

Assessment of Acid Sulfate Soil Materials in Ramsar Wetlands of the Murray-Darling Basin: Fivebough and Tuckerbil Swamps

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Cover Photograph:

Typical landscape in the Fivebough Swamp. Photograph taken at Site RSFS 6 in the Fivebough Swamp.

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EXECUTIVE SUMMARY

The Fivebough and Tuckerbil Swamps are located near Leeton in the Riverina region of New South Wales. Fivebough Swamp is 2 km north-east of Leeton, and Tuckerbil Swamp, less than 10 km from Fivebough, is approximately 12 km north-west of Leeton. The Fivebough Swamp is a permanent, but fluctuating, fresh-brackish, shallow wetland and Tuckerbil Swamp is a seasonal, shallow, brackish-saline wetland (Schultz *et al.* 2002). Both wetlands are of national and international importance because of the presence, abundance and diversity of waterbirds, including migratory shorebirds and threatened species (Schultz *et al.* 2002).

The Murray-Darling Basin Authority (MDBA), in partnership with its Partner Governments and scientists, instigated the Murray-Darling Basin Acid Sulfate Soil Risk Assessment Project (MDB ASSRAP), which aims to assess the spatial occurrence of, and risks posed by, acid sulfate soil materials at priority wetlands in the River Murray system, Ramsar wetlands and other key environmental sites in the Murray-Darling Basin. 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 Soil 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 the Fivebough and Tuckerbil Swamps Ramsar wetland. This Phase 1 report is aimed solely at determining whether or not acid sulfate soil materials are present in the Fivebough and Tuckerbil Swamps Ramsar wetland.

Sulfuric materials were not observed in these wetlands, and although 31% (i.e. 4) of the sampling sites contained sulfidic materials, the reduced inorganic sulfur concentrations of these samples were low (i.e. the highest S_{CR} was only 0.02%). A hypersulfidic soil material was present in one soil profile, and another three soil profiles contained hyposulfidic materials (with $S_{CR} < 0.10\%$). These results indicate that minimal acidity would be produced upon oxidation of sulfides in these materials.

While monosulfidic black ooze (MBO) was not observed at the time of sampling, all surficial soil materials contained water soluble sulfate in excess of the 100 mg/kg trigger value for MBO formation potential.

Based on the priority ranking criteria adopted by the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soil Risk Assessment Project, there was one high priority site based on the presence of a hypersulfidic material, and three moderate priority sites based on the presence of hyposulfidic materials with $S_{CR} < 0.10\%$. In addition, all 13 sampling sites had a high priority ranking for Phase 2 detailed assessment of MBO formation hazard.

The potential hazards at a wetland-scale posed by acid sulfate soil materials at the Fivebough and Tuckerbil Swamps Ramsar wetland sites are as below:

- Acidification: The data indicate that with low titratable actual acidities (TAA) and only a few sulfidic materials (where the highest S_{CR} was only 0.02% S) that the degree of acidification hazard is low.
- Deoxygenation: The water soluble sulfate contents of all thirteen surface soil materials were over the trigger value for potential MBO formation indicating the possible development of an appreciable deoxygenation hazard after prolonged wet conditions.
- Metal mobilisation: The low acidification hazard indicates that soil acidification is not likely to increase the solubility of metals. However, the potential for MBO formation identified in these wetlands may result in an appreciable metal release hazard depending on factors such as the potential for MBO formation and the metal loading in this wetland.

1. INTRODUCTION

1.1. *Wetland overview*

The Fivebough and Tuckerbil Swamps are located near Leeton in the Riverina region of New South Wales (Figure 1-1). Fivebough Swamp is 2 km north-east of Leeton, and Tuckerbil Swamp, less than 10 km from Fivebough, is approximately 12 km north-west of Leeton. Soils in the Fivebough Swamp are cracking grey clays with varying degrees of self-mulching properties. The surface of Tuckerbil Swamp is predominantly grey/dark grey clay to an average depth of 7.2 m. Data indicate the watertable is now within 2 m – 2.5 m of the surface in these swamps and there is a general rising groundwater trend in the area. Salinity is an issue in parts of the swamps. The sources of water are highly variable, coming from rainfall, stormwater and irrigation runoff, automatic overflow of drainage water from the contour drain, release of excess drainage water by Murrumbidgee Irrigation and escape water from the irrigation supply. Fivebough Swamp also receives water from treated sewage effluent discharges. Water levels in Fivebough and Tuckerbil Swamps fluctuate considerably from season to season. After heavy rainfall, water levels can rise rapidly. Water logging following excessive wet periods is common. Water levels gradually recede, exposing mudflats and providing a shallow water habitat (Glazebrook and Taylor 1998). The overview from the Ramsar Site Information Sheet (Schultz *et al.* 2002) is as follows:

Fivebough Swamp is a permanent, but fluctuating, fresh-brackish, shallow wetland and Tuckerbil Swamp is a seasonal, shallow, brackish-saline wetland. Both are of national and international importance because of the presence, abundance and diversity of waterbirds that have been recorded there, including migratory shorebirds and threatened species.

The typical landscape observed in the Fivebough and Tuckerbil Swamps is shown in Figure 1-2, and a typical soil profile is given in Figure 1-3. Further information on characteristics of the Fivebough and Tuckerbil Swamps can be found on the Ramsar Site Information Sheet (Schultz *et al.* 2002).

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 (Sullivan and Bush 1997; Bush 2000) and iron monosulfides (Bush and Sullivan 1997; Bush *et al.* 2000) can also be found.



Figure 1-1. Map of Ramsar Wetlands surveyed in the Murray-Darling Basin.

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 (Sammut *et al.* 1993; Sullivan *et al.* 2002a; Burton *et al.* 2006), high concentrations of aluminium and iron (Ferguson and Eyre 1999; Ward *et al.* 2002), and the release of other potentially toxic metals (Preda and Cox 2001; Sundström *et al.* 2002; Burton *et al.* 2008a; Sullivan *et al.* 2008a).

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. 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 (i.e. sulfuric materials with 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 assessment.

Despite decades of scientific investigation of the ecological (e.g. Living Murray Icon Site Environmental Management Plan: MDBC 2006a,b,c), hydrological, water quality (salinity) and geological 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. Lamontagne *et al.* 2004; Fitzpatrick *et al.* 2008a,b; Shand *et al.* 2008; Shand & Edmunds 2008; Simpson *et al.* 2008; Sullivan *et al.* 2008a). 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 MDBC (now the Murray-Darling Basin Authority – 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 materials at priority wetlands in the River Murray system, Ramsar wetlands and other key environmental sites 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 for immediate detailed acid sulfate soil assessment (Figure 1-1). Wetlands within these complexes were then identified and selected for further assessment.

Southern Cross GeoScience carried out a detailed assessment at 13 representative sites within the Fivebough and Tuckerbil Swamps Ramsar wetlands between 18th and 20th July 2008 to determine whether acid sulfate soils were present, or if there was a potential for acid sulfate soil to form within these wetlands (Figure 1-4). 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.



Figure 1-2. Typical landscape in the Fivebough and Tuckerbil Swamps (Site RSFS 2).



Figure 1-3. Typical grey brown clay in the Fivebough and Tuckerbil Swamps (Site RSFS 1).

