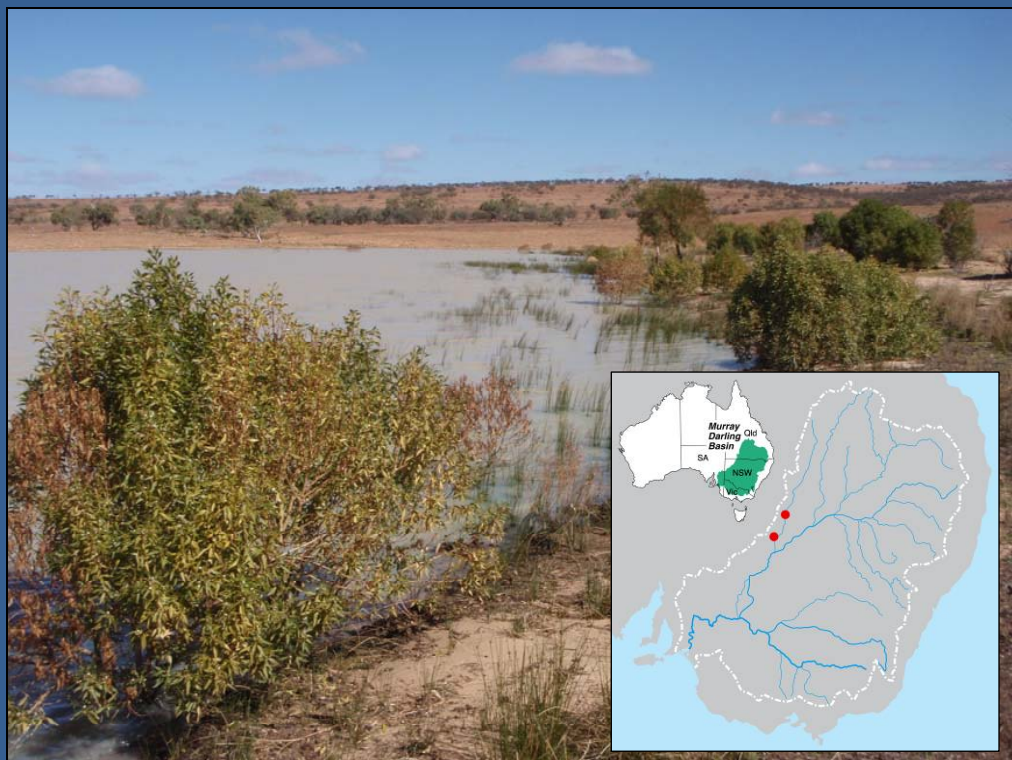


Assessment of Acid Sulfate Soil Materials in Ramsar Wetlands of the Murray-Darling Basin: Paroo River Wetlands

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Cover Photographs:

Typical wetland landscape in the Paroo River Wetlands at the time of sampling. Photograph taken at Site RSPL 4 in Paroo-Darling National Park.

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EXECUTIVE SUMMARY

The Paroo River Wetlands Ramsar site is located in far north west New South Wales and consists of two discrete units on the floodplain of the Paroo River. The Nocolèche Nature Reserve (71,133 ha) is approximately 180 km west of Bourke, whereas the Peery unit (67,171 ha), located in the Paroo-Darling National Park, is approximately 240 km south west of Bourke. Only listed in late 2007, the Paroo River Wetlands are Australia's 65th Ramsar wetland.

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 extent of, and risks posed by, acid sulfate soil materials 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 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 the Paroo River Wetlands. This Phase 1 report is aimed solely at determining whether or not acid sulfate soil materials are present in the Paroo River Wetlands.

Sulfuric soil materials were not observed in these wetlands, and although 12% (i.e. 2) of the sampling sites contained sulfidic materials, the reduced inorganic sulfur contents of these samples were very low (i.e. the highest S_{CR} was only 0.02%). A hypersulfidic soil material was present in one soil profile (this profile also contained a hyposulfidic material), and another soil profile contained a hyposulfidic material (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, three surficial soil materials sampled in the Paroo-Darling National Park (Peery Lake) contained water soluble sulfate in excess of the 100 mg kg^{-1} 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 Soils Risk Assessment Project, there was one high priority site based on the presence of a hypersulfidic material, and one moderate priority site based on the presence of a hyposulfidic material with $S_{CR} < 0.10\%$. In addition, three sampling sites had a high priority ranking for Phase 2 detailed assessment based on MBO formation hazard.

The potential hazards posed by acid sulfate soil materials at the Paroo River Wetlands 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) the degree of acidification hazard is low.
- Deoxygenation: The water soluble sulfate contents of three of the surface soil materials were over the trigger value for MBO formation indicating the possible development of an appreciable deoxygenation hazard at those locations after prolonged wet conditions.
- Metal mobilisation: The low acidification hazard indicates that soil acidification is not likely to produce excessive metal mobilisation. 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.

