acid sulfate soil materials are present in each wetland by:

a. Consulting with relevant wetland managers.

b. Field descriptions of soils and sampling, including pH (e.g. using Merck test strips) and specific electrical conductance (SEC) testing.

c. Photographic record of sites and soil profiles.

d. Sampling and sub-sampling in chip trays.

e. Field testing of water quality parameters (pH, specific electrical conductance (SEC), redox potential (Eh), dissolved oxygen (DO), alkalinity by titration, and turbidity).

f. Laboratory analyses to conclusively identify the presence or absence of sulfuric, sulfidic or MBO acid sulfate soil materials using incubation (“ageing pH”) in chip trays, pH peroxide testing and sulfur suite and partial acid base accounting: S_{CR} (sulfide % S), pH_{KCl}, and TAA (titratable actual acidity: moles $H^+ t^{-1}$), acid neutralising capacity (ANC) where soil materials were sulfidic, acid volatile sulfide (AVS) and water-extractable SO_4 (1:5 soil:water suspension).

g. Surface water and groundwater chemical and nutrient analyses.

Phase 2 is only pursued if results of Phase 1 dictate, and the MDB ASS Risk Assessment Advisory Panel recommend further detailed investigation. Phase 2 aims to determine the nature and severity of the environmental hazards posed by the acid sulfate soil materials, if present, by:

a. Continued incubation of samples in chip trays.

b. More detailed acid/base accounting (e.g. elemental sulfur).

c. Rapid metal release.

d. Contaminant and metalloid dynamics.

e. MBO formation potential.

f. Mineralogy by X-ray diffraction (XRD).

g. Major and trace elements by X-ray fluorescence spectroscopy (XRF).

h. Archiving of all soil samples in CSIRO archive (as chip trays and bulk samples).

Following a request from the Murray-Darling Basin Authority (MDBA), CSIRO Land and Water were engaged to conduct a Phase 1 detailed assessment of acid sulfate soils at the Banrock Station Wetland Complex.

1.4. Methods used to assess acid generation potential

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

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

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

$4FeS_2 + 15O_2 + 10H_2O \text{ ---> } 4FeOOH + 8H_2SO_4$

A range of secondary minerals, such as jarosite, sideronatrite and schwertmannite may also form, which act as stores of acidity i.e. they may produce acidity upon dissolution (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).

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. This method was developed specifically for analysing 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 (S_{CR} or CRS: 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 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 estimated by titration, and alkalinity present is expressed in $CaCO_3$ equivalents. By accepted definition (Ahern *et al.* 2004), any acid sulfate soil material with a $pH_{KCl} < 6.5$ has a zero ANC. The methods for determining ANC are given by Ahern *et al.* (2004).

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.

1.5. Classification of soil materials

Recently, the Acid Sulfate Soils Working Group of the International Union of Soil Sciences agreed to adopt in principle the following new descriptive terminology and classification definitions of acid sulfate soil materials proposed at the 6th International Acid Sulfate Soil and Acid Rock Drainage Conference in September 2008 in Guangzhou, China. This new classification system for acid sulfate soil materials (Sullivan *et al.* 2010) has also been adopted by the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soils Risk Assessment Project for use in the detailed assessment of acid sulfate soil in the Murray-Darling Basin.

The criteria to define the soil materials are as follows:

Acid Sulfate Soil materials

1) Sulfuric materials - soil materials currently defined as sulfuric by the Australian Soil Classification (Isbell 1996). Essentially, these are soil materials with a $pH_w < 4$ as a result of sulfide oxidation.

2) *Sulfidic materials – soil materials containing detectable sulfide minerals (defined as containing ≥ 0.01% sulfidic S). 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 ecology (e.g. sulfidic sediment). The method with the lowest detection limit is the Cr-reducible sulfide method, which currently has a detection limit of 0.01%; 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).*

3) Hypersulfidic material - Hypersulfidic material is a sulfidic material that is identified by having a field pH of 4 or more and by experiencing a substantial* drop in pH by at least 0.5 unit to 4 or less (1:1 by weight in water, or in a minimum of water to permit measurement) when a 2-10 mm thick layer is incubated aerobically at field capacity. The duration of the incubation is either: a) until the soil pH changes by at least 0.5 pH unit to below 4, or b) until a stable** pH is reached after at least 8 weeks of incubation.

> **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.*

4) Hyposulfidic material - Hyposulfidic material is a sulfidic material that is identified by having a field pH of 4 or more and by not experiencing a substantial* drop in pH by at least 0.5 unit to 4 or less (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.*

5) Monosulfidic materials - soil materials with an acid volatile sulfide content ≥ 0.01% S.

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 the 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 and would be identified during the present course of the Phase 1 detailed assessment.

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 $pH_w \geq 4$ but < 5.5 in the field.

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

2. METHODS AND MATERIALS

2.1. Banrock Station Wetland Complex characteristics

Banrock Station Wetland Complex lies on the River Murray floodplain in south-eastern Australia (Figure 1-1) 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 2-1).

The Wetland Complex straddles the boundary of the Mallee Trench and Mallee Gorge geomorphic tracts and supports a number of discrete depositional basins and active channels on an incised ancestral floodplain which is approximately 5 -10 m above sea level. The largest wetland basin is referred to as the main Banrock Lagoon (Butcher *et al.* 2009). It is an elongate lagoon (120 ha in size) that effectively by-passes lock 3, 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 Wetland Complex is located entirely on private land and management is the responsibility of Constellation Wines Australia. The Wetland Complex is used extensively for recreation and tourism and is the subject of a range of scientific research.

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 2-1, Table 2-1). The upstream toposequence was sited across the deepest part of the wetland, which in early 2008, dried 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 2-1). Both toposequences formed representative cross-sections from the high flood mark (Figure 2-2) to the dry wetland bed (Figure 2-2). 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 2-3). The wetland bed generally contained cracked clayey surface horizons with darker grey, moist heavy clays at depth (Figure 2-3). Black mottles were evident in the near surface at site RBA 4 (the deepest point in the wetland).

Figure 2-1 Map showing the sites assessed in the Banrock Station Wetland Complex, adjacent to the Banrock Station winery.

Table 2-1 Profile codes and global positioning system coordinates (WGS 84 datum, zone 54 south). Three wetland components / landscape types were targeted during this study and included – (i) Dry shoreline**, ii)** Dry bed **and iii)** Dry bed – lowest position**.**

Topo-sequence	Site No	Site Landscape Position	Sample type (near surface)	Date Sampled	Easting	Northing
RBA 1-5 **(near wetland inlet)**	RBA 1	Dry shoreline	Clayey sand	23/05/2008	439334	6214987
	RBA 2	Dry shoreline	Clayey sand	23/05/2008	439291	6214963
	RBA 3	Dry lakebed	Cracking clay	23/05/2008	439275	6214946
	RBA 4	Dry lakebed (lowest)	Cracking clay	23/05/2008	439273	6214945
	RBA 5	Dry lakebed	Cracking clay	23/05/2008	439240	6214949
RBA 6-8 **(near wetland outlet)**	RBA 6	Dry shoreline	Sandy loam	23/05/2008	438732	6216464
	RBA 7	Dry lakebed (lowest)	Cracking clay	23/05/2008	438738	6216472
	RBA 8	Dry shoreline	Clayey sand	23/05/2008	438606	6216568

Detailed site and soil profile descriptions for all sites and soil layers sampled are included in Appendix 1.

Further information on the natural characteristics of the Banrock Station Wetland Complex Ramsar Site can be found in Butcher et al. (2009) for ecological characteristics and (Crosbie et al. (2007) for surface and groundwater characteristics. Eight representative conceptual cross-sections across the wetland are presented in Appendix 3 to illustrate the sequential changes in soils caused by historical and controlled re-flooding.

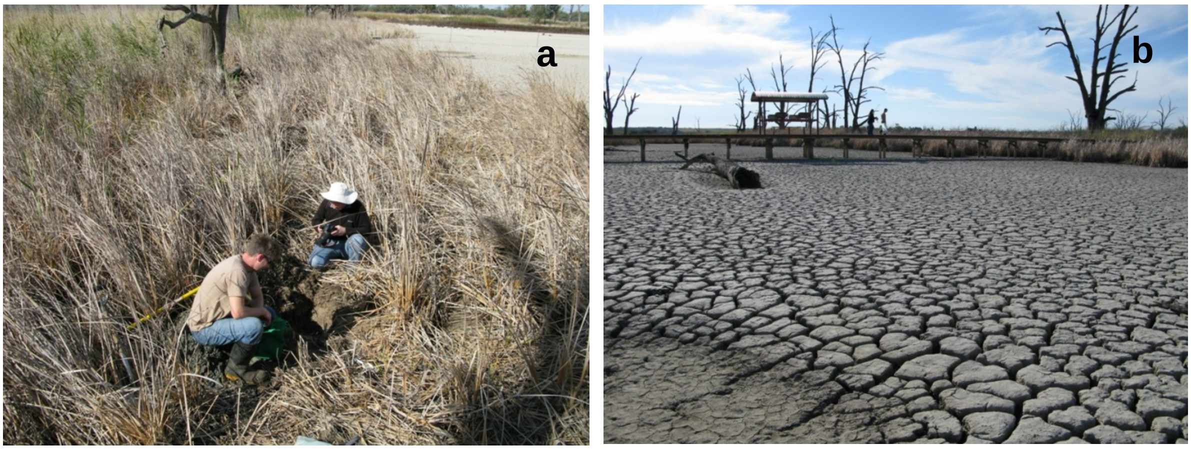

Figure 2-2 Dry wetland near the inlet creek to the main 'Banrock Lagoon'; May 2008. (a) Sampling sandy sulfuric materials from soil profile RBA 1, at the medium to high water mark in *Typha* and *Phragmites* reeds. (b) Dry, cracked, sulfidic clays occur in the near surface soils in the bed of the Banrock Station Wetland Complex.