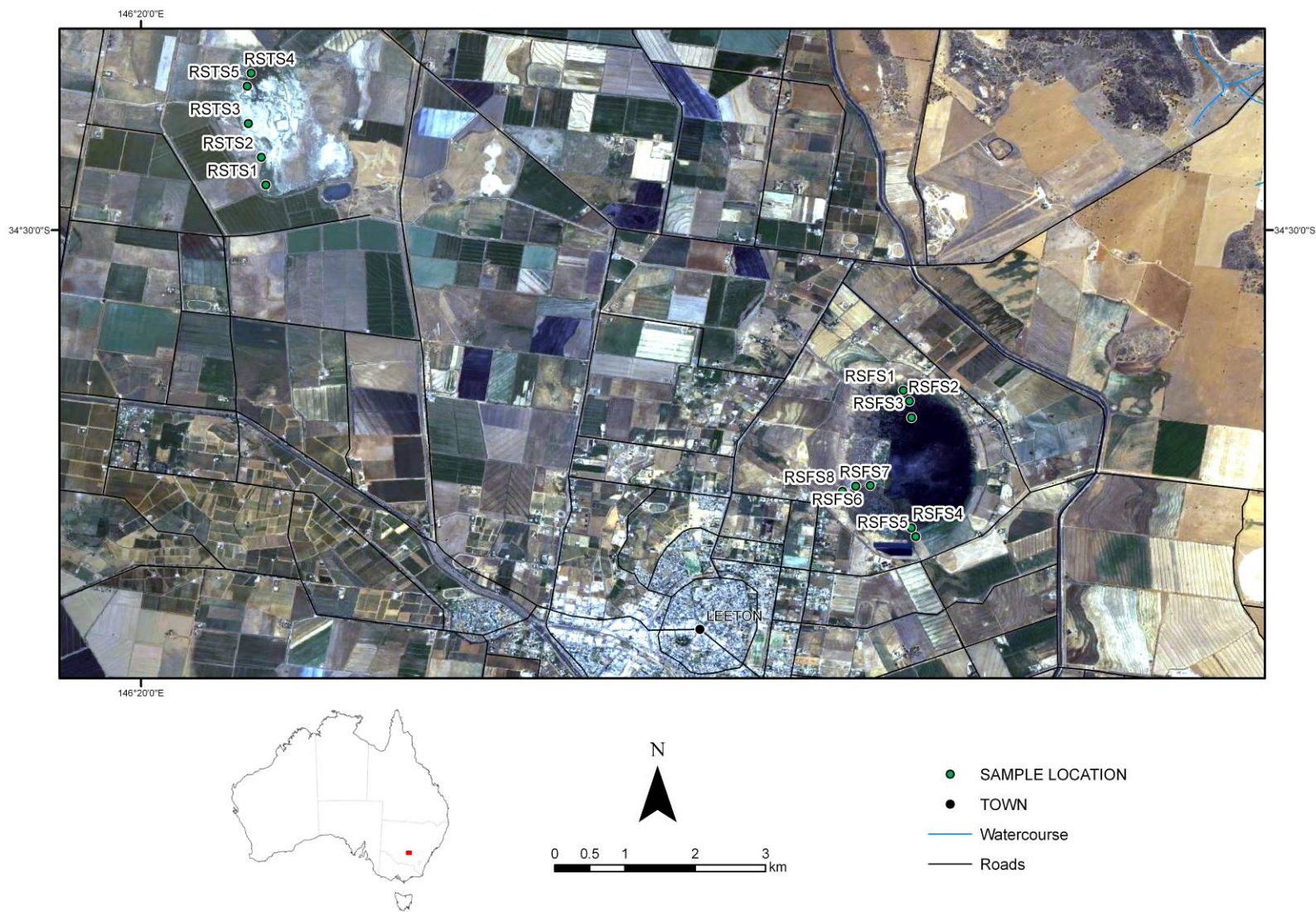


Figure 1-4. Map showing the areas assessed in the Fivebough (RSFS) and Tuckerbil (RSTS) Swamps.

1.3. Detailed Acid Sulfate Soil assessments using two stages

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^+ /tonne), 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).

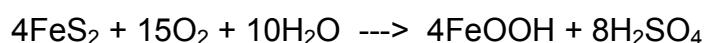
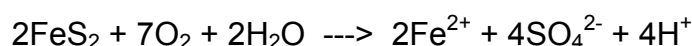
Following a request from the Murray-Darling Basin Authority (MDBA), Southern Cross GeoScience were engaged to conduct a Phase 1 detailed

assessment of acid sulfate soils at the Fivebough and Tuckerbil Swamps Ramsar wetlands.

1.4. Methodologies 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 (Sammut *et al.* 1993; Sullivan *et al.* 2002a; Burton *et al.* 2006), high concentrations of aluminium and iron (Ferguson and Eyre 1999; Ward *et al.* 2002), and the release of other potentially toxic metals (Preda and Cox 2001; Sundström *et al.* 2002; Burton *et al.* 2008a; Sullivan *et al.* 2008a).

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 (re-wetting).

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 acid-based accounting applicable to acid sulfate soils is described in Ahern *et al.* (2004) and summarised here. The equation below shows the calculation of Net Acidity (NA).

Net Acidity (NA) = Potential Sulfidic Acidity (PSA) + Titratable Actual Acidity (TAA) + Retained Acidity (RA) – Acid Neutralising Capacity (ANC)/Fineness Factor (FF)

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

- Potential sulfidic acidity (PSA) also known as the 'acid generation potential' (AGP) is most easily and accurately determined by assessing the Chromium reducible sulfur (S_{CR} or CRS) and then converting this to PSA (AGP) as described in Ahern *et al.* (2004).
- Titratable actual acidity (TAA) is a measure of the actual acidity in acid sulfate soil materials that have already oxidised. It measures the sum of both soluble and exchangeable acidity.
- Retained acidity (RA) is the acidity 'stored' in minerals such as jarosite, schwertmannite and other hydroxy sulfate minerals. Although these

minerals may be stable under acidic conditions, they can release acidity to the environment when these conditions change.

- Acid neutralising capacity (ANC) is measured in soils with pH_{KCl} values > 6.5 . These soils 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 expressed in CaCO_3 equivalents. By accepted definition (Ahern *et al.* 2004), any acid sulfate soil material with a $\text{pH}_{\text{KCl}} < 6.5$ has a zero ANC.
- Fineness factor (FF) 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 as 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 five descriptive terminology and classification definitions of acid sulfate soil materials proposed by Professor Leigh Sullivan and co-authors in a plenary lecture and Acid Sulfate Soils Working Group meeting at the 6th International Acid Sulfate Soil and Acid Rock Drainage Conference in September 2008 in Guangzhou, China (Sullivan *et al.* 2008b). This new classification system for acid sulfate soil materials (Sullivan *et al.* 2010) has also been recently (October 2008) adopted by the Scientific Reference Panel of the Murray–Darling Basin Acid Sulfate Soil Risk Assessment Project for use in the detailed assessment of acid sulfate soils in the Murray–Darling Basin.

The criteria to define the soil materials are as follows:

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 greater than or equal to 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 (i) has a field pH of 4 or more and (ii) is identified by experiencing a substantial* drop in pH 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 (i) has a field pH of 4 or more and (ii) does not experience a substantial* drop in pH 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 of 0.01% S or more.

Non-Acid Sulfate Soil materials

In addition the Scientific Reference Panel of the Murray–Darling Basin Acid Sulfate Soil 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 $\text{pH}_w \geq 4$ but < 5.5 in the field.
2. **Other soil materials** – soils that do not have acid sulfate soil (or other acidic) characteristics.

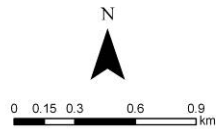
2. METHODS AND MATERIALS

2.1. Fivebough and Tuckerbil Swamps site characteristics

Locations sampled in this study were uniformly flat with either a lack of vegetation cover or more typically a vegetation cover of grasses and sedges (e.g. Figure 2-2 and 2-4). The soils at each site were grey-brown clays (e.g. Figure 2-2). Accordingly, the textures of the soil materials sampled ranged from light clay to medium-heavy clay (Appendix 2).

Surface water was present within the Fivebough Swamp when sampled. The Tuckerbil Swamp was dry at the time of sampling, except for standing water at one of the sites (Site RSTS 5). Groundwater was not intercepted in any of the Tuckerbil Swamp sampling pits. Monosulfidic black oozes (MBO) did not occur at any sites at the time of sampling.

A map giving the location of each of the sites sampled and the typical landscape in each of these areas is shown in Figures 2-1 – 2.4. A typical soil profile is also shown in Figure 2-2.



- SAMPLE LOCATION
- Watercourse
- Roads

Figure 2-1. Map showing the areas assessed in the Fivebough Swamp (Sites RSFS 1-8).



Figure 2-2. Typical landscape (Site RSFS 6) and grey brown clay (Site RSFS 1) in the Fivebough Swamp. Water quality samples were collected from and analysed for Site RSFS 6.