While this study showed the presence of acid sulfate soil materials in the Paroo River Wetlands, when considering the wetlands as a whole there is a low priority for further assessment to determine specific acid sulfate soil risks. As such, the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soils Risk Assessment Project agreed that Phase 2 detailed assessment of acid sulfate soil materials was not required for the Paroo River wetlands.

1. INTRODUCTION

1.1. Wetland overview

The Paroo River Wetlands Ramsar site is located in far north west New South Wales (Figure 1-1) and consists of two discrete units on the floodplain of the Paroo River, both of which were sampled in this study (Figures 1-2 and 1-3). The Nocolche Nature Reserve component (71,133 ha) is approximately 180 km west of Bourke and the Peery component (67,171 ha) is located within the Paroo-Darling National Park approximately 240 km south west of Bourke. Only listed in late 2007, the Paroo River Wetlands are Australia's 65th Ramsar wetland.

Relevant background information sourced from the Paroo River Wetlands Fact Sheet (Department of Environment and Water Resources 2007) follows:

The Paroo River Ramsar Site supports a number of threatened plant and animal species, significant native fish communities and is one of the most important wetland systems for migratory waterbirds in south-eastern Australia. The climate in the Paroo catchment is semi-arid to arid with an annual average rainfall of 250 mm. As well as receiving water from upstream, the site includes many small wetlands and claypans that fill from local rainfall. The site also includes artesian mound springs; those at Peery Lake are the largest active complex in NSW.

Typical wetlands in this Ramsar wetland at the time of sampling are shown in Figures 1-4 and 1-5. Further information on characteristics of the Paroo River Wetlands from the Ramsar Site Information Sheet and the Paroo River Wetlands Fact Sheet can be found at NSW DEC (2006) and DEWR (2007) respectively.

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.

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).



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

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.* 2006; Fitzpatrick *et al.* 2008a,b; Shand *et al.* 2008a,b; 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 extent 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 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 17 representative sites within the Paroo River Wetlands in August 2008 to determine whether acid sulfate soils were present, or if there was a potential for acid sulfate soil to form within these wetlands (Figures 1-2 and 1-3). 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.