Figure 2-3 (a) Soil profile RBA 1 showing light orange to brown sandy soils that typically fringe the wetland. Sulfuric material occurs in the top 50 cm of this sandy soil profile. (b) Soil profile RBA 3 shows cracked, light grey clay with a thin, white salt crust at the surface. Sulfidic materials occur throughout soil profile RBA 3.

2.2. Field sampling of soils

A detailed field investigation was undertaken on the 23rd of May 2008 to assess the current and potential environmental hazards due to the presence of acid sulfate soils at the Ramsar site. A total of 30 soil samples were assessed from the eight sites (soil profiles) located on two toposequences that traversed the two main water bodies (the main 'Banrock Lagoon' and the 'Eastern Lagoon'). Where possible the profiles were chosen to represent: (i) the lowest point in the landscape, (ii) a moderately elevated site just above the observed or interpreted normal flow level, and (iii) an elevated site above the normal flow level (Figure 2-3; Table 2-1). All sites were dry at the time of sampling.

Soil samples were collected from at least 5 sampling depths (to a maximum depth of 90 cm) using a range of implements (i.e. spades, and augers). Samples were packed into plastic bags and or plastic jars in which retained air was minimised. All soil samples were maintained at ≤ 4°C prior to analysis.

Site and profile descriptions including global positioning system (GPS) coordinates are presented in Appendix 1. The soil texture and Munsell colour of each sampled soil layer is presented in Appendix 1. Digital photographs were also taken to document each site and soil profile characteristics (e.g. Figure 2-3).

2.3. Laboratory soil analysis methods

All soil samples were oven-dried at 80°C prior to analysis. Any coarse material (> 2 mm) present was removed by sieving, and then samples were ring mill ground.

Several parameters were examined to determine whether acid sulfate soil materials were likely to be present, or if there was a potential for acid sulfate soil materials to form. The parameters measured in this study included pH (pH_W, pH_{OX}, pH_{KCl} and $pH_{INCUBATION}$), titratable actual acidity (TAA), water soluble sulfate and chromium reducible sulfur (S_{CR}).

The existing acidity of each soil layer (pH_W) was assessed by measuring the pH in a saturated paste (1:1 soil:water mixture). The pH_{OX} was determined following oxidation with 30 % hydrogen peroxide (H_2O_2) (Method Code 23Bf) (Ahern *et al.* 2004). The KCl extractable pH (pH_{KCl}) was measured in a 1:40 1.0 M KCl extract (Method Code 23A), and the titratable actual acidity (TAA) (i.e. sum of soluble and exchangeable acidity) was determined by titration of the KCl extract to pH 6.5 (Method Code 23F) (Ahern *et al.* 2004). TAA is a measure of the actual acidity in soil materials. The pH following incubation ($pH_{INCUBATION}$) was determined on duplicate moistened sulfidic soil materials (i.e. $S_{CR} \geq 0.01\%$ S) placed in chip trays using pH indicator strips. The duration of the incubation was until a stable pH was reached after at least 8 weeks of incubation.

Water soluble sulfate (1:5 soil:water extract) was prepared following the procedures described in Rayment and Higginson (1992), and analysed by ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry). The pyritic sulfur content was quantified using the chromium reduction analysis method of Burton *et al.* (2008b).

Acid neutralising capacity, measured by the ANC_{BT} method (Method Code 19A2) (Ahern *et al.* 2004) was determined for sulfidic samples to enable net acidity to be estimated by the acid base account method of Ahern *et al.* (2004).

Standard quality assurance (QA) procedures were followed including the monitoring of blanks, duplicates and standards in each batch.

2.4. Criteria for ranking soil material for inclusion in Phase 2 of the detailed assessment process

The Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soils Risk Assessment Project agreed to recommend that soil materials be assigned the following priorities to undertake the Phase 2 detailed assessment:

High Priority

1) All sulfuric materials.
2) All hypersulfidic materials as recognised by either i) incubation of sulfidic materials (pH<4) or ii) a positive net acidity result with a Fineness Factor of 1.5 being used.
3) All hyposulfidic materials with S_{CR} contents ≥ 0.10% S.
4) All surface soil materials (i.e. within 0-20 cm) with water soluble sulfate (1:5 soil:water) contents >100 mg kg^{-1} SO_4.
5) All monosulfidic materials.

Moderate Priority

All hyposulfidic materials with S_{CR} contents < 0.10% S.

No Further Assessment

1) Other acidic soil materials.
2) All other soil materials.

It is important to note, while the criteria identifying samples for Phase 2 analysis is clearly defined, samples only go through to Phase 2 when consideration is given to the wetland as a whole.

3. RESULTS

3.1. Summary of Banrock Station Wetland Complex field and laboratory results

3.1.1. Soil pH testing (pH_W, pH_{OX}, $pH_{INCUBATION}$ and pH_{KCl})

From the eight sites assessed 30 samples were collected for routine laboratory analysis. Data are presented in Appendix 2 and summarised in Table 3-1 and Figure 3-1 to Figure 3-8.

The pH_W values ranged from strongly acidic (minimum pH_W of 2.6) to basic (maximum pH_W of 9.3), and a median pH_W of 5.8. Strongly acidic soils with a pH_W of less than 4.0 were identified at sites RBA 1 and RBA 2, and classify as sulfuric materials. Soil samples with moderately low pH_w values (<5.5) were also identified at three other sites (RBA 6, RBA 7 and RBA 8).

The pH_{OX} values ranged between 1.3 and 8.8. Almost half (13) of the soil samples experienced a significant drop in pH to obtain a pH_{OX} <2.5, indicating they may have potential to acidify to pH < 4 as a result of sulfide oxidation. Peroxide treatment results were generally supported by ongoing incubation experiments, and S_{CR} data.

The $pH_{INCUBATION}$ values for the 20 soil samples containing sulfidic material (i.e. $S_{CR} \geq 0.01\%$ S) ranged between 2.5 and 7.0. Of these 20 samples four classified as hypersulfidic material because they contained a positive net acidity. The remaining sulfidic soil samples classified as hyposulfidic material.

The pH_{KCl} values ranged between 3.6 and 7.6. The results indicate that 20 soil samples are likely to contain Titratable actual acidity (TAA) as they had a pH_{KCl} < 6.5. Five of these samples are also likely to contain retained acidity (RA) as they had a pH_{KCl} < 4.5.

Table 3-1 Summary data for pH testing and S suite analysis.

parameter	units	minimum	median	maximum	n[1]
pH_W[2]		2.6	5.8	9.3	30
pH_{OX}[3]		1.3	2.9	8.8	30
pH_{KCl}[4]		3.6	5.4	7.6	30
$pH_{INCUBATION}$[5]		2.5	5.3	7.0	20
TAA[6]	mole $H^+ t^{-1}$	0	14	59	20
Water soluble SO_4[7]	mg SO_4 kg^{-1}	83	1239	20337	30
S_{CR}[8]	% S	<0.01	0.1	0.23	30
ANC[9]	% $CaCO_3$	0	0	2.0	20
Net Acidity[10]	mole $H^+ t^{-1}$	-121	16	83	30

[1]n: number of samples. [2]pH_W: pH in saturated paste with water. [3]pH_{OX}: after treatment with 30% H_2O_2. [4]pH_{KCl}: pH of 1:40 1 M KCl extract. [5]$pH_{INCUBATION}$: pH after at least 8 weeks of incubation sulfidic soil materials (i.e. $S_{CR} \geq 0.01\%$ S). [6]TAA: Titratable actual acidity. [7]Water soluble sulfate: in 1:5 soil:water extract. [8]S_{CR}: Chromium reducible sulfur. [9]ANC: Acid neutralising capacity – by definition, where pH_{KCl} < 6.5 ANC = 0. [10]Net acidity - here does not include allowance for retained acidity.

3.1.2. Chromium reducible sulfur (S_{CR})

The chromium reducible sulfur (S_{CR}) data for the Banrock Station Wetland Complex are presented in Appendix 2 and summarised in Table 3-1. Chromium reducible sulfur contents ranged from <0.01% to 0.23%, with a median of 0.1%. Twenty of the 30 samples analysed had measurable S_{CR} (> 0.01 wt. % S_{CR}), with five of these having a S_{CR} of > 0.1 wt. %.

3.1.3. Titratable actual acidity (TAA)

The titratable actual acidity (TAA) data is presented in Appendix 2 and summarised in Table 3-1 and Figure 3-1. The TAA ranged between zero and 59 mole H^+ t^{-1}, with a median of 14 mole H^+ t^{-1}. There was no TAA in 10 of the 30 soil profiles as these layers had a pH_{KCl} ≥ 6.5. Unlike the observed distribution of water soluble SO_4 data, there was usually a slight increase in the TAA with depth to 50 cm (Figure 3-1).