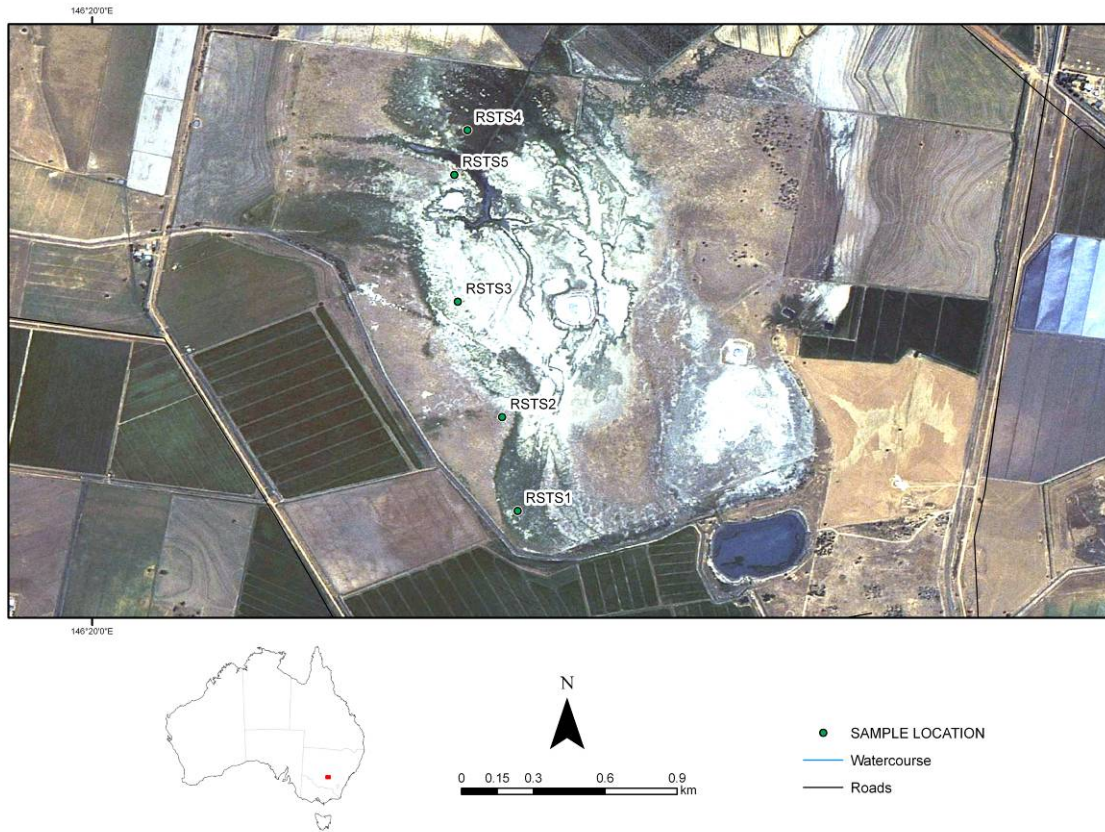


Figure 2-3. Map showing the areas assessed in the Tuckerbil Swamp (Sites RSTS 1-5).



Figure 2-4. Typical landscape (Site RSTS 2) and standing water at Site RSTS 5 in the Tuckerbil Swamp. Water quality samples were collected from and analysed for Site RSTS 5.

2.2. Field sampling of soils and waters

Field sampling of the Fivebough and Tuckerbil Swamps was undertaken between the 18th and 20th July 2008. A total of 67 soil layers were collected and analysed from 13 representative soil profiles within the Fivebough and Tuckerbil Swamps Ramsar wetlands to assess the current and potential environmental hazard due to the presence of acid sulfate soils (Figure 1-4).

Representative soil profiles were collected from three locations within the Fivebough Swamp (Figure 2-1). At each of these locations soil profiles were sampled along a toposequence. 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. Representative soil profiles were collected from five locations along a transect within the Tuckerbil Swamp (Figure 2-3).

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 in which retained air was minimised. All soil samples were maintained at $\leq 4^{\circ}\text{C}$ 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 2. Digital photographs were also taken to document each site and soil profile characteristics. Photographs of representative sites can be found in Section 2.1.

Surface water quality data was collected from four locations in the Fivebough Swamp (Sites RSFS 2, 3, 4 and 6) and one location in the Tuckerbil Swamp (Site RSTS 5). Groundwater samples were collected from three sites in the Fivebough Swamp (Sites RSFS 5, 7 and 8).

Surface water pH, specific electrical conductivity (SEC), dissolved oxygen (DO) and redox potential (Eh) were determined in the field using calibrated electrodes linked to a TPS 90-FLMV multi-parameter meter. Turbidity was measured using a calibrated TPS WP88 Turbidity meter. Alkalinity was also determined in the field by acid titration.

Surface water samples were collected in 1L polypropylene containers. Filtered (0.45 μm) and unfiltered surface water samples were collected at each location. All filtered samples were acidified with a couple of drops of concentrated nitric acid (HNO_3). Samples were stored at $< 4^{\circ}\text{C}$ and sent to CSIRO for analysis.

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_{FOX} , pH_{KCl} and $pH_{INCUBATION}$), titratable actual acidity (TAA), water soluble sulfate, chromium reducible sulfur (S_{CR}) and acid neutralising capacity (ANC).

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_{FOX} 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. Laboratory water analysis

The water quality parameters measured by CSIRO included (i) pH, EC, alkalinity, (ii) dissolved organic carbon, (iii) major anions/nutrients (Cl, Br, F, NO_2 , NO_3 , PO_4 , SO_4 , NH_4 , total N & P, B, S), (iv) major cations (Na, K, Ca, Mg), and (v) trace metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Zn). EC, pH, alkalinity, nutrient (N and P) and major ion analyses were undertaken on unfiltered samples (centrifuged and no visible suspended solids present). Dissolved metals were analysed on filtered samples.

2.5. Criteria for ranking soil materials for inclusion in Phase 2 of the detailed assessment process

The Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soil 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 1) incubation of sulfidic materials or 2) a positive net acidity result with a Fineness Factor of 1.5 being used).
- 3) All hyposulfidic materials with S_{CR} contents $\geq 0.10\%$ S.
- 4) All surface soil materials (i.e. within 0-20 cm) with water soluble sulfate (1:5 soil:water) contents ≥ 100 mg/kg 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 that, 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 Fivebough and Tuckerbil Swamps field and laboratory results

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

The pH_W , pH_{FOX} , pH_{KCl} and $pH_{INCUBATION}$ data for the Fivebough and Tuckerbil Swamps Ramsar wetland sites examined are presented in Table 7-2 and 7-3 (Appendix 2) and summarised in Table 3-1. The pH_W values ranged between 6.06 and 9.19, with the majority of the samples having a $pH_W > 7.5$. None of the soils in the Fivebough and Tuckerbil Swamps would be classified as being sulfuric materials as all soils had a $pH_W > 4$.

The pH_{FOX} values ranged between 2.81 and 9.39. The majority of the soils either showed a pH drop or minimal change in pH after treatment with peroxide (e.g. Figures 3-1 – 3-4), with a maximum decrease of 3.3 pH units. One of the surface soils in the Tuckerbil Swamp (i.e. RSTS 4.3 (0-5 cm)) had a $pH_{FOX} < 4$, and the S_{CR} data also shows this layer contains detectable sulfide ($S_{CR} = 0.02\% S$).

The $pH_{INCUBATION}$ values of the sulfidic soil materials (i.e. $S_{CR} \geq 0.01\% S$) ranged between 5.3 and 9.0. None of the sulfidic soil materials acidified to $pH < 4$ after at least 8 weeks of incubation. However, one sulfidic soil material (i.e. RSTS 4.3 (0-5 cm)) was classified as hypersulfidic as it had a positive net acidity (see Section 2.5).

Table 3-1. Summary soil data for peroxide testing and sulfur suite.

Parameter	Units	Minimum	Median	Maximum	n ¹
pH_W ²		6.06	8.39	9.19	67
pH_{FOX} ³		2.81	8.35	9.39	67
pH_{KCl} ⁴		5.31	8.04	9.78	67
$pH_{INCUBATION}$ ⁵		5.3	8.2	9.0	4
TAA ⁶	mole H ⁺ /tonne	0.00	0.00	30.08	67
Soluble SO ₄ ⁷	mg SO ₄ /kg	56	526	12299	67
S_{CR} ⁸	Wt. %S	<0.01	<0.01	0.02	67
ANC ⁹	%CaCO ₃	0.00	0.47	5.14	4
Net Acidity ¹⁰	mole H ⁺ /tonne	-678.6	4.1	30.8	15

¹ n: number of samples. ² pH_W : pH in saturated paste with water. ³ pH_{FOX} : pH after treatment with 30% H₂O₂. ⁴ pH_{KCl} : pH of 1:40 1 M KCl extract. ⁵ $pH_{INCUBATION}$: pH after least 8 weeks of incubation. ⁶ TAA: Titratable Actual Acidity. ⁷ 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.

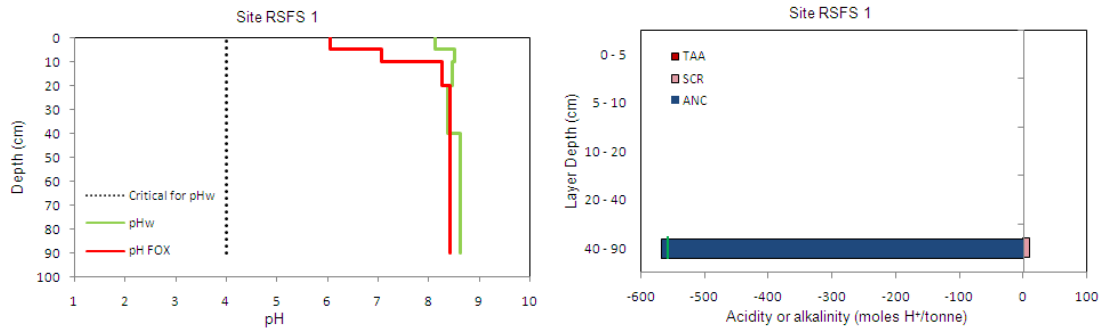


Figure 3-1. Soil pH and acid base accounting data for soil profile RSFS 1. Left Plot: Soil (pH_w: green line) and peroxide pH (pH_{FOX}: red line). Right Plot: S_{CR} (pink bar), ANC (blue bar) and Net Acidity for sulfidic layers (green line). (Note: ANC was only required to be determined for sulfidic layers).