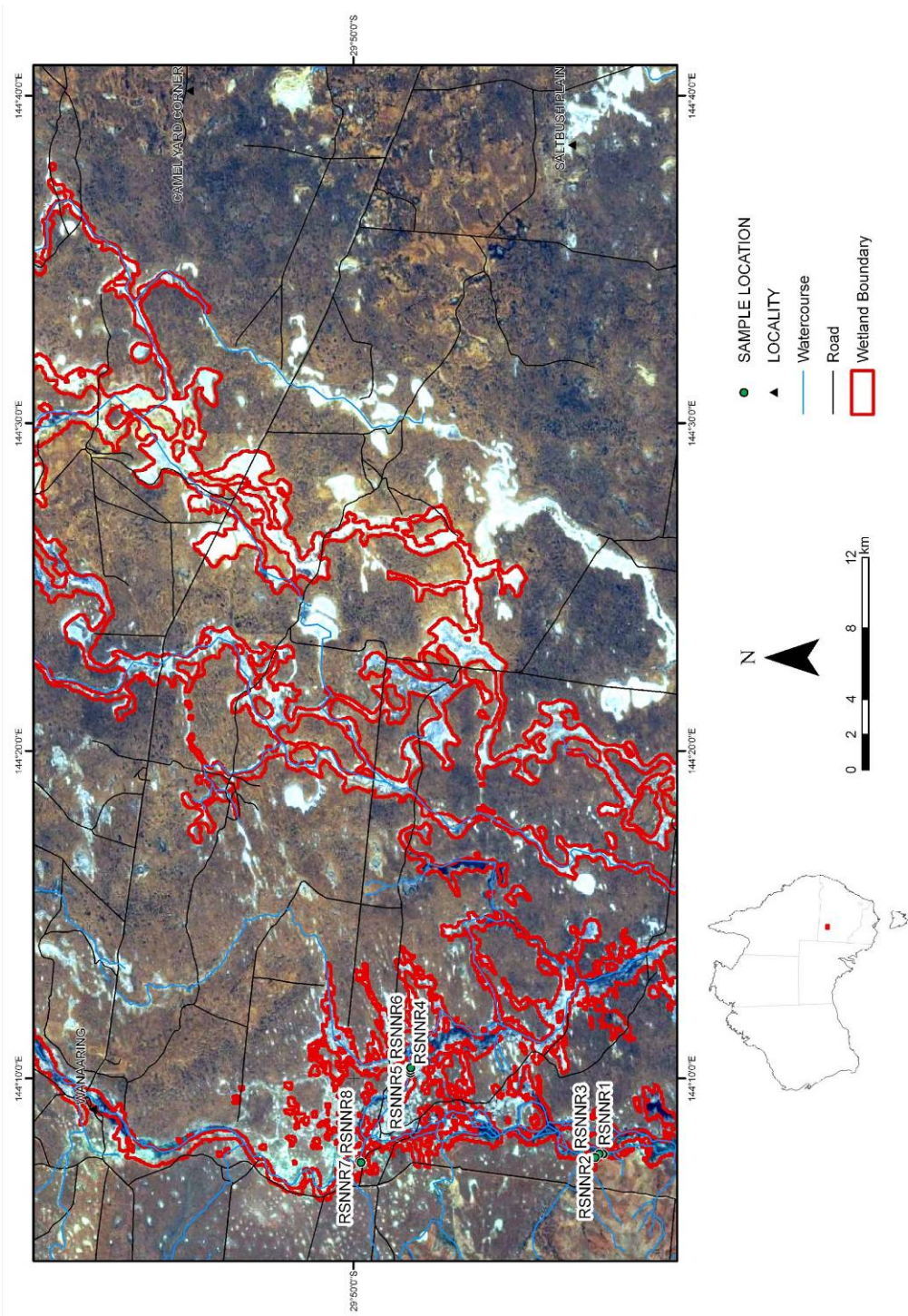


Figure 1-2 Map showing the Paroo River Wetlands Ramsar site (Nocoleche Nature Reserve).