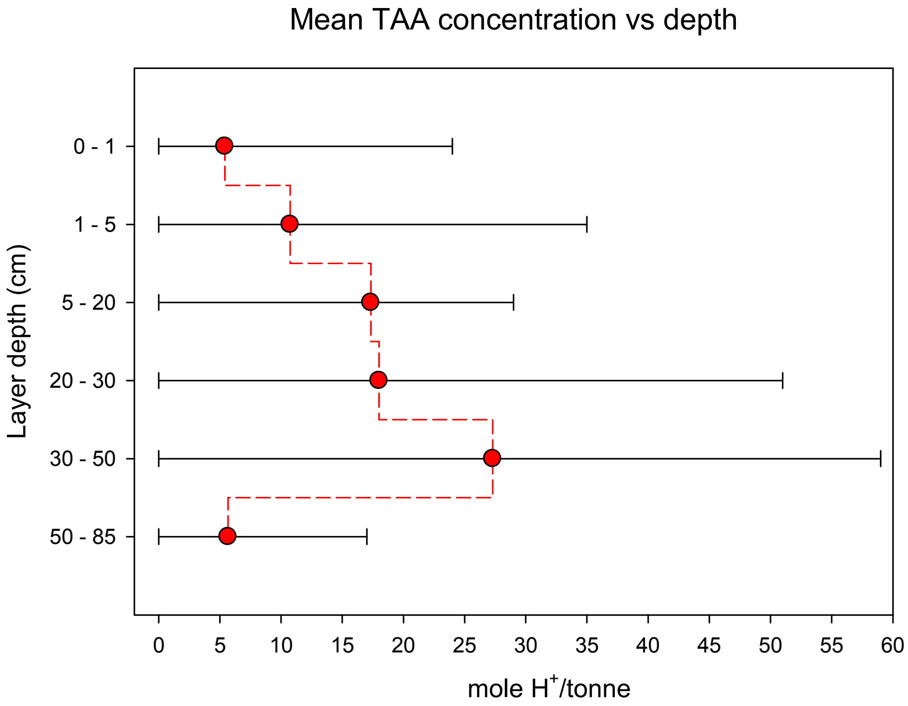

Figure 3-1 Variation in TAA (mole H^+ t^{-1}) across depth intervals for all sites assessed at the Banrock Station Wetland Complex. Mean values are indicated by red dots. Error bars show the range of values for each depth interval.

3.1.4. Acid neutralising capacity (ANC)

The acid neutralising capacity (ANC) data for the Banrock Station Wetland Complex samples are presented in Appendix 2 and summarised in Table 3-1. The ANC was only determined for sulfidic samples to enable the net acidity for sulfidic materials to be estimated by the acid-base accounting. The ANC ranged between zero and 2.0% $CaCO_3$ for the 20 sulfidic soil materials. Thirteen of the sulfidic samples had a pH_{KCl} below 6.5 which by definition indicated that they contain zero effective ANC.

3.1.5. Net acidity

The net acidity data for the Banrock Station Wetland Complex samples are presented in Appendix 2 and summarised in Figure 3-1. The net acidity thresholds used to characterise the acid sulfate soil materials in this assessment include low net acidity (<19 mole $H^+ t^{-1}$), moderate net acidity (19-100 mole $H^+ t^{-1}$) and high net acidity (>100 mole $H^+ t^{-1}$). Acid-base accounting calculations showed the net acidity ranged between -121 and 83 mole $H^+ t^{-1}$, with a median net acidity of 16 mole $H^+ t^{-1}$ (Table 3-1).

The acidification hazard is considered moderate for acid sulfate soil material from profiles RBA 1 (between 0-50 cm depth), RBA 2 (between 30-60 cm depth), RBA 3 (between 0-5 cm depth) and RBA 7 (between 0-50 cm depth). The acidification hazard posed by the acid sulfate soil materials is considered low for all the other soil profiles assessed.

The down profile distribution of acid sulfate soil characteristics are displayed in Figure 3-2 to Figure 3-8.

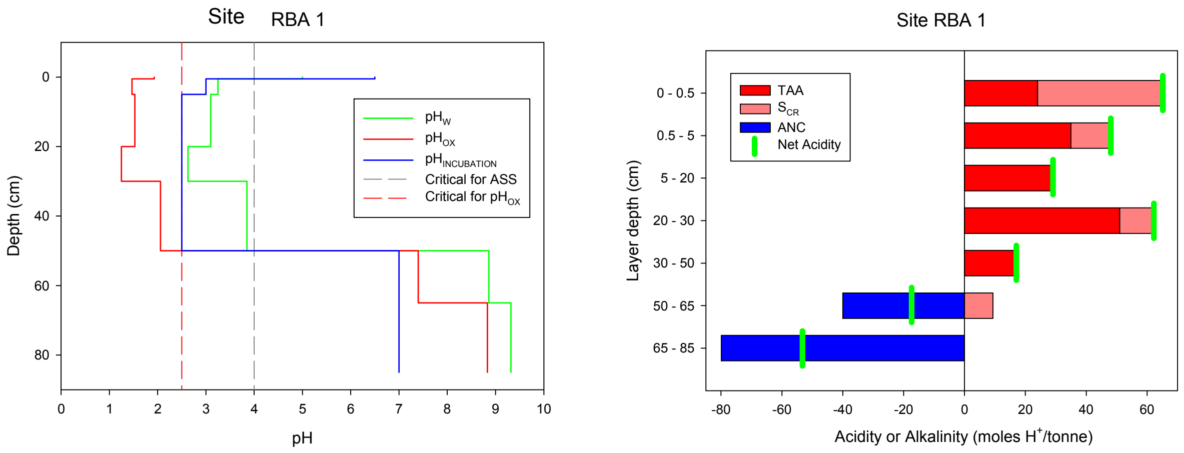

Figure 3-2 (Left plot) Vertical profile distribution of soil pH_W (green line), pH_{OX} (red line) and $pH_{INCUBATION}$ (blue line) data for site RBA 1. The vertical dashed lines indicate critical values for (grey) ASS classification and (red) pH_{OX}. (Right plot) Vertical profile distribution of TAA (red bar), S_{CR} (pink bar), ANC (blue bar) and net acidity (green vertical lines).

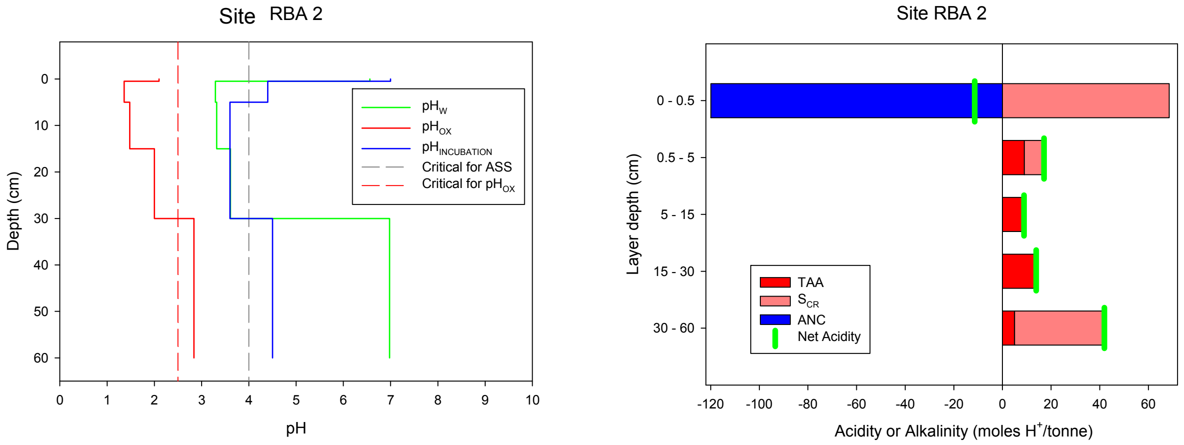

Figure 3-3 (Left plot) Vertical profile distribution of soil pH_W (green line), pH_{OX} (red line) and $pH_{INCUBATION}$ (blue line) data for site RBA 2. The vertical dashed lines indicate critical values for (grey) ASS classification and (red) pH_{OX}. (Right plot) Vertical profile distribution of TAA (red bar), S_{CR} (pink bar), ANC (blue bar) and net acidity (green vertical lines).

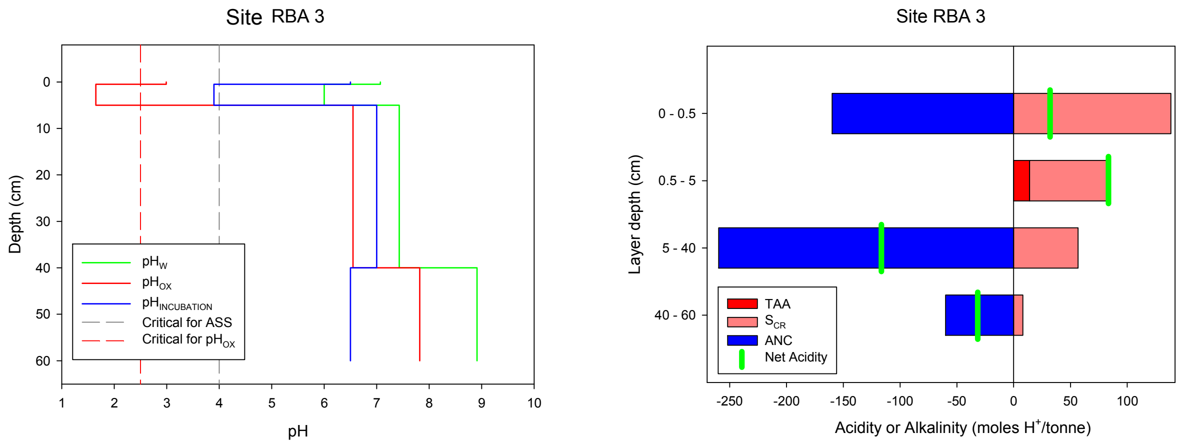

Figure 3-4 (Left plot) Vertical profile distribution of soil pH_W (green line), pH_{OX} (red line) and $pH_{INCUBATION}$ (blue line) data for site RBA 3. The vertical dashed lines indicate critical values for (grey) ASS classification and (red) pH_{OX}. (Right plot) Vertical profile distribution of TAA (red bar), S_{CR} (pink bar), ANC (blue bar) and net acidity (green vertical lines).