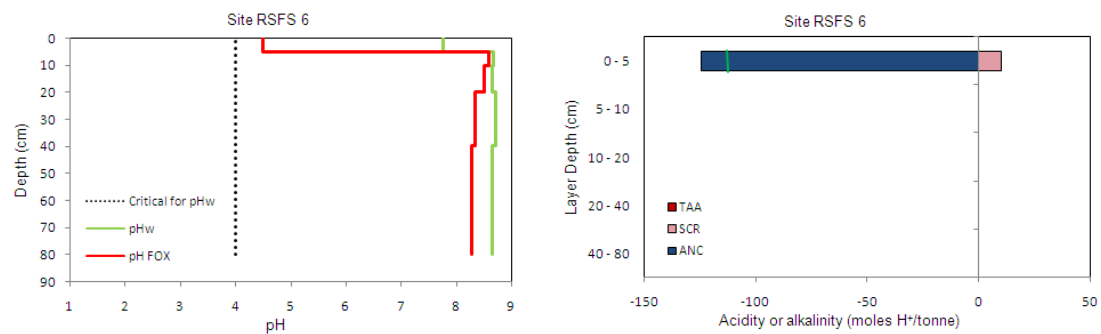


Figure 3-2. Soil pH and acid base accounting data for soil profile RSFS 6. Left Plot: Soil (pH_w: green line) and peroxide pH (pH_{FOX}: red line). Right Plot: S_{CR} (pink bar), ANC (blue bar) and Net Acidity for sulfidic layers (green line). (Note: ANC was only required to be determined for sulfidic layers).

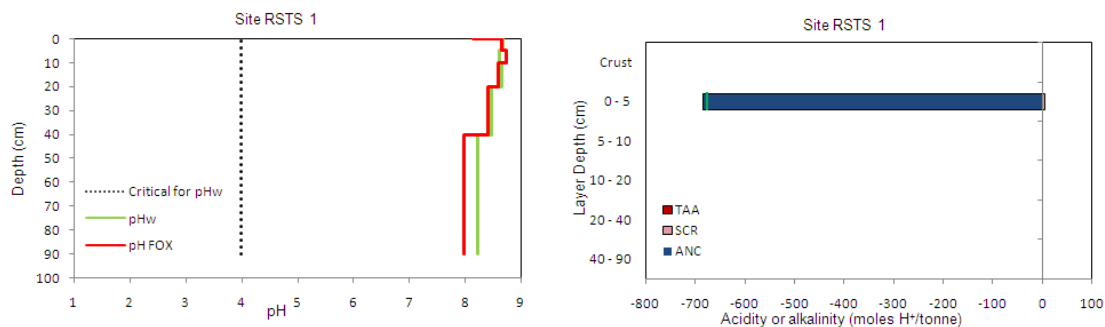


Figure 3-3. Soil pH and acid base accounting data for soil profile RSTS 1. Left Plot: Soil (pH_w: green line) and peroxide pH (pH_{FOX}: red line). Right Plot: S_{CR} (pink bar), ANC (blue bar) and Net Acidity for sulfidic layers (green line). (Note: ANC was only required to be determined for sulfidic layers).

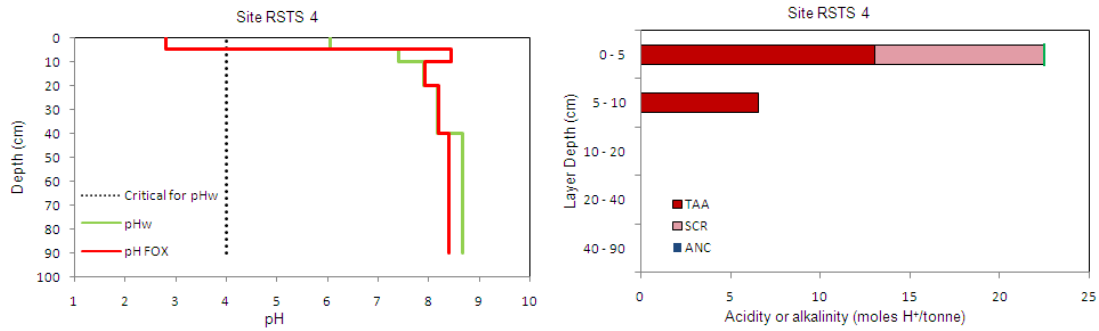


Figure 3-4. Soil pH and acid base accounting data for soil profile RSTS 4. Left Plot: Soil (pH_w: green line) and peroxide pH (pH_{FOX}: red line). Right Plot: TAA (red bar), S_{CR} (pink bar) and Net Acidity for sulfidic layers (green line). (Note: ANC was only required to be determined for sulfidic layers and was zero at this site for these layers).

3.1.2. Chromium Reducible Sulfur (S_{CR})

The chromium reducible sulfur (S_{CR}) data for the Fivebough and Tuckerbil Swamps are presented in Tables 7-2 and 7-3 (Appendix 2) and summarised in Table 3-1. Sulfidic soil materials (i.e. S_{CR} ≥ 0.01% S) were largely absent from all sampling sites, with only 4 materials of the 67 samples collected equal to or greater than the sulfidic criterion. Two sites in both the Fivebough Swamp and Tuckerbil Swamp contained sulfidic materials. Sites RSFS 1 (40-90 cm), RSFS 6 (0-5 cm) and RSTS 4 (0-5 cm) all had a S_{CR} of 0.02% S. Site RSTS 1 (0-5 cm) had a S_{CR} equal to the sulfidic criterion of 0.01% S.

3.1.3. Acid Neutralising Capacity

The acid neutralising capacity (ANC) data for the Fivebough and Tuckerbil Swamps are presented in Tables 7-2 and 7-3 (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 5.14 %CaCO₃ for the four sulfidic soil materials.

3.1.4. Net Acidity

The net acidity data for the Fivebough and Tuckerbil Swamps are presented in Tables 7-2 and 7-3 (Appendix 2) and summarised in Table 3-1. The net acidity was only determined for sulfidic soil materials and soil materials with no ANC (i.e. pH_{KCl} < 6.5). The net acidity thresholds used to characterise the acid sulfate soil materials in this assessment include low net acidity (< 19 mole H⁺/tonne), moderate net acidity (19-100 mole H⁺/tonne) and high net acidity (> 100 mole H⁺/tonne). Acid-base accounting calculations showed the net acidity ranged between -679 and 31 mole H⁺/tonne, with a median net

acidity of 4 mole H⁺/tonne. All had low net acidities, except two soil materials (i.e. RSFS 5.5 (10-20 cm) and RSTS 4.3 (0-5 cm)) which had moderate net acidities.

The acidification risk from acid sulfate soil disturbance posed by the sulfidic soil materials is low, except for the single hypersulfidic soil material (i.e. RSTS 4.3 (0-5 cm)) which had a moderate net acidity of 22 mole H⁺/tonne.

3.1.5. Water soluble SO₄

The water soluble SO₄ data for the Fivebough and Tuckerbil Swamps is presented in Tables 7-2 and 7-3 (Appendix 2) and summarised in Table 3-1. The water soluble SO₄ in the soils in the Fivebough and Tuckerbil Swamps ranged between 56 and 12,299 mg/kg. The water soluble sulfate contents of all surface soil materials exceeded the trigger value of 100 mg/kg indicating that the formation of monosulfidic surface materials may be a potential problem upon rewetting. All layers in nine of 13 profiles had soluble SO₄ contents exceeding the trigger value. A decrease in water soluble SO₄ content with depth was often observed at the Tuckerbil Swamp (e.g. Figure 3-5), however, the water soluble SO₄ trend varied with depth at the Fivebough Swamp sites.

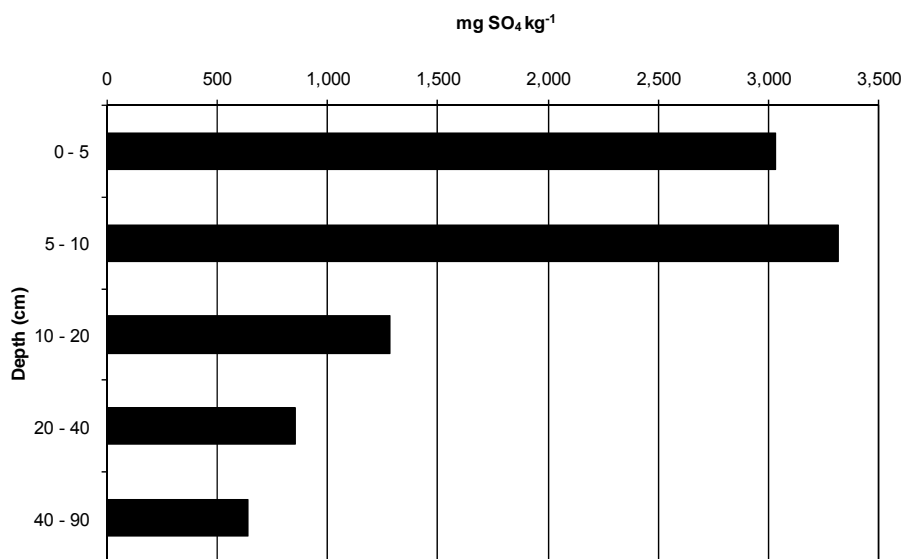


Figure 3-5. Variation in water soluble SO₄ (mg SO₄ kg⁻¹) with depth at the Tuckerbil Swamp (Site RSTS 4).