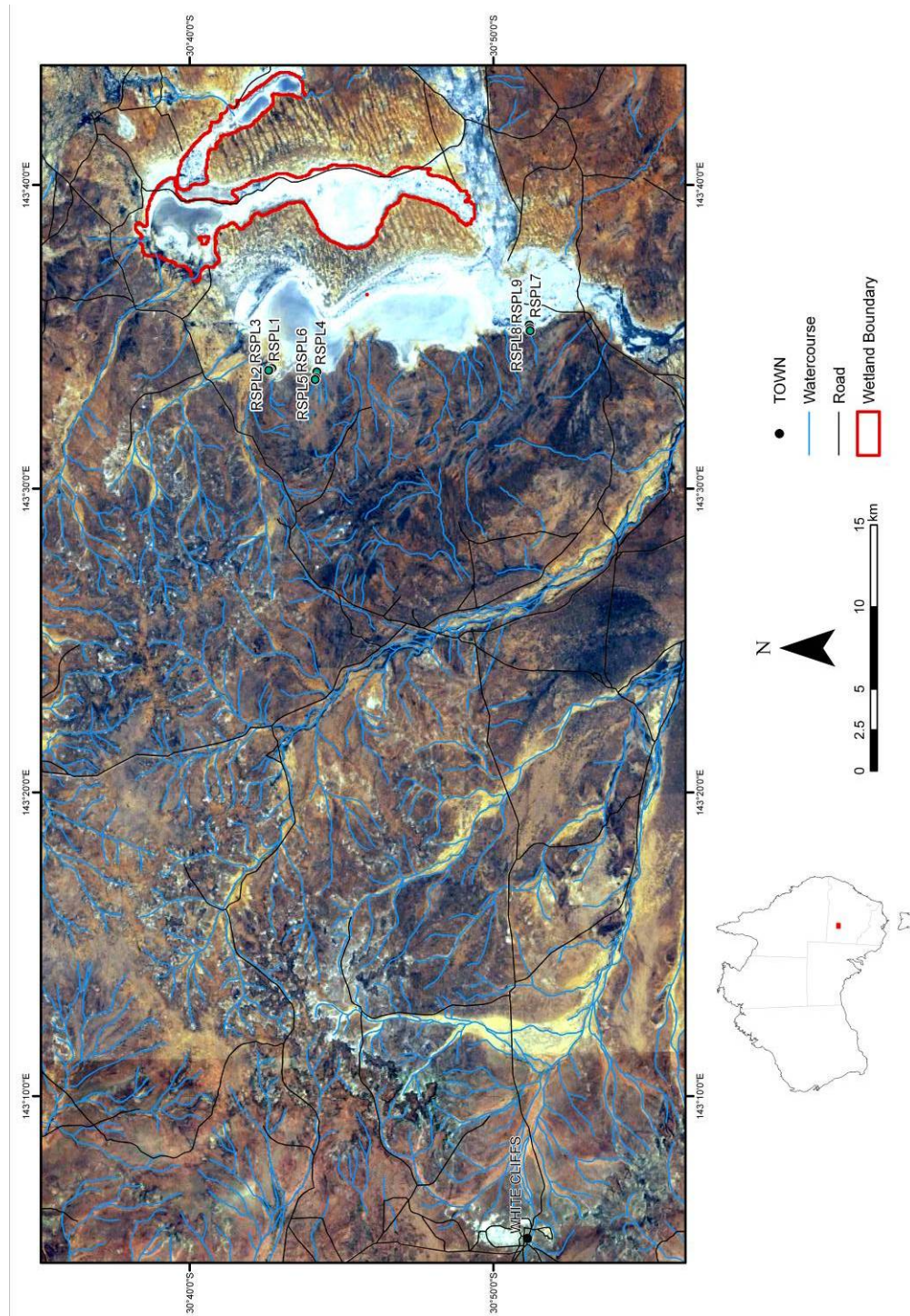


Figure 1-3 Map showing the Paroo River Wetlands Ramsar site (Paroo-Darling National Park (Peery Lake)).



Figure 1-4 Typical wetland landscape in the Paroo River Wetlands Ramsar site at the time of sampling (Site RSPL 4).



Figure 1-5 Typical wetland landscape in the Paroo River Wetlands Ramsar site at the time of sampling showing some of the bird life (Site RSPL 1).

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 being developed by the MDB ASS Risk Assessment Project Scientific Reference Panel 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 managers of that wetland.
- 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:

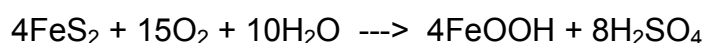
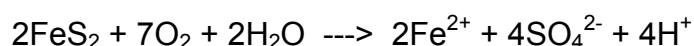
- a. Continued incubation of samples in chip trays.
- b. More detailed acid/base accounting (e.g. elemental sulfur).
- c. Rapid metal release.
- d. Contaminant and metalloid dynamics.
- e. MBO formation potential.
- f. Mineralogy by X-ray diffraction (XRD).
- g. Major and trace elements by X-ray fluorescence 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 Paroo River Wetlands Ramsar site.

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 (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) as shown below:

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

* ANC = Acid Neutralizing Capacity

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

Potential Sulfidic Acidity

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 (S_{CR} or CRS: Method Code 22B) and its conversion to PSA.

Existing Acidity

This 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 materials that have already oxidised. TAA measures the sum of both soluble and exchangeable acidity. The Retained Acidity 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 Retained Acidity are given by Ahern *et al.* (2004).

Acid Neutralising Capacity (ANC)

Soils with pH 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 CaCO₃ equivalents. By accepted definition (Ahern *et al.* 2004), any acid sulfate soil material with a pH < 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.

Water extractable sulfate (1:5 soil:water suspension)

A 1:5 soil:water extract is prepared using 5g oven dried (80°C) soil following the procedures described in Rayment and Higginson (1992). After shaking end-over-end for 4 hours, the suspensions are subject to 10 minutes centrifugation at 4000 rpm. The supernatant is filtered (0.45 µm) and sulfate concentration determined by turbidimetric analysis using a HACH spectrophotometer (or suitable alternative analytical technique for sulfate). Soluble sulfate content is expressed on a dry mass basis. Sulfate contents >10 mg L⁻¹ in water of inland water bodies such as wetlands and rivers give a strong indication that the soil materials underlying those water bodies are able to sulfidise (Sullivan *et al.* 2002a, Baldwin *et al.* 2007, Sullivan *et al.* 2008a) forming monosulfidic black oozes (MBOs) or sulfidic sediments. In dry soils where there are no overlying water bodies, it is considered that water soluble sulfate contents of greater than or equal to 100 mg kg⁻¹ in the surface soil layers (i.e. soil layers in the top 20 cm of the soil profile) would be able to create similar sulfate contents in overlying water bodies as a result of inundation. Therefore this soil sulfate content of greater than or equal to 100

mg kg⁻¹ in surface soil layers has been selected to indicate whether or not surface soil materials from dry wetlands should be examined in the Phase 2 of the detailed assessment for the capacity of these soil materials to form monosulfidic soil materials upon inundation using the approach of Sullivan *et al.* (2008a).

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 by Sullivan *et al.* (2008b) 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 has also been recently (October 2008) 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:

- 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 (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.

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). Also the acidity present in field soils may 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. Paroo River Wetlands site characteristics

Locations sampled in this study were uniformly flat with a lack of vegetation cover except for the occasional lignum clumps and red gums (e.g. Figure 2-2). The wetlands were generally filled with water when sampled. Peery Lake was approximately 98% full and is the first time this lake has been filled in the last 10 years. The groundwater was not intercepted in the non-inundated sampling sites.

The texture of the soil materials sampled was highly variable ranging from sands (especially along the shorelines) to heavy clays. The consistence of some of the clayey subsoils were exceptionally strong precluding sampling of some of the deeper subsoil layers. 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, the typical landscape and soil profile in each of these areas is shown below in Figures 2-1 – 2-4.