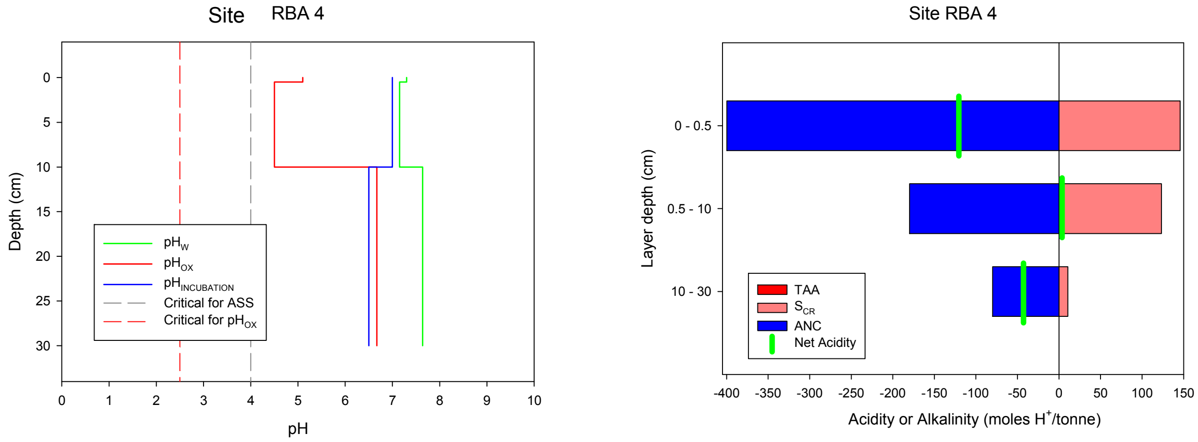

Figure 3-5 (Left plot) Vertical profile distribution of soil pH_W (green line), pH_{OX} (red line) and $pH_{INCUBATION}$ (blue line) data for site RBA 4. The vertical dashed lines indicate critical values for (grey) ASS classification and (red) pH_{OX}. (Right plot) Vertical profile distribution of TAA (red bar), S_{CR} (pink bar), ANC (blue bar) and net acidity (green vertical lines).

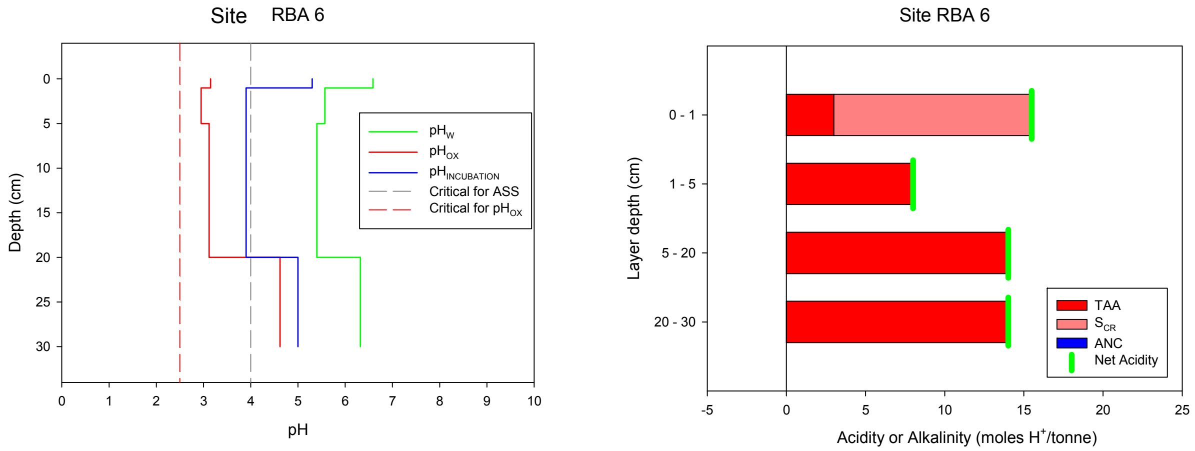

Figure 3-6 (Left plot) Vertical profile distribution of soil pH_W (green line), pH_{OX} (red line) and $pH_{INCUBATION}$ (blue line) data for site RBA 6. The vertical dashed lines indicate critical values for (grey) ASS classification and (red) pH_{OX}. (Right plot) Vertical profile distribution of TAA (red bar), S_{CR} (pink bar), ANC (blue bar) and net acidity (green vertical lines).

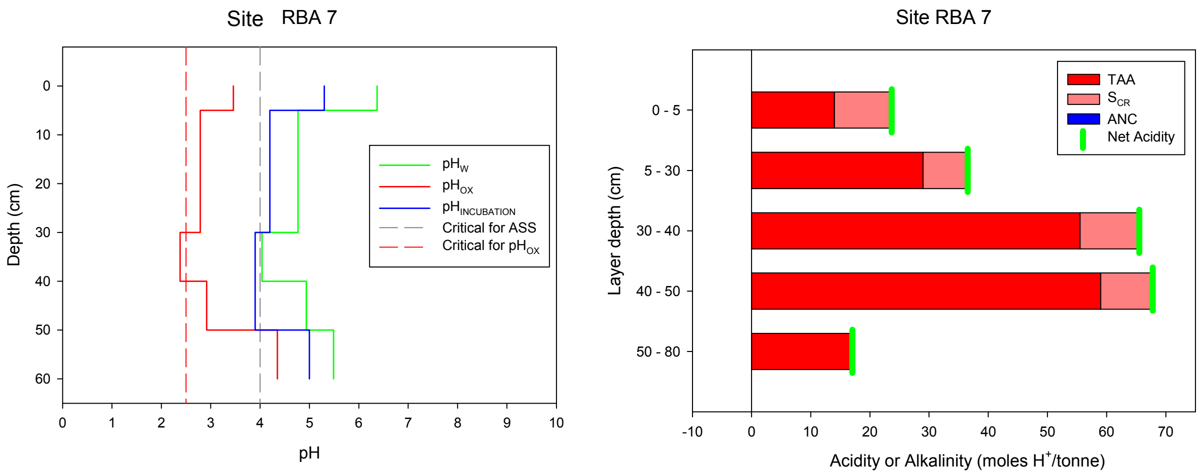

Figure 3-7 (Left plot) Vertical profile distribution of soil pH_W (green line), pH_{OX} (red line) and $pH_{INCUBATION}$ (blue line) data for site RBA 7. The vertical dashed lines indicate critical values for (grey) ASS classification and (red) pH_{OX}. (Right plot) Vertical profile distribution of TAA (red bar), S_{CR} (pink bar), ANC (blue bar) and net acidity (green vertical lines).

3.1.6. Water soluble SO_4

Water soluble sulfate data for the Banrock Station Wetland Complex is presented in Appendix 2 and summarised in Table 3-1 and Figure 3-8. The water soluble sulfate values ranged between 83 and 20,337 mg kg^{-1} SO_4 and generally decreased in concentration with increasing depth. Near surface soils contained the highest water soluble sulfate contents and were generally an order of magnitude higher than the trigger value of 100 mg kg^{-1} SO_4, indicating that the formation of monosulfides may be a potential problem upon rewetting in this wetland. Only two of the 30 soil samples analysed had a water soluble sulfate content below 100 mg kg^{-1} SO_4.

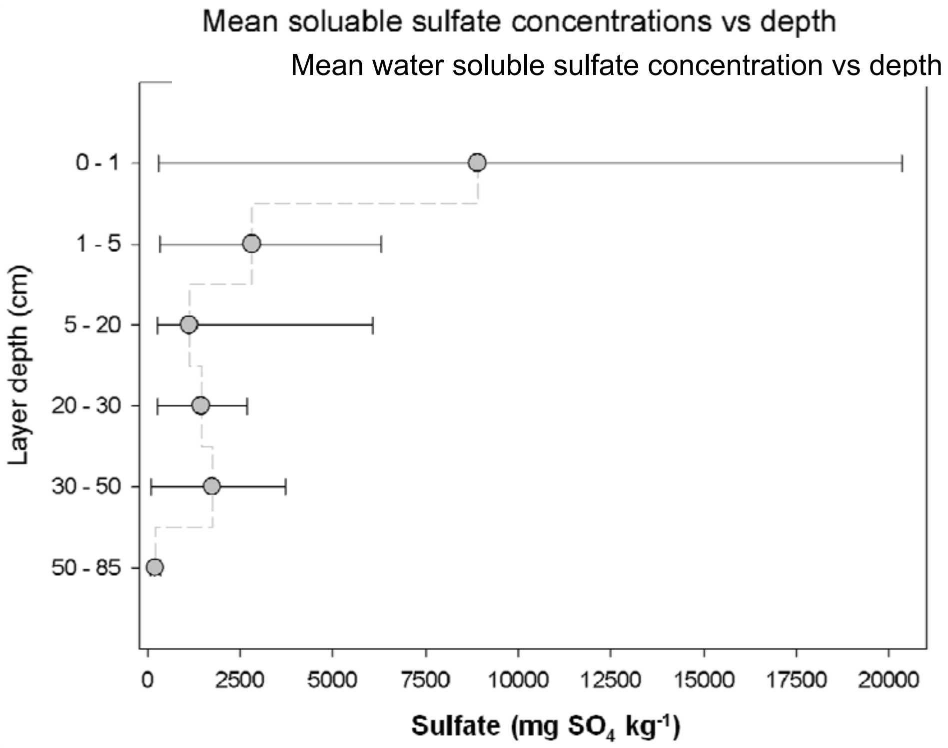

Figure 3-8 Variation in water soluble sulfate (mg SO_4 kg^{-1}) across depth intervals for all sites assessed at the Banrock Station Wetland Complex.

4. HAZARD ASSESSMENT

4.1. Interpretation of soil data

The actual acidity and potential sulfidic acidity within the Banrock Station Wetland Complex Ramsar site is substantial, and spatially extensive (Table 4-1). Sulfuric material was identified at two of the eight sites assessed (RBA 1 and RBA 2) with net acidity of sulfuric material ranging between 9 and 62 mole $H^+ t^{-1}$. Hypersulfidic material was identified at five sites and contained net acidity values ranging between 1 and 83 mole $H^+ t^{-1}$. The remaining soil profile contained other acidic soil material (RBA 8). The acidification hazard from acid sulfate soil is therefore considered as moderate.