3.1.6. Titratable actual acidity (TAA)

The titratable actual acidity (TAA) data for the Fivebough and Tuckerbil Swamp is presented in Tables 7-2 and 7-3 (Appendix 2) and summarised above in Table 3-1. The TAA ranged between zero and 30 mole H⁺/tonne,

with the majority of the soil layers having zero or very low TAA. There was zero TAA in nine of the 13 soil profiles as all layers had a $\text{pH}_{\text{KCl}} \geq 6.5$. As observed with water soluble SO_4 data, there was usually a decrease in the TAA with depth (e.g. Figure 3-6).

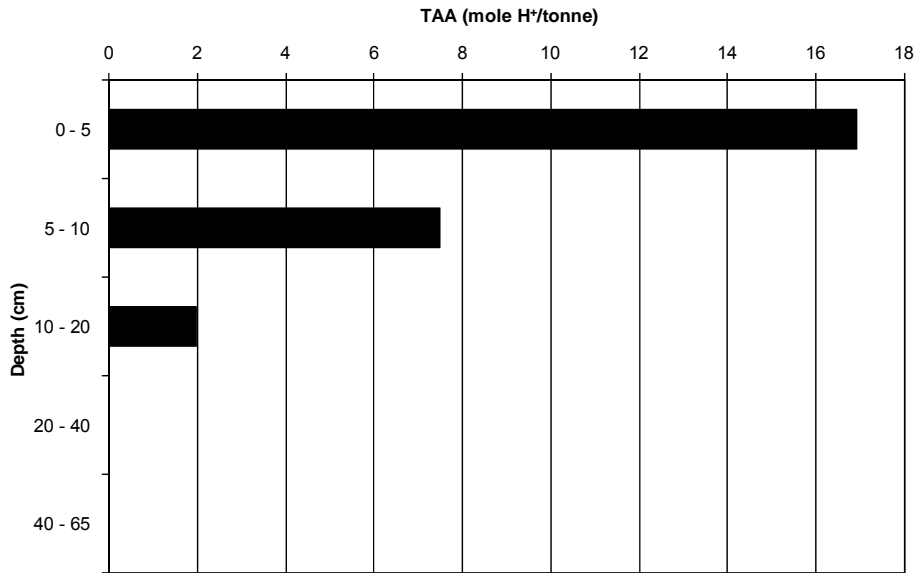


Figure 3-6. Variation in TAA (mole H⁺/tonne) with depth at site RSTS 5.

3.2. Hydrochemistry

Surface water quality data was collected from four locations in the Fivebough Swamp (Sites RSFS 2, 3, 4 and 6) and a single location in the Tuckerbil Swamp (Site RSTS 5). Groundwater samples were collected from three locations in the Fivebough Swamp (Sites RSFS 5, 7 and 8).

A summary of the surface water characteristics measured in the field are presented below in Table 3-2 and the results of the laboratory analyses are presented in Appendix 3.

The field pH of the surface waters ranged between 7.10 and 8.40 (Table 3-2) with two sites (i.e. Sites RSFS 2 and 3) exceeding the most relevant ANZECC/ARMCANZ (2000) trigger value of 8.0. The water data indicates that the surface water has not been affected by acidification. The surface water soluble sulfate concentrations were low, ranging between 5 and 86 mg/L (Table 7-5, Appendix 3).

Table 3-2. Summary of surface water hydrochemical characteristics (field).

	pH	SEC μS/cm	DO % sat.	Eh mV	Turbidity NTU	Alkalinity (mg/L as HCO ₃)
Minimum	7.10	435	9.5	-63	6.3	130
Median	7.52	1004	54.4	244	27.6	245
Maximum	8.40	1128	75.1	425	267	347
n ¹	5	5	5	5	5	5

¹ n: number of samples

The field pH of the groundwater ranged between 7.89 and 7.92 indicating that the groundwater has not been affected by acidification (Table 3-3). The groundwater had water soluble sulfate concentrations ranging between 39 and 5,472 mg/L (Table 7-7, Appendix 3).

Table 3-3. Summary of groundwater hydrochemical characteristics (field).

	pH	SEC μS/cm	DO % sat.	Eh mV	Turbidity NTU	Alkalinity (mg/L as HCO ₃)
Minimum	7.89	7.44	17.0	249	n.a. ²	230
Mean	7.91	10.80	40.2	310	n.a.	707
Maximum	7.92	14.15	63.3	370	n.a.	1230
n ¹	2	2	2	2	0	3

¹ n: number of samples

² n.a.: not applicable. Turbidity was measured only for surface water samples

4. HAZARD ASSESSMENT

4.1. Interpretation of soil and water data

Sulfuric soil materials were not encountered in any of the sampling sites (Table 4-1).

A hypersulfidic soil material occurred in the surface soil (i.e. 0-5 cm) at one of the 13 sampling locations (Table 4-1). The acidification risk from acid sulfate soil disturbance posed by the single hypersulfidic material is moderate as this material had a net acidity of 22 mole H⁺/tonne.

Three profiles containing hyposulfidic soil materials with S_{CR} < 0.10% were also present within the wetland.

The soluble sulfate contents of all surficial soil materials sampled exceeded the trigger value of 100 mg/kg indicating that the formation of monosulfidic materials may occur upon rewetting (Table 4-1).

The water data indicates that the surface water has not been affected by acidification.

Table 4-1. Type and prevalence of acid sulfate soil materials.

Type of actual or potential acid sulfate soil material	Number of sampling sites containing actual or potential acid sulfate soil materials (Total sites = 13)	Proportion of total sampling sites (%)
Sulfuric	0	0
Hypersulfidic	1	8
Hyposulfidic (S _{CR} ≥ 0.10%)	0	0
Monosulfidic (observed)	0	0
Monosulfidic (potential)	13	100
Hyposulfidic (S _{CR} < 0.10%)	3	23
Other acidic (pH _w &/or pH _{INCUBATION}) 4 – 5.5	0	0
Other soil materials	9	69

5. CONCLUSIONS

This report provides the results of Phase 1 of a two-phased detailed assessment procedure to determine the hazards posed by acid sulfate soil materials in the Fivebough and Tuckerbil Swamps Ramsar site. This Phase 1 report is aimed solely at determining whether or not acid sulfate soil materials are present in the Fivebough and Tuckerbil Swamps Ramsar site.

Sulfuric materials were not observed in these wetlands, and although 31% (i.e. 4) of the sampling sites contained sulfidic materials, the reduced inorganic sulfur concentrations of these samples were low (i.e. the highest S_{CR} was only 0.02%). A hypersulfidic soil material was present in one soil profile, and another three soil profiles contained hyposulfidic materials (with $S_{CR} < 0.10\%$). These results indicate that minimal acidity would be produced upon oxidation of sulfides in these materials.

While monosulfidic black ooze (MBO) was not observed at the time of sampling, all surficial soil materials contained soluble sulfate in excess of the 100 mg/kg trigger value for MBO formation potential.

Based on the priority ranking criteria adopted by the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soil Risk Assessment Project, there was one high priority site based on the presence of a hypersulfidic material, and three moderate priority sites based on the presence of hyposulfidic materials with $S_{CR} < 0.10\%$. In addition, all 13 sampling sites had a high priority ranking for Phase 2 detailed assessment of MBO formation hazard.

The potential hazards at a wetland-scale posed by acid sulfate soil materials at the Fivebough and Tuckerbil Swamps Ramsar wetland sites are as below:

- **Acidification:** The data indicate that with low titratable actual acidities (TAA) and only a few sulfidic materials (where the highest S_{CR} was only 0.02% S) that the degree of acidification hazard is low.
- **Deoxygenation:** The water soluble sulfate contents of all thirteen surface soil materials were over the trigger value for MBO formation indicating the possible development of an appreciable deoxygenation hazard after prolonged wet conditions.
- **Metal mobilisation:** The low acidification hazard indicates that soil acidification is not likely to increase the solubility of metals. However, the potential for MBO formation identified in these wetlands may result in an appreciable metal release hazard depending on factors such as the potential for MBO formation and the metal loading in this wetland.

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7. APPENDICES

APPENDIX 1. Site and sample descriptions.

Table 7-1. Fivebough and Tuckerbil Swamps site and sample descriptions.