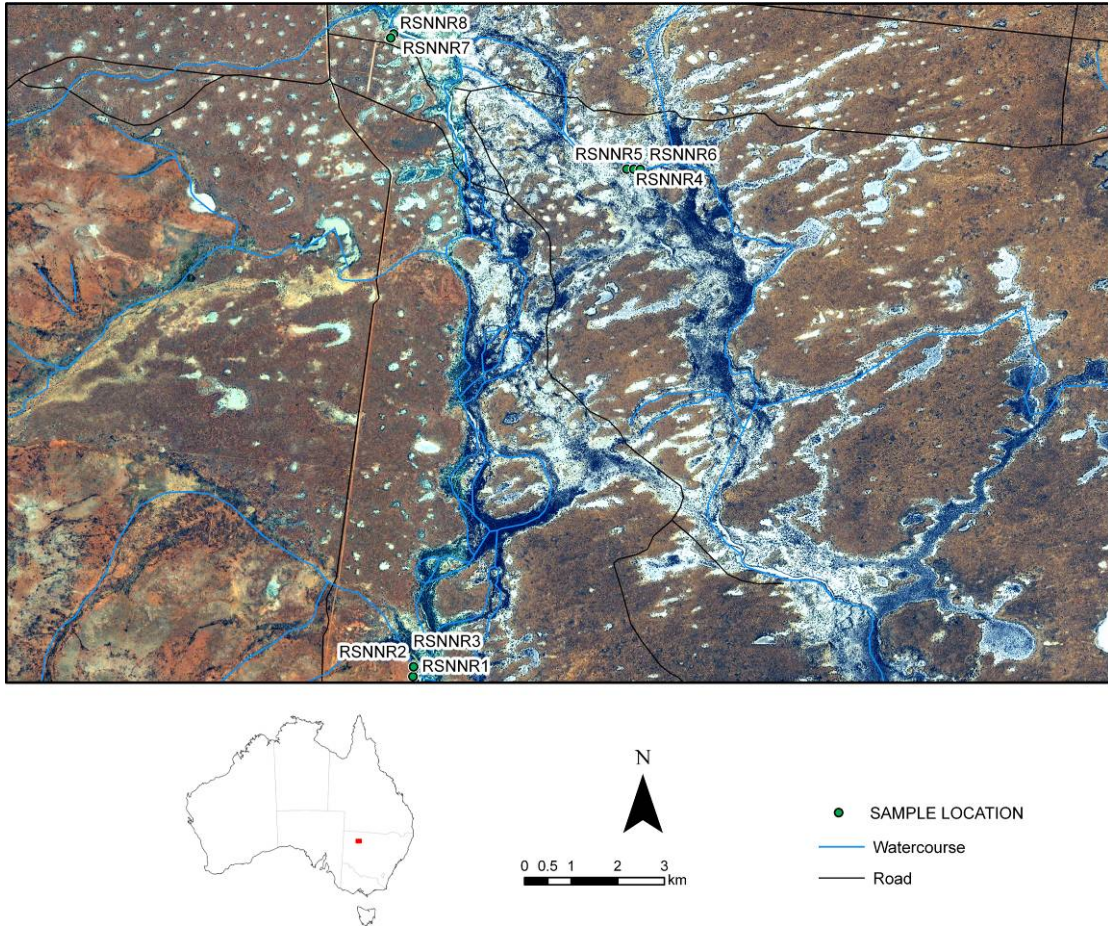


Figure 2-1 Map showing the areas assessed in the Nocoleche Nature Reserve in the Paroo River Wetlands (Sites RSNNR 1-8).



Figure 2-2 Typical landscape (Site RSNNR 8) and Calbocaro waterhole (Site RSNNR 4) in the Nocoleche Nature Reserve. Landscape typically bare ground surrounded by lignum clumps and red gums. Water quality of Calbocaro waterhole (Site RSNNR 4) analysed.