Minor amounts of monosulfidic material (as dark grey mottles) were observed at one site (RBA 4) located in the lowest point of the main 'Banrock Lagoon'. The concentration of water soluble sulfate in near surface soil layers was well above trigger value of 100 mg kg^{-1} SO_4 at all sites. The potential for monosulfide formation is therefore considered significant upon rewetting at all eight sites (Table 4-1).

Table 4-1 Summary of acid sulfate soil types in the Banrock Station Wetland Complex Ramsar site.

Type of acid sulfate soil material	Number of sampling sites containing acid sulfate soil material (Total sites = 8)	Portion of total sampling sites (%)
Sulfuric	2	25
Hypersulfidic	5	62.5
Hyposulfidic ($S_{CR} \geq 0.10\%$)	3	37.5
Monosulfidic (observed)	1	12.5
Monosulfidic (potential)	8	100
Hyposulfidic ($S_{CR} < 0.10\%$)	5	62.5
Other acidic (pH_w &/or $pH_{INCUBATION}$) 4 – 5.5	3	37.5
Other soil materials	1	12.5

5. CONCLUSIONS

This report provides the results of Phase 1 of a two-phase assessment procedure to determine the hazards posed by acid sulfate soil materials in the Banrock Station Wetland Complex Ramsar site. The Phase 1 report is aimed solely at determining whether or not acid sulfate soil materials are present and ranking the soils according to the criteria adopted by the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soils Risk Assessment Project.

In this study 30 soil layers and mineral samples were collected from eight geographically well-distributed and locally representative sites (soil profiles) from the Banrock Station Wetland Complex Ramsar site and analysed using a combination of standard methods: **(i)** soil morphology, **(ii)** field pH testing, **(iii)** peroxide testing, **(iv)** acid-base accounting (ABA) and **(v)** soil incubation. No surface water or soil pit water was available for sampling at the time of the site survey.

The results indicate that acid sulfate soil materials were spatially extensive at the time of sampling. Sulfuric material was identified at 25% (i.e. two of the eight) of sampling sites, and represented a current acidity hazard. Hypersulfidic material was identified at 62.5% (i.e. 5) of sites, indicating potential for further acidification to occur upon continued oxidation of the wetland soils. The net acidity values measured indicated that the level of the acidity hazard was moderate. While monosulfidic material was observed at only one soil profile, the potential for monosulfides to form upon reflooding was considered high due to the water soluble sulfur contents of near surface soils at all eight sites being well in excess of the 100 mg kg^{-1} trigger value.

Based on the priority ranking criteria all eight sites qualified as high priority for Phase 2 detailed assessment. There were two high priority sites identified based on the presence of sulfuric material and five other high priority sites based on the presence of hypersulfidic material. One high priority site was also identified based on the presence of hyposulfidic materials with S_{CR} > 0.10%. In addition, all eight sampling sites had a high priority ranking for Phase 2 detailed assessment based on monosulfide formation hazard.

The potential hazards at a wetland-scale posed by acid sulfate soil materials at the Banrock Station Wetland Complex Ramsar site are as below (Table 5-1):

- Acidification: Titratable actual acidity (TAA) data indicated that a moderate acidity hazard existed in the wetland soils at the time of sampling. A moderate potential acidity hazard also existed in the wetland due to the presence of hypersulfidic materials identified. As such, the degree of acidification hazard is moderate.
- Deoxygenation: The water soluble sulfate contents of all eight surface soil materials were over the trigger value for monosulfide formation indicating the possible development of an appreciable deoxygenation hazard after prolonged wet conditions.
- Metal mobilisation: The moderate acidification hazard indicates that soil acidification is likely to increase the solubility of metals. The potential for monosulfide formation identified in these wetlands may also result in an appreciable metal release hazard depending on factors such as the metal loading in this wetland.

Table 5-1 Summary of acid sulfate soil hazards identified for the different wetland components and soil types identified within the Banrock Station Wetland Complex Ramsar site.

Wetland component	**Type of soil material**	**Hazard**		
		Acidification	**Metal mobilisation**	**De-oxygenation of water**
Dry shoreline	Clayey sands – **Sulfuric**	Moderate	Moderate	Moderate
Dry lakebed	Cracking clay – ***Hypersulfidic***	Moderate	Moderate	Moderate
Dry lakebed (lowest position)	Cracking clay – ***Hypersulfidic***	Moderate	Moderate	Moderate

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7. APPENDIX 1. SITE AND SAMPLE DESCRIPTIONS

GENERAL				POSITION			LOCALITY				
Location name	**Sampling date**	**Site code**	**Layer code**	**Z**	**X**	**Y**	**Topo-sequence Locality (position)**	**Obs. method**	**Site (Local name)**	**Site Water Status**	**Site Description**
Banrock	23/05/2008	RBA 4	**RBA 4.1**	54H	439273	6214945	3	Field		D	
Banrock	23/05/2008	RBA 4	**RBA 4.2**	54H	439273	6214945					
Banrock	23/05/2008	RBA 4	**RBA 4.3**	54H	439273	6214945					
Banrock	23/05/2008	RBA 5	**RBA 5.1**	54H	439240	6214949	3			D	
Banrock	23/05/2008	RBA 6	**RBA 6.1**	54H	438732	6216464	1	Field		D	
Banrock	23/05/2008	RBA 6	**RBA 6.2**	54H	438732	6216464					
Banrock	23/05/2008	RBA 6	**RBA 6.3**	54H	438732	6216464					
Banrock	23/05/2008	RBA 6	**RBA 6.4**	54H	438732	6216464					
Banrock	23/05/2008	RBA 7	**RBA 7.1**	54H	438738	6216472	3	Field		D	*Phragmites* about 10m north of the boardwalk opposite site 6. Embankment about 0.6m high next to the main outlet channel - cross section of bank
Banrock	23/05/2008	RBA 7	**RBA 7.2**	54H	438738	6216472					
Banrock	23/05/2008	RBA 7	**RBA 7.3**	54H	438738	6216472					
Banrock	23/05/2008	RBA 7	**RBA 7.4**	54H	438738	6216472					
Banrock	23/05/2008	RBA 7	**RBA 7.5**	54H	438738	6216472					
Banrock	23/05/2008	RBA 8	**RBA 8.1**	54H	438606	6216568	2	Field		D	*Phragmites* about 70m from the start of the boardwalk

Toposequence Locality (position)*: 1 – High to mid point on shoreline or embankment; 2 – Mid to low point of dry shoreline near normal water level; 3 – lowest point in wetland or creek channel.

	DEPTH			SOIL COLOUR			TEXTURE
Layer code	**Upper depth (cm)**	**Lower depth (cm)**	**Depth to water**	**Soil Moist. Status**	**Soil Colour**	**Munsell**	**Class**
RBA 1.1	0	0.2	?	M	White salts on the boardwalk pylon		Fine
RBA 1.2	0	0.5		M	white	10YR 8/1	Fine
RBA 1.3	0.5	5		D	light grey	2.5Y 7/1	Medium
RBA 1.4	5	20		M	light grey	2.5Y 7/2	Medium
RBA 1.5	20	30		M	greyish brown	2.5Y 5/2	Medium
RBA 1.6	30	50		M	greenish grey	10Y 6/1	Medium
RBA 1.7	50	65		M	greenish grey	5GY 5/1	Fine
RBA 1.8	65	85		M	greenish grey	5GY 5/1	Fine
RBA 1.9	grab	grab					Fine
RBA 1.10	grab	grab					Fine
RBA 2.1	0	0.5	?	D	light grey	2.5Y 7/2	Fine
RBA 2.2	0.5	5		D	light grey	2.5Y 7/1	Medium
RBA 2.3	5	15		D	light grey	2.5Y 7/2	Medium
RBA 2.4	15	30		M	light greenish grey	10Y 7/1	Medium
RBA 2.5	30	60		M	greenish grey	10Y 6/1	Fine
RBA 3.1	0	0.5	?	D	light grey	2.5Y 7/2	Fine
RBA 3.2	0.5	5		D	light grey	2.5Y 7/2	Fine
RBA 3.3	5	40		D	greenish grey	10Y 6/1	Fine
RBA 3.4	40	60		D	greenish grey	10Y 5/1	Fine
RBA 4.1	0	0.5	?	M	olive grey	5Y 4/2	Fine
RBA 4.2	0.5	10		M	dark grey	5Y 4/1	Fine
RBA 4.3	10	30		M	greenish grey	10GY 5/1	Fine
RBA 5.1	0	3	?	D	light grey	5Y 7/1	Fine
RBA 6.1	0	1	?	D	light greenish grey	10Y 7/1	Fine
RBA 6.2	1	5		D	light brownish grey	2.5YR 6/2	Fine
RBA 6.3	5	20		D	greenish grey	10Y 6/1	Fine
RBA 6.4	20	30		D	greenish grey	10Y 6/1	Fine
RBA 7.1	0	5	?	D	light grey	2.5Y 7/1	Medium
RBA 7.2	5	30		D	pale yellow	2.5Y 7/4	Medium
RBA 7.3	30	40		D	pale yellow	2.5Y 7/4	Medium
RBA 7.4	40	50		M	grey	5Y 5/1	Fine
RBA 7.5	50	80		M	greenish grey	10Y 5/1	Fine
RBA 8.1	0	10	?	D	light grey	2.5Y 7/2	Medium