Profile	Date	Location	GPS Co-ords Zone East. North.	Location Remarks	Profile remarks
RSFS1	18/07/08	Leeton, Fivebough	55 447762 6179984	Northern end of swamp, in the "ephemeral" section of the swamp. Driest profile in transect ~60 m from water's edge. Heavy grazing pressure, short pasture grasses and herbs.	Dug to 90 cm.
RSFS2	18/07/08	Leeton, Fivebough	55 447835 6179832	In water towards the centre of the swamp from FS1. Surface water sample taken.	Gouge Auger holes (6-8) ranged in depth from 60-80 cm.
RSFS3	18/07/08	Leeton, Fivebough	55 447861 6179597	Further out in swamp. Water shallow with various islands. Vegetation is drowned pasture grasses, Bathurst bur and other woody species that could be roly-poly.	
RSFS4	18/07/08	Leeton, Fivebough	55 447868 6178032	In south eastern corner of swamp. Heavy cover of water couch and Cumbungi. Some standing water – surface water sample taken. Pungent odour coming from sediments.	Dug to 90 cm.
RSFS5	18/07/08	Leeton, Fivebough	55 447920 6177911	Approx. 200 m to the SE of RSFS4. Heavy cover of water couch. Very boggy underfoot however no standing water. Groundwater sample taken. No water quality measurements recorded.	Dug to 90 cm
RSFS6	19/07/08	Leeton, Fivebough	55 447382 6178633	Site is permanently wet swamp are to SW of main Swamp. Permanently flooded by sewage treatment water. Approximately 50m from bird watching tower. Cover of water couch and cumbungi. Surface water sample taken.	Dug to 80 cm
RSFS7	19/07/08	Leeton, Fivebough	55 447212 6178621	West of RSFS6 approximately 200 m. Sampled in relatively bare patch in Cumbungi. Spare couch grass as well. Water in patches but not deep enough to sample. Groundwater sample taken.	Dug to 90 cm.

Table 7-1 (continued). Fivebough and Tuckerbil Swamps site and sample descriptions.

Profile	Date	Location	GPS Co-ords Zone East. North.	Location Remarks	Profile remarks
RSFS8	20/07/08	Leeton, Fivebough	55 447057 6178548	Western most hole on 3 rd transect west of RSFS7. Approximately 5 m from edge of Cumbungi within permanently wetted swamp. Groundcover of sedges and pasture grasses.	Moist on top
RSTS1	19/07/08	Leeton, Tuckerbil	55 440259 6182850	Very degraded swamp. Cattle grazing here with apparent access to whole swamp. RSTS1 up southern end of swamp in dead trees. Groundcover of short pasture grasses. Salt exposed on bare surfaces.	Grey brown clays to yellowish brown clays at ~70 cm.
RSTS2	19/07/08	Leeton, Tuckerbil	55 440203 6183240	Further north towards standing pools of water. Low cover of spiky roly-poly like bushes and pasture grasses. No salt evident at this site.	Iron lining root holes near surface (<20 cm). Grading from grey brown to yellow brown at 30 cm. Carbonate nodules at depth (>70 cm). Dug to 90 cm.
RSTS3	19/07/08	Leeton, Tuckerbil	55 440047 6183719	Further up swamp. No standing water here, profile dug on open claypan section which has less heavily trampled by cattle. Minor salt crust evident on bare surfaces.	Extensive iron staining <40 cm. Gravel >60 cm. Dug to 90 cm.
RSTS4	19/07/08	Leeton, Tuckerbil	55 440076 6184433	At northern end of swamp, ~ 30 m from man-made drainage channel. Groundcover of short pasture grasses. Very soft under foot.	
RSTS5	20/07/08	Leeton, Tuckerbil	55 440032 6184247	Sample taken in what appears to be the most permanent water hole in swamp. Very soft under foot. Some chewed down Cumbungi present.	Sample top approximately 65 cm.

APPENDIX 2. Field and laboratory analytical soil data.

Table 7-2. Fivebough Swamp field and laboratory analytical soil data.

Site / Sample	Depth (cm)	Texture	Colour	Mottle % / Colour	pH _w	pH _{FOX}	pH _{FOX} reaction	pH _{KCl}	pH _{INCUBATION} ¹	TAA mole H ⁺ /tonne	CRS %Scr	ANC %CaCO ₃	Net Acidity mole H ⁺ /tonne	Sulfate (mg SO ₄ /kg)
RSFS / 1.3	0 - 5	FSLC	10YR3/1		8.13	6.06	XXXX	8.04		0.00	< 0.01	-	-	144.71
	1.4	5 - 10	FSLMC	10YR3/1	8.51	7.08	XXXX	8.45		0.00	< 0.01	-	-	121.34
	1.5	10 - 20	FSMC	10YR3/1	8.48	8.27	XXXX	7.70		0.00	< 0.01	-	-	174.86
	1.6	20 - 40	MC	10YR3/2	8.39	8.42	XXXX	8.05		0.00	< 0.01	-	-	210.22
	1.7	40 - 90	LMC	2.5Y5/2	8.63	8.41	XXXX	8.46	7.9	0.00	0.015	4.26	-557.54	65.65
RSFS / 2.3	0 - 5	SLC	10YR4/1		8.33	6.81	XXXX	8.47		0.00	< 0.01	-	-	163.28
	2.4	5 - 10	SLC	10YR4/1	8.61	7.30	XXXX	8.14		0.00	< 0.01	-	-	76.61
	2.5	10 - 20	SMC	10YR4/1	8.57	8.13	XXXX	7.41		0.00	< 0.01	-	-	85.62
	2.6	20 - 40	SLC	10YR5/1	8.60	8.19	XXXX	8.30		0.00	< 0.01	-	-	116.85
	2.7	40 - 80	MC	10YR5/1	8.50	8.23	XXXX	8.45		0.00	< 0.01	-	-	110.68
RSFS / 3.3	0 - 5	SLMC	10YR4/1		8.38	8.46	XX	8.23		0.00	< 0.01	-	-	126.97
	3.4	5 - 10	SLMC	10YR4/1	8.68	8.24	XXXX	7.37		0.00	< 0.01	-	-	75.00
	3.5	10 - 20	SLMC	10YR4/1	8.75	8.50	XXXX	8.49		0.00	< 0.01	-	-	56.06
	3.6	20 - 40	SLMC	10YR4/1	20% 10YR6/2	8.82	8.53	XXXX	8.56	0.00	< 0.01	-	-	121.32
	3.7	40 - 90	LMC	2.5Y7/3	30% 10YR5/1	8.78	8.60	XXXX	8.55	0.00	< 0.01	-	-	119.72
RSFS / 4.3	0 - 5	FSLC	10YR3/1		6.25	4.91	XX	5.55		11.45	< 0.01	-	11.45	918.81
	4.4	5 - 10	SMC	10YR3/1	7.28	6.31	XX	6.17		4.07	< 0.01	-	4.07	648.24
	4.5	10 - 20	SMC	10YR3/1	7.35	6.69	XX	6.34		3.42	< 0.01	-	3.42	960.53
	4.6	20 - 40	SMC	10YR4/1	7.54	7.38	XX	6.52		0.00	< 0.01	-	-	654.21
	4.7	40 - 90	SMC	10YR5/1	7.90	7.88	XXXX	6.78		0.00	< 0.01	-	-	522.08
RSFS / 5.3	0 - 5	FSLC	10YR4/2		7.52	4.29	XX	6.13		1.85	< 0.01	-	1.85	326.58
	5.4	5 - 10	SMC	10YR4/1	7.78	8.88	XXXX	6.02		3.50	< 0.01	-	3.50	152.61
	5.5	10 - 20	SMC	10YR4/1	8.11	8.19	XXXX	5.92		30.80	< 0.01	-	30.80	97.77
	5.6	20 - 40	SMC	10YR4/1	8.39	8.36	XXXX	5.66		7.93	< 0.01	-	7.93	175.15
	5.7	40 - 90	SMC	10YR6/1	8.47	8.50	XXXX	8.58		0.00	< 0.01	-	-	356.47
RSFS / 6.3	0 - 5	FSLC	2.5Y4/2		7.76	4.50	XX	8.36	8.5	0.00	0.016	0.93	-114.07	677.60
	6.4	5 - 10	SMC	2.5Y5/2	8.68	8.59	XXXX	8.14		0.00	< 0.01	-	-	526.10
	6.5	10 - 20	SMC	2.5Y5/2	8.65	8.50	XXXX	8.24		0.00	< 0.01	-	-	795.32
	6.6	20 - 40	MC	2.5Y5/2	8.72	8.35	XXXX	8.03		0.00	< 0.01	-	-	863.60
	6.7	40 - 80	MC	2.5Y5/2	8.65	8.29	XXXX	8.80		0.00	< 0.01	-	-	1012.83
RSFS / 7.3	0 - 5	SMC	2.5Y4/2		9.19	9.39	XX	9.78		0.00	< 0.01	-	-	1178.86
	7.4	5 - 10	SMC	2.5Y5/2	9.09	8.85	XXXX	9.02		0.00	< 0.01	-	-	1143.55
	7.5	10 - 20	MC	2.5Y5/2	8.88	8.95	XX	8.71		0.00	< 0.01	-	-	2398.36
	7.6	20 - 40	SMC	2.5Y5/2	8.69	8.83	XX	8.87		0.00	< 0.01	-	-	3086.83
	7.7	40 - 90	SMHC	2.5Y6/3	8.56	8.62	X	8.89		0.00	< 0.01	-	-	2740.27
RSFS / 8.3	0 - 5	SMC	10YR4/1		7.68	8.86	XX	6.73		0.00	< 0.01	-	-	129.78
	8.4	5 - 10	SMC	10YR4/1	8.28	8.47	XXXX	7.23		0.00	< 0.01	-	-	104.82
	8.5	10 - 20	MC	10YR3/1	8.39	8.52	XXXX	7.78		0.00	< 0.01	-	-	367.89
	8.6	20 - 40	MC	10YR4/1	8.36	8.38	XX	8.16		0.00	< 0.01	-	-	1008.34
	8.7	40 - 90	SMC	10YR5/1	8.75	8.84	XX	8.82		0.00	< 0.01	-	-	1084.97