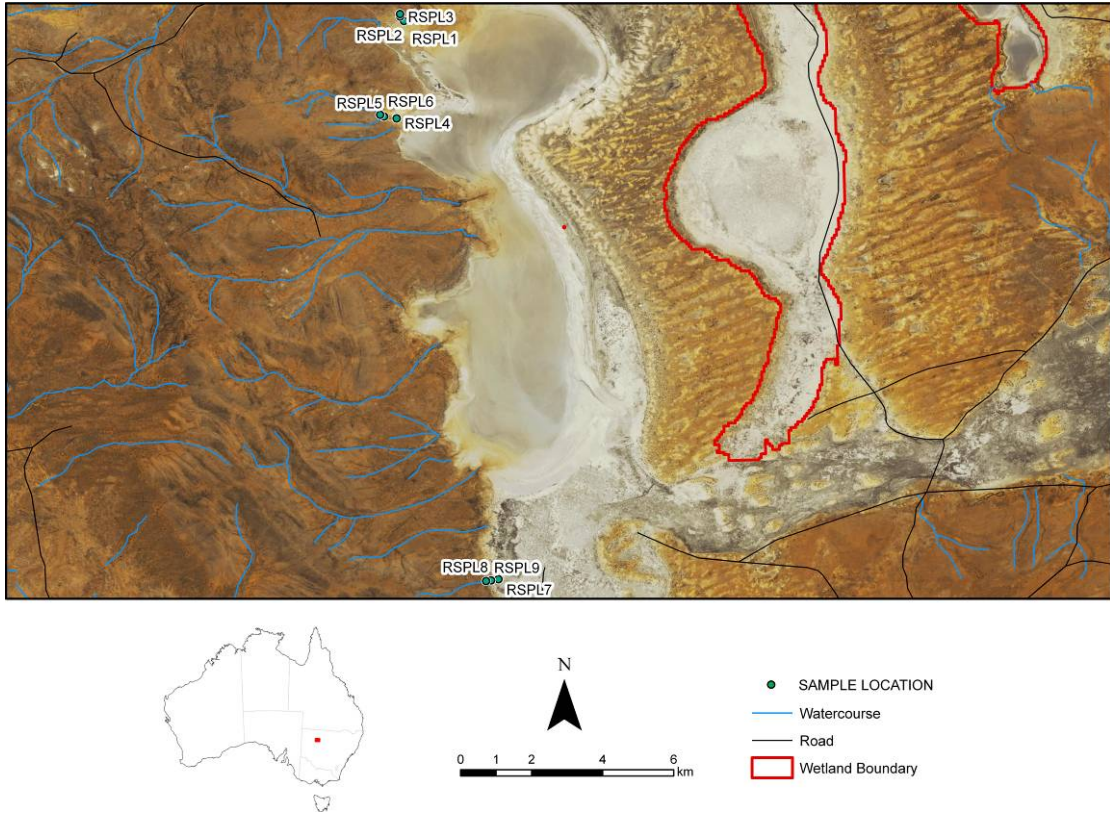


Figure 2-3 Map showing the areas assessed at in the Paroo-Darling National Park (Peery Lake) in the Paroo River Wetlands (Sites RSPL 1-9).



Figure 2-4 Typical landscape (Site RSPL 9) and soil profile at Site RSPL 2 in the Paroo-Darling National Park.

2.2. Field sampling of soils and waters

Field sampling of the Paroo River Wetlands was undertaken between 2nd – 3rd August 2008 at the Nocolèche Nature Reserve sites, and between 7th – 8th August 2008 at the Paroo-Darling National Park sites. A total of 86 soil layers were collected and analysed from 17 representative soil profiles within the Paroo River Wetlands to assess the current and potential environmental hazard due to the presence of acid sulfate soils (Figures 1-2 and 1-3).

Representative soil profiles were collected from 3 locations within the Nocolèche Nature Reserve, and from 3 locations within the Paroo-Darling National Park (Peery Lake). At all except one of these locations 3 soil profiles were sampled along a toposequence. 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. Only two soil profiles were collected at one of the locations in the Nocolèche Nature Reserve (Sites RSNR 7-8).

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 for a selection of representative sites can be found in Section 2.1.

Surface water quality data was collected from 7 locations in the Paroo River Wetlands. Four surface water samples were collected from the Nocolèche Nature Reserve sites (Sites RSNR 1, 2, 4 & 7) and 3 samples were collected from the Paroo-Darling National Park sites (Sites RSNR 1, 4 & 7). No groundwater samples were collected as the groundwater was not intercepted in the non-inundated sampling sites.

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 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_{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, 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, 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 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 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 $\geq 100 \text{ mg SO}_4 \text{ kg}^{-1}$.
- 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 Paroo River Wetlands 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 Paroo River Wetland sites examined is presented in Table 7-2 and 7-3 (Appendix 2) and summarised in Table 3-1. The pH_W values ranged between 5.86 and 10.80, with the majority of the samples having a pH_W > 6.5. None of the soils in the Paroo River Wetlands would be classified as being sulfuric materials as all soils had a pH_W > 4.

The pH_{FOX} values ranged between 3.09 and 9.32. The majority of the soils showed a pH drop after treatment with peroxide (e.g. Figure 3-1 and 3-2), with a maximum decrease of 3.9 pH units. The pH_{FOX} results also indicate that some of the surface soils in the Paroo River Wetlands may have the potential to acidify to pH < 4 as a result of sulfide oxidation. However, the S_{CR} data shows that none of these layers contain detectable sulfide (i.e. S_{CR} ≥ 0.01% S). While such decreases in pH after treatment with peroxide are often used to indicate the presence of sulfide minerals in coastal acid sulfate soil materials, the S_{CR} data from these studies suggest that pH decreases in inland acid sulfate soil materials after peroxide has been added are often due to non-acid sulfate soil factors such as the oxidation of organic matter. None of the sulfidic soil materials (i.e. S_{CR} ≥ 0.01% S) acidified to a pH of less than 4 after at least 8 weeks of incubation.