	COLOUR			LAYER MORPHOLOGY
Layer code	**Moist. Status**	**Mottle Colour**	**Munsell**	**Description**
RBA 1.1				White salts on the boardwalk pylon
RBA 1.2	M			Very fluffy white salts on the soil surface of the dark, friable algal mat that is under the boardwalk (protected from the rain)
RBA 1.3	D			Brownish sand with about 40% dead *Phragmites* stalk and roots intermixed
RBA 1.4	M			Mainly yellowish sand with odd clay lens intermixed, making up about 30% of soil
RBA 1.5	M			Pale orange to brown sand with black clay layers
RBA 1.6	M			Greenish (odd olive) sandy loam, slightly stinky
RBA 1.7	M	very dark greyish green	5G 3/2	Green, light clay with brown mottles (ca. 10%) and dark olive green mottles (ca. 2-5%)
RBA 1.8	M	strong brown	7.5YR 5/8	Green heavy clay with brown mottles (ca. 5%)
RBA 1.9				Brown black rusted metal fragments/flakes with orange yellow mottles, found on the surface of the algal mat
RBA 1.10				Bright orange yellow powder gel?
RBA 2.1	D			Crust with roots and white salts holding the sandy surface together. Friable, slightly moist
RBA 2.2	D			Light grey, clean, fine sand. *Typha* roots intermittent
RBA 2.3	D			Light grey, yellowish brown fine to medium sand with occasional *Typha* root material, more abundant than upper layer
RBA 2.4	M	strong brown	7.5YR 5/8	Greyish sandy clay grading to light clay with depth. Fine (elongate and thin, about 1mm to 5mm across) yellow orange mottles make up about 5% or less of soil and occur near sandy areas (root channels or cracks or benthic organic-rich holes)
RBA 2.5	M	reddish yellow	7.5YR 6/8	Greyish green heavy clay identical to RBA 1.8 with possibly more green mottles. Orange mottles make up 1% of soil and occur around fine root channels or tubes of about 0.5 to 1mm diameter, and elongate up to 10 to 30mm long
RBA 3.1	D			Light grey white crust. Quite hard to lift from the column
RBA 3.2	D			grey, hard y clay. Some yellow brown mottles <1%
RBA 3.3	D	strong brown	7.5YR 5/8	Light grey, very hard dry clay. Light brown yellow mottles along sandy fills cracks and thin root channels ca. 2-5%
RBA 3.4	D	olive	5Y 4/4	Green grey wet moist clay with some sparkles - probably gypsum crystals. Very bright olive green mottles ca. 2-5% are possibly nontronite (RF)

	COLOUR			LAYER MORPHOLOGY
Layer code	**Moist. Status**	**Mottle Colour**	**Munsell**	**Description**
RBA 4.1	M			Soft grey brown to white crust
RBA 4.2	M			Dark grey olive green brown heavy clay with orange mottles along cracks and root channels ca. <5%
RBA 4.3	M	strong brown	7.5YR 5/8	Dark grey slightly olive green heavy clay with bright yellow orange coatings (<0.1mm thick) around root channels and cracks surfaces. Cracks may be layering but are discontinuous
RBA 5.1	D			Soil and crust from underneath pile of fish bones
RBA 6.1	D	reddish yellow	7.5YR 7/8	Orange coating (<1mm thick) on surface of the crust. The crust is 0.5 to 1cm thick, light grey silty clay
RBA 6.2	D			grey dark brown clay, hard, slightly damp, with brown grey sandy areas. The clay has orange mottles along root channels
RBA 6.3	D	reddish yellow	7.5YR 6/8	Light grey clay with light orange yellow mottles around root channels. Dry and hard
RBA 6.4	D	reddish yellow	7.5YR 6/8	Light brown grey clay with light orange mottles along root channels and along crack surfaces
RBA 7.1	D			*Phragmites* root mat. Brown and very light. 90% Organic Matter
RBA 7.2	D			*Phragmites* root mat. Brown and very light. 90% Organic Matter
RBA 7.3	D			*Phragmites* root mat. Brown and very light. 80% Organic Matter
RBA 7.4	M	strong brown	7.5YR 5/8	Dark grey brown heavy clay
RBA 7.5	M	reddish yellow	7.5YR 6/8	Dark grey brown clay. From below the *Phragmites* embankment
RBA 8.1	D			Light brown orange mottled sandy loam - medium sand getting more clayey with depth

8. APPENDIX 2. FIELD AND LABORATORY ANALYTICAL SOIL DATA

	Layer depth		$pH_{INCUBATION}$		pH		ASS Classification (Manual Ranking)
Layer code	Upper depth	Lower depth	10 weeks	19 weeks	pHw	pH_{OX}	14/12/2010
RBA 1.1	0	0.2					Other soil material
RBA 1.2	0	0.5	7	6.5	5	1.93	Hyposulfidic
RBA 1.3	0.5	5	4	3	3.25	1.47	Sulfuric
RBA 1.4	5	20	3	2.5	3.1	1.53	Sulfuric
RBA 1.5	20	30	3	2.5	2.63	1.25	Sulfuric
RBA 1.6	30	50	3	2.5	3.85	2.06	Sulfuric
RBA 1.7	50	65	7	7	8.86	7.40	Hyposulfidic
RBA 1.8	65	85	7	7	9.32	8.83	Other soil material
RBA 1.9	grab	grab					Other soil material
RBA 1.10	grab	grab					Other soil material
RBA 2.1	0	0.5	7	7	6.56	2.10	Hyposulfidic (SCR >0.1%)
RBA 2.2	0.5	5	5	4.4	3.29	1.36	Sulfuric
RBA 2.3	5	15	3	3.6	3.32	1.48	Sulfuric
RBA 2.4	15	30	3	3.6	3.61	2.00	Sulfuric
RBA 2.5	30	60	3.9	4.5	6.98	2.84	Hypersulfidic
RBA 3.1	0	0.5	7	6.5	7.07	2.99	Hyposulfidic (SCR >0.1%)
RBA 3.2	0.5	5	4	3.9	6	1.65	Hypersulfidic
RBA 3.3	5	40	5	7	7.43	6.55	Hyposulfidic
RBA 3.4	40	60	7	6.5	8.91	7.82	Hyposulfidic
RBA 4.1	0	0.5	7	7	7.3	5.10	Hyposulfidic (SCR >0.1%)
RBA 4.2	0.5	10	7	7	7.15	4.50	Hyposulfidic (SCR >0.1%)
RBA 4.3	10	30	7	6.5	7.64	6.67	Hyposulfidic

	Layer depth		$pH_{INCUBATION}$		pH		ASS Classification (Manual Ranking)
Layer code	Upper depth	Lower depth	10 weeks	19 weeks	pHw	pH_{OX}	14/12/2010
RBA 5.1	0	3	4	3	6.39	1.90	Hypersulfidic
RBA 6.1	0	1	7	5.3	6.59	3.15	Hyposulfidic
RBA 6.2	1	5	4	3.9	5.57	2.95	Hypersulfidic
RBA 6.3	5	20	4.4	3.9	5.4	3.12	Hypersulfidic
RBA 6.4	20	30	5.8	5	6.32	4.62	Other Acidic
RBA 7.1	0	5	6.1	5.3	6.37	3.46	Hyposulfidic
RBA 7.2	5	30	5.8	4.2	4.77	2.79	Hyposulfidic
RBA 7.3	30	40	5	3.9	4.04	2.38	Hypersulfidic
RBA 7.4	40	50	5.3	3.9	4.94	2.92	Hypersulfidic
RBA 7.5	50	80	5.3	5	5.49	4.35	Other Acidic
RBA 8.1	0	10			4.69	2.24	Other Acidic

	Layer depth		S - Suite								
Layer code	**Upper depth**	**Lower depth**	**Texture**	**Sulfate*** (mgSO$_4$ kg^{-1})	**pH$_{KCl}$**	**TAA** (as mole H+ t^{-1})	**S$_{CR}$** (%S$_{CR}$)	**S$_{CR}$** (moles H$^+$ t^{-1})	**ANC** (%CaCO$_3$)	**ANC** (as moles H$^+$ t^{-1})	**NET ACIDITY (based on %S$_{CR}$)** (mole H$^+$ t^{-1})
Samples							**LLD 0.01**				
RBA 1.1	0	0.2	Fine								
RBA 1.2	0	0.5	Fine	20337	5.62	24	0.07	41.16	0.0	0.00	65.16
RBA 1.3	0.5	5	Medium	6308	4.33	35	0.02	13.10	0.0	0.00	48.10
RBA 1.4	5	20	Medium	1789	4.09	29	0.00	0.00	0.0	0.00	29.00
RBA 1.5	20	30	Medium	2691.	3.62	51	0.02	11.23	0.0	0.00	62.23
RBA 1.6	30	50	Medium	1344	4.26	17	0.00	0.00	0.0	0.00	17.00
RBA 1.7	50	65	Fine	214	6.54	0	0.02	9.36	0.2	39.96	-17.28
RBA 1.8	65	85	Fine	83	6.97	0	0.00	0.00	0.4	79.92	-53.28
RBA 1.9	grab	grab	Fine							0.00	
RBA 1.10	grab	grab	Fine							0.00	
RBA 2.1	0	0.5	Fine	14260	6.96	0	0.11	68.61	0.6	119.88	-11.31
RBA 2.2	0.5	5	Medium	1642	5.15	9	0.01	8.11	0.0	0.00	17.11
RBA 2.3	5	15	Medium	1067	5.13	9	0.00	0.00	0.0	0.00	9.00
RBA 2.4	15	30	Medium	1133	4.62	14	0.00	0.00	0.0	0.00	14.00
RBA 2.5	30	60	Fine	94	5.70	5	0.06	36.80	0.0	0.00	41.80
RBA 3.1	0	0.5	Fine	2796	7.21	0	0.22	138.46	0.8	159.84	31.90
RBA 3.2	0.5	5	Fine	2209	5.25	14	0.11	69.23	0.0	0.00	83.23
RBA 3.3	5	40	Fine	967	7.52	0	0.09	56.76	1.3	259.74	-116.40
RBA 3.4	40	60	Fine	158	6.84	0	0.01	8.11	0.3	59.94	-31.85