¹ Soil reaction rating scale for pH_{FOX} test: slight reaction (X), moderate reaction (XX), high reaction (XXX), and very vigorous reaction, gas evolution and heat generation commonly >80°C (XXXX) (Ahern *et al.* 2004).

Table 7-3. Tuckerbil Swamp field and laboratory analytical soil data.

Site / Sample	Depth (cm)	Texture	Colour	Mottle % / Colour	pH _w	pH _{FOX}	pH _{FOX} reaction	pH _{KCl}	pH _{INCUBATION} ¹	TAA mole H ⁺ /tonne	CRS %Scr	ANC %CaCO ₃	Net Acidity mole H ⁺ /tonne	Sulfate (mg SO ₄ /kg)
RSTS / 1.1	Salt crust	n.a.	n.a.		8.29	8.14	XXXX	9.14		0.00	< 0.01	-	-	12299.37
1.3	0 - 5	SLMC	10YR4/1		8.68	8.66	XXXX	8.91	9.0	0.00	0.010	5.14	-678.55	589.17
1.4	5 - 10	SMC	10YR4/1		8.62	8.74	XXXX	8.84		0.00	< 0.01	-	-	480.09
1.5	10 - 20	SMC	10YR4/1		8.65	8.59	XXX	8.67		0.00	< 0.01	-	-	988.20
1.6	20 - 40	MC	10YR4/1	10% 10YR7/6	8.48	8.41	XXXX	6.74		0.00	< 0.01	-	-	749.64
1.7	40 - 90	MC	10YR8/3	20% 10YR4/1	8.22	7.97	XXXX	6.60		0.00	< 0.01	-	-	266.98
RSTS / 2.3	0 - 5	LMC	10YR4/1		8.72	8.91	XXXX	8.70		0.00	< 0.01	-	-	286.92
2.4	5 - 10	LMC	10YR4/1	7% 5YR5/8	8.75	8.51	XXXX	7.91		0.00	< 0.01	-	-	525.16
2.5	10 - 20	SMC	10YR4/2		8.52	8.50	XXXX	7.33		0.00	< 0.01	-	-	898.69
2.6	20 - 40	MC	2.5Y5/2		8.26	8.22	XXXX	7.45		0.00	< 0.01	-	-	2131.39
2.7	40 - 90	MC	2.5Y6/3		8.73	8.47	XXXX	8.38		0.00	< 0.01	-	-	239.43
RSTS / 3.2	Crust	i.s.	i.s.		8.14	8.41	XXXX	8.91		0.00	< 0.01	-	-	11219.48
3.3	0 - 5	LC	10YR4/2	10% 5YR5/8	8.02	8.18	XXXX	8.72		0.00	< 0.01	-	-	5318.99
3.4	5 - 10	LC	10YR4/2	20% 10YR8/6	7.65	7.95	XXXX	7.10		0.00	< 0.01	-	-	1869.36
3.5	10 - 20	LC	2.5Y5/3	15% 10YR2/1	7.63	7.85	XXX	6.85		0.00	< 0.01	-	-	3113.69
3.6	20 - 40	LC	2.5Y5/3	10YR2/1	7.77	7.70	XX	7.09		0.00	< 0.01	-	-	7642.26
3.7	40 - 90	MC	2.5Y7/3		8.15	7.87	XXX	8.68		0.00	< 0.01	-	-	2331.44
RSTS / 4.3	0 - 5	LMC	10YR4/1		6.06	2.81	XX	5.53	5.3	13.05	0.015	0.00	22.48	3032.67
4.4	5 - 10	LMC	10YR4/1		7.41	8.45	XXX	5.79		6.56	< 0.01	-	6.56	3317.50
4.5	10 - 20	SLMC	10YR4/1	2% 5YR5/8	7.90	7.94	XXXX	6.56		0.00	< 0.01	-	-	1281.34
4.6	20 - 40	LMC	2.5Y5/2		8.18	8.21	XXX	6.78		0.00	< 0.01	-	-	851.01
4.7	40 - 90	LMC	2.5Y5/2	30% 2.5Y7/3	8.67	8.40	XXXX	8.52		0.00	< 0.01	-	-	638.92
RSTS / 5.3	0 - 5	LC	2.5Y2 5/1		6.29	6.04	XX	5.31		16.92	< 0.01	-	16.92	553.46
5.4	5 - 10	LC	10YR4/1	3% 7.5YR6/8	7.09	7.37	XXXX	5.62		7.51	< 0.01	-	7.51	194.94
5.5	10 - 20	SLC	10YR4/1		7.59	8.25	XXXX	6.28		2.00	< 0.01	-	2.00	160.55
5.6	20 - 40	SLMC	10YR5/1	7.5YR5/8	8.32	7.56	XXXX	6.68		0.00	< 0.01	-	-	108.84
5.7	40 - 65	SLMC	2.5Y6/3		8.74	8.49	XXXX	7.96		0.00	< 0.01	-	-	140.28

¹ Soil reaction rating scale for pH_{FOX} test: slight reaction (X), moderate reaction (XX), high reaction (XXX), and very vigorous reaction, gas evolution and heat generation commonly >80°C (XXXX) (Ahern *et al.* 2004).

APPENDIX 3. Field and laboratory hydrochemistry data.

Table 7-4. Fivebough and Tuckerbil Swamps field surface water hydrochemistry data.

Site	Units	RSFS 2	RSFS 3	RSFS 4	RSFS 6	RSTS 5	Minimum	Median	Maximum	Range	n
Water type		Surface	Surface	Surface	Surface	Surface					
pH		8.40	8.02	7.10	7.52	7.12	7.10	7.52	8.40	7.10 - 8.40	5
SEC	$\mu\text{S cm}^{-1}$	1004	1059	924	1128	435	924	1004	1128	924 - 1128	5
DO	% sat	75.1	54.4	9.5	22.5	62.5	9.5	54.4	75.1	9.5 - 75.1	5
Eh	mV	425	384	-63	94	244	-63	244	425	-63 - 425	5
Turbidity	NTU	33.6	10.9	27.6	6.3	267.0	6.3	27.6	267	6.3 - 267	5
Alkalinity	(mg L^{-1} as HCO_3^-)	347	320	245	218	130	218	245	347	218 - 347	5
Temperature	$^{\circ}\text{C}$	7.4	8.3	10.7	2.2	8.5	2.2	8.3	10.7	2.2 - 10.7	5

Table 7-5. Fivebough and Tuckerbil Swamps surface water laboratory analytical hydrochemistry data.