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

Parameter	Units	Minimum	Median	Maximum	¹ n
pH _W ²		5.86	7.78	10.80	86
pH _{FOX} ³		3.09	6.81	9.32	86
pH _{KCl} ⁴		4.71	7.03	9.70	86
pH _{INCUBATION} ⁵		7.0	7.4	7.4	3
TAA ⁶	mole H ⁺ /tonne	0.00	8.11	20.17	86
Soluble sulfate ⁷	mg SO ₄ kg ⁻¹	10.0	40.2	78,600	86
S _{CR} ⁸	Wt. %S	<0.01	<0.01	0.02	86
ANC* ⁹	%CaCO ₃	0	0.50	1.47	3
Net Acidity ¹⁰	mole H ⁺ /tonne	-187.2	8.2	20.2	43

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.

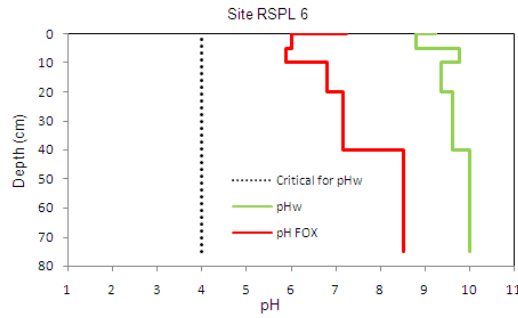


Figure 3-1 Soil pH data for soil profile RSPL 6. Soil (pH_W: green line) and peroxide pH (pH_{FOX}: red line). (Note: no sulfidic layers were present in soil profile RSPL 6 and the TAA was zero for all soil layers).

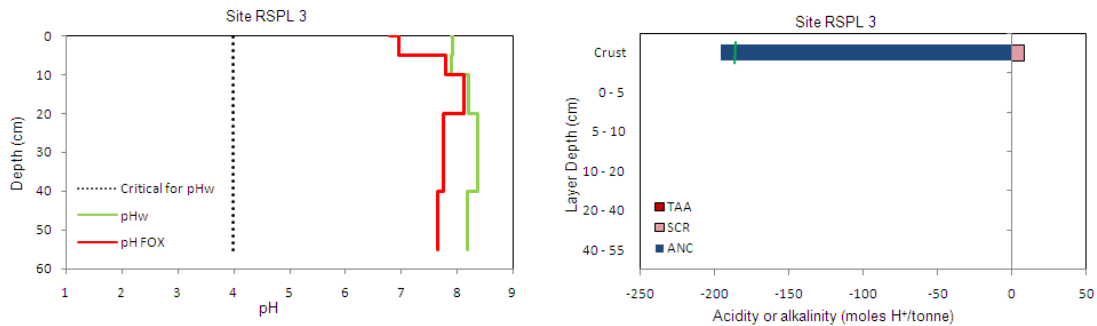


Figure 3-2 Soil pH and acid base accounting data for soil profile RSPL 3. Left Plot: Soil (pH_W: green line) and peroxide pH (pH_{FOX}: red line). Right Plot: S_{CR} (pink bar), ANC (blue bar) and Net Acidity for sulfidic layers (green line). (Note: ANC was only required to be determined for sulfidic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

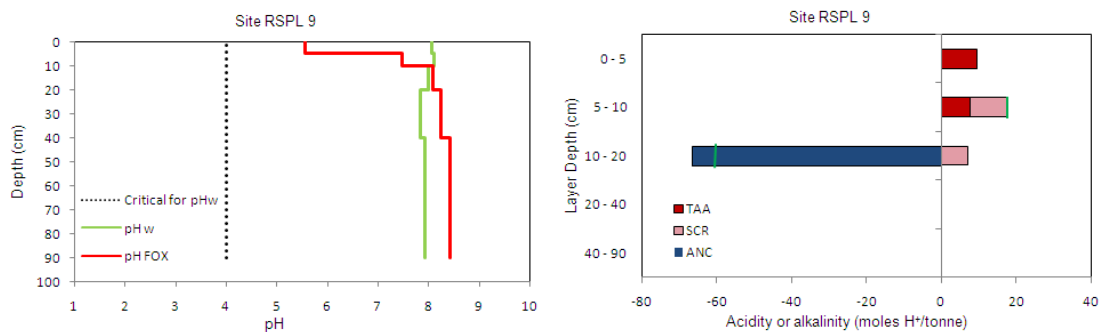


Figure 3-3 Soil pH and acid base accounting data for soil profile RSPL 9. Left Plot: Soil (pH_W: green line) and peroxide pH (pH_{FOX}: red line). Right Plot: TAA (red bar), S_{CR} (pink bar), ANC (blue bar) and Net Acidity for sulfidic layers (green line). (Note: ANC was only required to be determined for sulfidic layers and was zero for the 5-10 cm soil layer).