	Layer depth		S - Suite								
Layer code	**Upper depth**	**Lower depth**	**Texture**	**Sulfate*** (mgSO$_4$ kg^{-1})	**pH$_{KCl}$**	**TAA** (as mole H+ t^{-1})	**S$_{CR}$** (%S$_{CR}$)	**S$_{CR}$** (moles H$^+$ t^{-1})	**ANC** (%CaCO$_3$)	**ANC** (as moles H$^+$ t^{-1})	**NET ACIDITY (based on %S$_{CR}$)** (mole H$^+$ t^{-1})
Samples							**LLD 0.01**				
RBA 4.1	0	0.5	Fine	6846	7.62	0	0.23	145.95	2.0	399.60	-120.45
RBA 4.2	0.5	10	Fine	6073	7.62	0	0.20	123.49	0.9	179.82	3.61
RBA 4.3	10	30	Fine	237	6.88	0	0.02	10.60	0.4	79.92	-42.68
RBA 5.1	0	3	Fine	4892	6.61	0	0.09	54.26	0.4	79.92	0.98
RBA 6.1	0	1	Fine	301	6.22	3	0.02	12.47	0.0	0.00	15.47
RBA 6.2	1	5	Fine	715	5.57	8	0.00	0.00	0.0	0.00	8.00
RBA 6.3	5	20	Fine	564	5.22	14	0.00	0.00	0.0	0.00	14.00
RBA 6.4	20	30	Fine	282	5.27	14	0.00	0.00	0.0	0.00	14.00
RBA 7.1	0	5	Medium	452	5.70	14	0.02	9.67	0.0	0.00	23.67
RBA 7.2	5	30	Medium	3439	5.08	29	0.01	7.48	0.0	0.00	36.48
RBA 7.3	30	40	Medium	3448	4.58	56	0.02	9.98	0.0	0.00	65.48
RBA 7.4	40	50	Fine	3718	4.20	59	0.01	8.73	0.0	0.00	67.73
RBA 7.5	50	80	Fine	356	5.08	17	0.00	0.00	0.0	0.00	17.00
RBA 8.1	0	10	Medium	338	5.17	6	0.00	0.00	0.0	0.00	6.00

Analyses were completed by Southern Cross University, Lismore. The methods are mostly as described by Ahern *et al.* (2004). ***Acid Sulfate Soils Laboratory Methods Guidelines*.** QLD DNRME. All analysis is based on dry weight - samples dried and ground immediately upon arrival (unless supplied dried and ground). Results at or below detection limits are replaced with '0' for calculation purposes. See methods section for additional details. 1 - TAA = total actual acidity. 2 - Soluble sulfate measured on a 1:5 soil:water extract. 3 - S$_{CR}$ = reduced inorganic sulfur measured as % chromium reducible sulfur. 4 - ANC = acid neutralising capacity expressed as equivalent % CaCO$_3$. 5 - Net Acidity = Potential Sulfidic Acidity (i.e. S$_{CR}$ or S$_{ox}$) + Actual Acidity + Retained Acidity - measured ANC/FF. Note that retained acidity is frequently significant on samples with pH$_{KCl}$ < 4.5, but has not yet been measured on these samples.

9. APPENDIX 3: BANROCK STATION WETLAND COMPLEX RAMSAR SITE – ACID SULFATE SOIL CONCEPTUAL MODELS

Background information

Despite decades of scientific investigation of the ecological e.g. Living Murray Icon Site Environmental Management Plan (Murray-Darling Basin Commission 2006d), hydrological, water quality (salinity) and pedological features of wetlands in the Murray-Darling Basin (MDB), we have only in the past year advanced far enough to appreciate the wide spectrum of ASS subtypes and processes that are operating in these contemporary environmental settings, especially from continued lowering of water levels (e.g. Fitzpatrick *et al.* 2008b; Fitzpatrick *et al.* 2008c; Fitzpatrick *et al.* 2008d; Lamontagne *et al.* 2004; Shand *et al.* 2008a; Shand *et al.* 2008b; Simpson *et al.* 2008).

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

ASS form naturally in both coastal and freshwater environments where sulfate is present in the surface or groundwater along with large amounts of organic matter such as decaying vegetation in waterlogged areas.

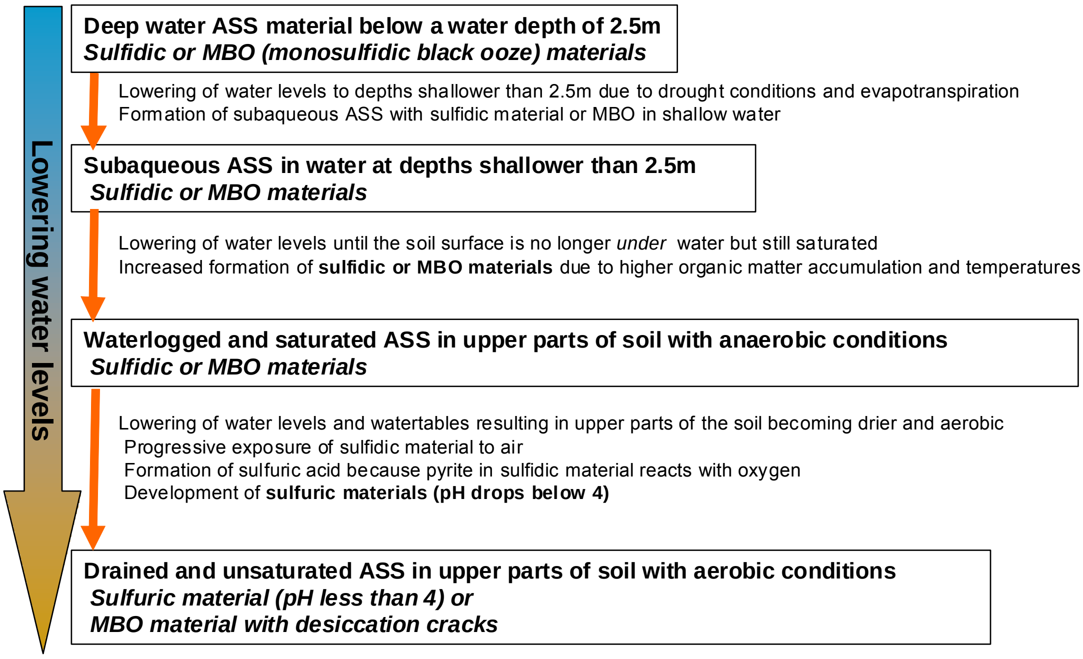

Figure 9-1 Generalised conceptual model showing the sequential transformation of four classes of ASS due to lowering of water levels from “Deep-water ASS” → “Subaqueous ASS” → “Waterlogged and saturated ASS” (all containing sulfidic material with high sulfide concentrations and pH>4) to → “Drained and unsaturated ASS” containing sulfuric material (pH<4) in the upper soil layers (from Fitzpatrick *et al.* 2008b; Fitzpatrick *et al.* 2008c; Fitzpatrick *et al.* 2009).

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 is likely to have accumulated in subaqueous or submerged soils. Current drought conditions have led to a considerable drop in water levels in the river channel 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 9-1).

Conceptual models for acid sulfate soil transformations over time and management

In this appendix, we summarise all current field and laboratory investigations to assess the acid sulfate soil properties, hazard and management scenarios with respect to the drained soils and rewetted subaqueous soils at the Banrock Station Wetland Complex Ramsar site. Based on these investigations and historical/palaeo-pedological knowledge of the Murray-Darling Basin (MDB), we have constructed a series of eight conceptual models that illustrate how various Acid Sulfate Soil (ASS) materials in subaqueous and dried conditions have sequentially changed – and will change over time. To illustrate these sequential changes, we have constructed the following series of conceptual cross-sectional models across the wetland, based on Fitzpatrick *et al.* (2009):

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

It is anticipated that this Ramsar wetland will commence a drying phase in October 2008.

(i) Before the 1880s (5,500 BC to 1880s) the Banrock Station 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 9-2).

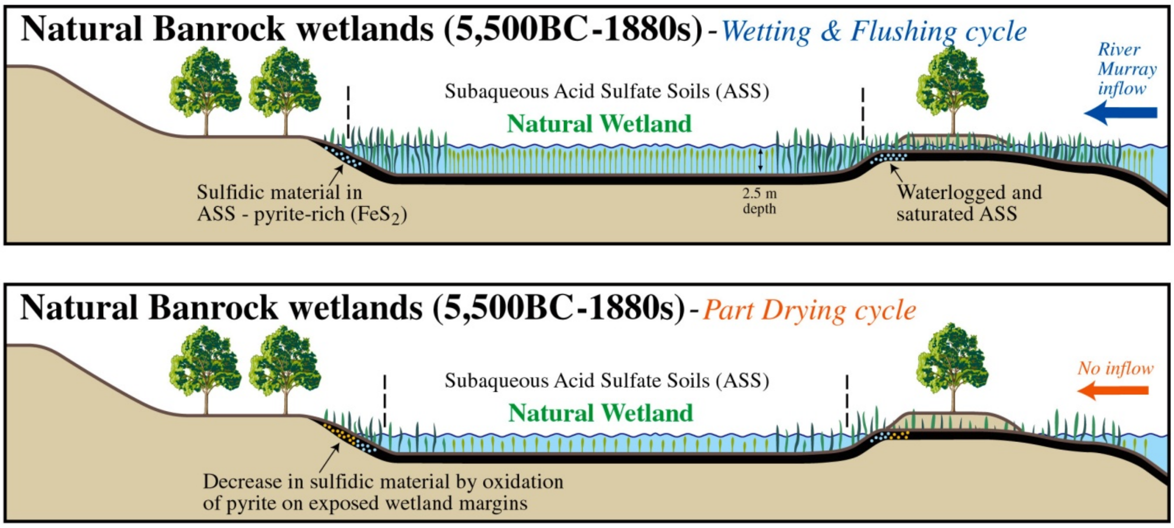

Figure 9-2. Generalised schematic cross section models for Banrock Station Wetland Complex; illustrating natural wetting and flushing (upper panel), and partial drying (lower panel) cycle conditions during pre-colonial times (5,500 BC - 1880s).