Parameter	Units	RSFS 2	RSFS 3	RSFS 4	RSFS 6	RSTS 5	Minimum	Median	Maximum	Range	n
pH		8.80	8.94	8.86	8.35	7.74	7.74	8.80	8.94	7.74 - 8.94	5
E.C.	dS/m	1.10	1.06	0.94	1.32	0.33	0.33	1.06	1.32	0.33 - 1.32	5
Alkalinity	meq/L	6.09	5.30	4.26	3.46	1.84	1.84	4.26	6.09	1.84 - 6.09	5
Ammonia ($\text{NH}_4\text{-N}$)	mg/L	0.020	0.045	0.074	0.030	0.089	0.020	0.045	0.089	0.020 - 0.089	5
Oxides of Nitrogen ($\text{NO}_x\text{-N}$)	mg/L	0.056	0.047	0.016	0.033	0.147	0.016	0.047	0.147	0.016 - 0.147	5
Nitrate ($\text{NO}_3\text{-N}$)	mg/L	0.056	0.047	0.016	0.027	0.147	0.016	0.047	0.147	0.016 - 0.147	5
Nitrite ($\text{NO}_2\text{-N}$)	mg/L	<0.005	<0.005	<0.005	0.006	<0.005	<0.005	<0.005	0.006	<0.005 - 0.006	5
Phosphate ($\text{PO}_4\text{-P}$)	mg/L	0.088	0.123	0.024	0.025	0.004	0.004	0.025	0.123	0.004 - 0.123	5
Fluoride (F)	mg/L	0.22	0.24	0.23	<0.2	0.17	<0.2	0.22	0.24	<0.2 - 0.24	5
Chloride (Cl)	mg/L	139.14	153.80	160.67	255.93	32.00	32.00	153.80	255.93	32.00 - 255.93	5
Bromide (Br)	mg/L	0.28	0.34	0.34	0.64	0.11	0.11	0.34	0.64	0.11 - 0.64	5
Sulfate (SO_4^{2-})	mg/L	39.49	43.96	7.58	86.25	5.09	5.09	39.49	86.25	5.09 - 86.25	5
Calcium (Ca)	mg/L	35.07	40.70	26.17	40.31	16.73	16.73	35.07	40.70	16.73 - 40.70	5
Potassium (K)	mg/L	26.17	24.21	22.41	20.66	8.18	8.18	22.41	26.17	8.18 - 26.17	5
Magnesium (Mg)	mg/L	25.43	25.56	25.32	26.01	9.22	9.22	25.43	26.01	9.22 - 26.01	5
Sodium (Na)	mg/L	181.18	179.71	144.08	210.00	40.10	40.10	179.71	210.00	40.10 - 210.00	5
Sulfur (S)	mg/L	16.42	17.39	4.31	31.51	2.62	2.62	16.42	31.51	2.62 - 31.51	5
Total Organic Carbon (NPOC)	mg/L	36.63	35.22	27.19	19.88	11.27	11.27	27.19	36.63	11.27 - 36.63	5
Total Nitrogen (TN)	mg/L	2.880	2.590	1.730	1.400	1.100	1.100	1.730	2.880	1.100 - 2.880	5
Aluminium (Al)	mg/L	0.098	0.091	0.047	0.048	0.342	0.047	0.091	0.342	0.047 - 0.342	5
Boron (B)	mg/L	0.238	0.218	0.212	0.240	0.103	0.103	0.218	0.240	0.103 - 0.240	5
Copper (Cu)	mg/L	< 0.005	0.006	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.006	< 0.005 - 0.006	5
Iron (Fe)	mg/L	0.155	0.170	0.531	0.245	0.480	0.155	0.245	0.531	0.155 - 0.531	5
Manganese (Mn)	mg/L	0.029	0.127	0.240	0.650	0.338	0.029	0.240	0.650	0.029 - 0.650	5
Phosphorus (P)	mg/L	4.336	3.972	0.722	1.094	< 0.03	< 0.03	1.094	4.336	< 0.03 - 4.336	5
Zinc (Zn)	mg/L	< 0.003	0.020	< 0.003	0.010	0.015	< 0.003	0.010	0.020	< 0.003 - 0.020	5
Molybdenum (Mo)	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	5
Cobalt (Co)	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	5
Nickel (Ni)	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	5
Chromium (Cr)	mg/L	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	5
Cadmium (Cd)	mg/L	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	5
Lead (Pb)	mg/L	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	5
Selenium (Se)	mg/L	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	5

Table 7-6. Fivebough Swamp field groundwater hydrochemistry data.

Site	Units	RSFS 5	RSFS 7	RSFS 8	Minimum	Maximum	Range	n
Water type		Groundwater	Groundwater	Groundwater				
pH		n.a.	7.92	7.89	7.89	7.92	7.89 - 7.92	2
SEC	$\mu\text{S cm}^{-1}$	n.a.	14.2	7.4	7.4	14.2	7.4 - 14.2	2
DO	% sat	n.a.	17.0	63.3	17.0	63.3	17.0 - 63.3	2
Eh	mV	n.a.	249	370	249	370	249 - 370	2
Turbidity	NTU	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0
Alkalinity	(mg L^{-1} as HCO_3)	230	1230	660	230	1230	230 - 1230	3
Temperature	$^{\circ}\text{C}$	n.a.	9.6	9.1	9.1	9.6	9.1 - 9.6	2

Table 7-7. Fivebough Swamp groundwater laboratory analytical hydrochemistry data.

Parameter	Units	RSFS 5	RSFS 7	RSFS 8	Minimum	Median	Maximum	Range	n
pH		8.68	8.67	7.61	7.61	8.67	8.68	7.61 - 8.68	3
E.C.	dS/m	1.10	21.62	9.69	1.10	9.69	21.62	1.10 - 21.62	3
Alkalinity	meq/L	5.19	10.14	6.90	5.19	6.90	10.14	5.19 - 10.14	3
Ammonia ($\text{NH}_4\text{-N}$)	mg/L	0.243	0.132	0.114	0.114	0.132	0.243	0.114 - 0.243	3
Oxides of Nitrogen ($\text{NO}_x\text{-N}$)	mg/L	0.595	0.262	0.245	0.245	0.262	0.595	0.245 - 0.595	3
Nitrate ($\text{NO}_3\text{-N}$)	mg/L	0.399	0.255	0.239	0.239	0.255	0.399	0.239 - 0.399	3
Nitrite ($\text{NO}_2\text{-N}$)	mg/L	0.197	0.007	0.006	0.006	0.007	0.197	0.006 - 0.197	3
Phosphate ($\text{PO}_4\text{-P}$)	mg/L	0.002	0.075	0.047	0.002	0.047	0.075	0.002 - 0.075	3
Fluoride (F)	mg/L	< 0.2	< 2	< 1	< 0.2	< 1	< 2	< 0.2 - < 2	3
Chloride (Cl)	mg/L	157.67	7019.93	2663.59	157.67	2663.59	7019.93	157.67 - 7019.93	3
Bromide (Br)	mg/L	0.35	21.16	7.96	0.35	7.96	21.16	0.35 - 21.16	3
Sulfate (SO_4^{2-})	mg/L	39.16	5472.37	1543.81	39.16	1543.81	5472.37	39.16 - 5472.37	3
Calcium (Ca)	mg/L	40.32	155.47	192.94	40.32	155.47	192.94	40.32 - 192.94	3
Potassium (K)	mg/L	16.23	14.28	6.93	6.93	14.28	16.23	6.93 - 16.23	3
Magnesium (Mg)	mg/L	23.66	730.00	230.00	23.66	230.00	730.00	23.66 - 730.00	3
Sodium (Na)	mg/L	200.00	8600.00	2100.00	200.00	2100.00	8600.00	200.00 - 8600.00	3
Sulfur (S)	mg/L	15.69	1800.00	530.00	15.69	530.00	1800.00	15.69 - 1800.00	3
Total Organic Carbon (NPOC)	mg/L	28.05	32.68	29.16	28.05	29.16	32.68	28.05 - 32.68	3
Total Nitrogen (TN)	mg/L	3.940	1.750	2.110	1.750	2.110	3.940	1.750 - 3.940	3
Aluminium (Al)	mg/L	0.873	0.202	0.193	0.193	0.202	0.873	0.193 - 0.873	3
Boron (B)	mg/L	0.351	6.458	1.906	0.351	1.906	6.458	0.351 - 6.458	3
Copper (Cu)	mg/L	0.014	< 0.05	< 0.03	< 0.03	< 0.05	0.014	< 0.03 - 0.014	3
Iron (Fe)	mg/L	0.739	0.807	0.545	0.545	0.739	0.807	0.545 - 0.807	3
Manganese (Mn)	mg/L	0.395	0.730	0.064	0.064	0.395	0.730	0.064 - 0.730	3
Phosphorus (P)	mg/L	0.063	< 0.3	0.197	< 0.3	0.063	0.197	< 0.3 - 0.197	3
Zinc (Zn)	mg/L	0.049	< 0.03	< 0.02	< 0.02	< 0.03	0.049	< 0.02 - 0.049	3
Molybdenum (Mo)	mg/L	< 0.01	< 0.1	< 0.06	< 0.01	< 0.06	< 0.1	< 0.01 - < 0.1	3
Cobalt (Co)	mg/L	< 0.01	< 0.1	< 0.06	< 0.01	< 0.06	< 0.1	< 0.01 - < 0.1	3
Nickel (Ni)	mg/L	0.010	< 0.1	< 0.07	< 0.07	< 0.1	0.010	< 0.07 - 0.010	3
Chromium (Cr)	mg/L	< 0.008	< 0.08	< 0.04	< 0.008	< 0.04	< 0.08	< 0.008 - < 0.08	3
Cadmium (Cd)	mg/L	< 0.003	< 0.03	< 0.02	< 0.003	< 0.02	< 0.03	< 0.003 - < 0.03	3
Lead (Pb)	mg/L	< 0.03	< 0.3	< 0.2	< 0.03	< 0.2	< 0.3	< 0.03 - < 0.3	3
Selenium (Se)	mg/L	< 0.1	< 1	< 0.6	< 0.1	< 0.6	< 1	< 0.1 - < 1	3