During wetter periods the wetlands underwent regular wetting and flushing cycles (Figure 9-2 - upper panel). Waters received by the wetlands were transferred via channels, overland flow, and by infiltration. Wetlands accumulated sulfidic materials from sulfate contained in upstream and groundwaters. However, during dry periods such as droughts (Figure 9-2 - lower panel) when river flows were lower, the wetland 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 the supposed formation of sulfuric materials. In wetter times and 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 (e.g. “burned-off”) and removal from scouring floods.

(ii) During the 1880s to 1930s period, European colonists moderated the flows of the River Murray by the installation of various irrigation network systems (Figure 9-3). During this period the wetland was “managed for flood irrigation” (e.g. citrus and dairy).

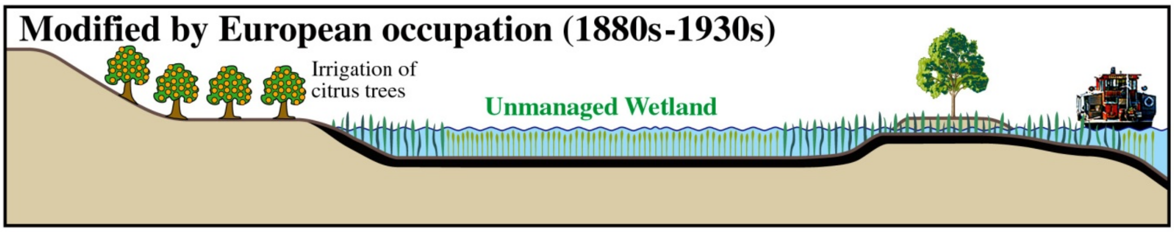

Figure 9-3 Generalised schematic cross section model for the Banrock Station Wetland Complex; illustrating modification of water flows by European occupation (1880s- 1930s).

(iii) During the 1925 to 1993 period the river and wetland systems were first managed using locks (Figure 9-4). The installation of locks has allowed considerable build-up of sulfidic and MBO material in the wetland due to: (i) the evaporative concentration of sulfate containing nutrient/salt loads in stable pool levels and groundwater sources, (ii) the lack of scouring and seasonal flooding. Ultra-fine monosulfidic black ooze (MBO) material accumulates in low-flow backwaters and along the vegetated edges of the wetland (Figure 9-4).

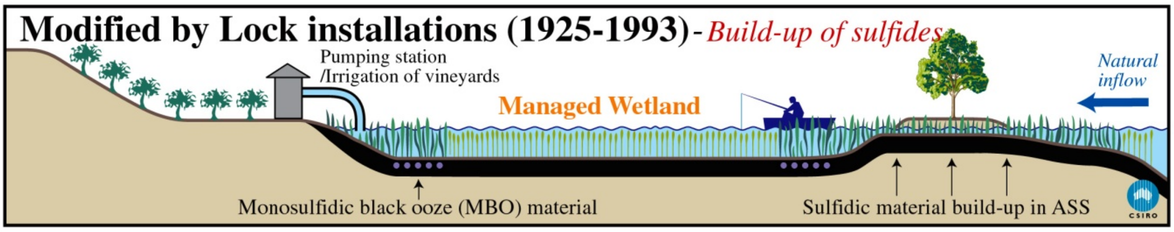

Figure 9-4 Generalised schematic cross section model for the Banrock Station Wetland Complex; illustrating modification of water flows by lock installations causing the build up of sulfides under continues subaqueous ASS conditions from 1925-1993.

(iv) During the 1993 to 2006 period, partial drying cycles and substantial rewetting cycles occurred due to the installation of flow control structures (sluice gates) (Figure 9-5). During partial drying periods (Figure 9-5 - top panel) the wetland partly dried in places, causing likely oxidation of sulfidic (hypersulfidic) 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 supposed formation of sulfuric materials - similar to the natural system described in Figure 9-2. 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 regularly kept-in-check by oxidation (e.g. “burned-off”).

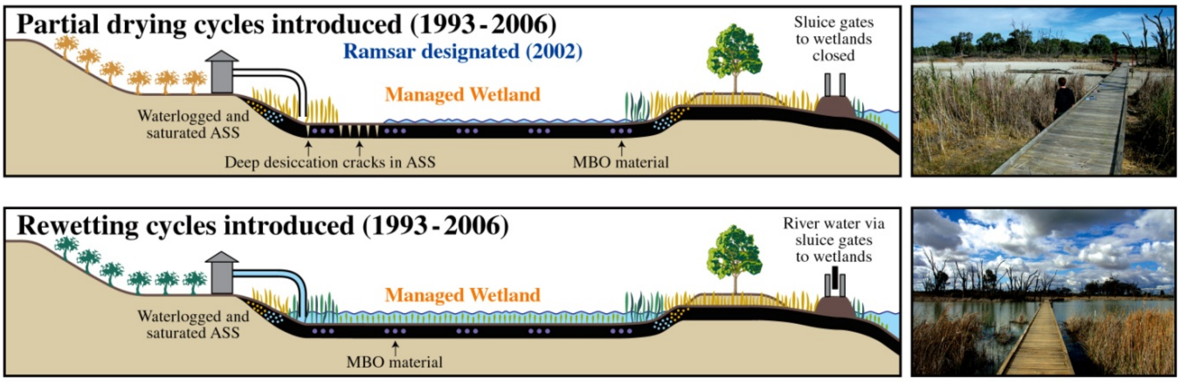

Figure 9-5 Generalised schematic cross section models for the Banrock Station Wetland Complex; illustrating the installation of sluice gates to manage the partial drying cycle (upper panel) and the rewetting/ flushing cycle (lower panel) during 1993 to 2006). The Banrock Station Wetland Complex was designated a Ramsar site in 2002.

(v) During the 2007 to June 2008 period (18 months) when complete (unprecedented) drying of the whole wetland took place (Figure 9-6) because of the extreme drought conditions from 2006 to 2008 when the river level continued to lower, and the wetland effectively became hydraulically disconnected from the river channel. During this period subaqueous ASS transformed to waterlogged ASS (i.e. ASS that are wet or saturated long enough to produce periodically anaerobic conditions, thereby influencing the growth of plants: e.g. hydric soils with sulfidic material) and eventually to dried ASS. This resulted in the formation of sulfuric material (pH less than 4 to depths up to 50cm) 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 cause the release of Fe, Al, Mg, Si (and others) and the formation of sulfate-rich salt efflorescences in and near soil surfaces (Figure 9-6). The continued drying of the wetlands has caused further desiccation, and the precipitation of sulfate-rich salt efflorescences in desiccation cracks and on the sandy edges of the wetland. Areas with MBO continued to dry out, also causing desiccation cracks to develop in the fine textured material.

In 2006, the pump used for irrigation purposes was removed from the Ramsar wetland (Figure 9-6).

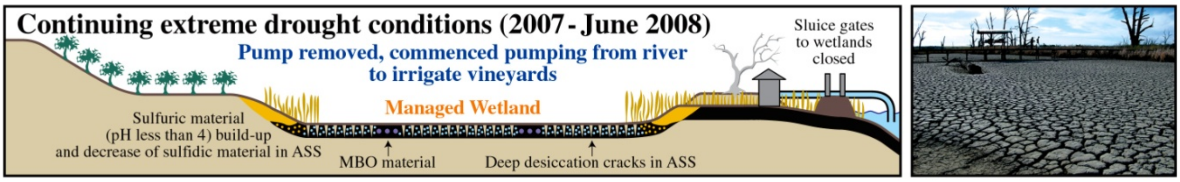

Figure 9-6 Generic conceptual model for the Banrock Station Wetland Complex illustrating the formation of: (i) sulfuric material (pH <4) by oxidation of sulfides in sulfidic material on the edges of the wetland, (ii) sulfate-rich salt efflorescences and (iii) deep desiccation cracks; due to continued lowering of water levels under persistent extreme drought conditions during 2007 – 2008.

(vi) During June 2008 to October 2008 period (5 months) when complete rewetting took place by pumping water into the wetland (Figure 9-7), sulfuric, sulfidic and MBO materials, including sulfate-rich salt efflorescences become diluted and mobilised. Once appropriate wetland/redox conditions resume, sulfidic materials reform, while metal salts bioaccumulate, or accumulate in sediments. Under this management scenario, there is control of the distribution and eventual fate of sulfates, MBO and salts.

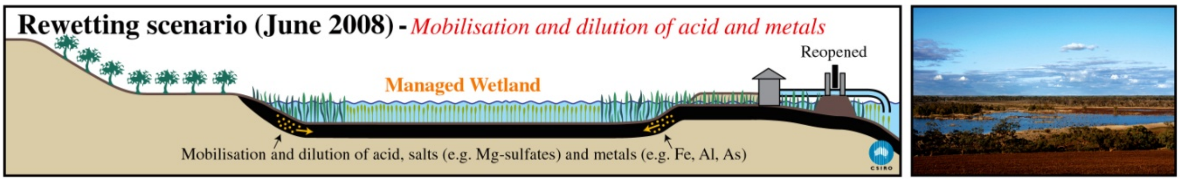

Figure 9-7. Generic conceptual model for the Banrock Station Wetland Complex showing the complete re-wetting of the whole wetland in June 2008 with inundation of sulfuric materials, which occur on the edges of the wetland

Management of this now-managed wetland will involve carefully maintaining water level by controlling in-flows and out-flows. Under this management scenario, sulfuric materials and metal salts will be contained in the wetland, thus allowing targeted and controlled management to occur to re-instigate and maintain wetland quality.

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