3.1.2. Chromium Reducible Sulfur (S_{CR})

The S_{CR} data for the Paroo River Wetland sites examined is presented in Table 7-2 and 7-3 (Appendix 2) and summarised in Table 3-1. Sulfidic soil materials (i.e. $S_{CR} \geq 0.01\%$ S) were largely absent from all sampling sites, with only 3 materials of the 86 samples collected equal to or greater than the sulfidic criterion. Sulfidic materials were only found in the Paroo-Darling National Park (Peery Lake) and not in the Nocolèche Nature Reserve. The crust layer at Site RSPL 3 and a surface layer at Site RSPL 9 (10-20 cm) both had a S_{CR} content of 0.01% S. Another surface layer at Site RSPL 9 (5-10 cm) had a S_{CR} content of 0.02% S

3.1.3. Acid Neutralising Capacity

The acid neutralising capacity (ANC) ranged between zero and 1.47 %CaCO₃ for the 3 sulfidic soil materials (see Table 3-1).

3.1.4. Net Acidity

The acidification hazard from acid sulfate soil disturbance posed by the 3 sulfidic soil materials is low. 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). The only hypersulfidic soil material (RSPL 9.4) had a low net acidity of 17.5 mole H⁺/tonne (Figure 3-3).

3.1.5. Water soluble SO₄

The water soluble SO₄ data for the Paroo River Wetland sites examined is presented in Table 7-2 and 7-3 (Appendix 2) and summarised in Table 3-1. The water soluble SO₄ content in the soils in the Paroo River Wetlands ranged between 10 and 78,600 mg kg⁻¹. The highest water soluble SO₄ content was found in the crust layer at Site RSPL 6. The water soluble SO₄ contents in 3 surface soil materials in the Paroo-Darling National Park (Peery Lake) were greater than the trigger value of 100 mg kg⁻¹ (Table 7-3, Appendix 2) suggesting that the formation of monosulfidic materials may pose risks after inundation of these wetlands. The water soluble SO₄ content was often observed to be greatest at depth (i.e. > 40 cm) (Figure 3-4).

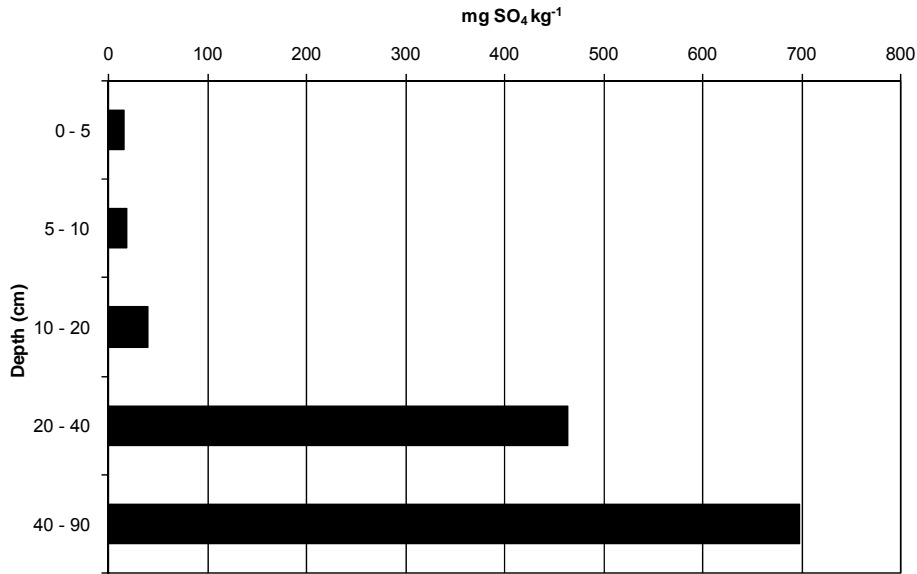


Figure 3-4 Variation in water soluble SO₄ (mg SO₄ kg⁻¹) with depth at site RSNNR 2.

3.1.6. Titratable actual acidity (TAA)

The TAA data for the Paroo River Wetland sites examined is presented in Table 7-2 and 7-3 (Appendix 2) and summarised above in Table 3-1. The TAA ranged between 0 and 20 mole H⁺/tonne. All except 3 layers from soils collected from the Paroo-Darling National Park had a TAA of 0 mole H⁺/tonne, as indicated by a pH_{KCl} > 6.5. Nocolèche Nature Reserve differed in that all except 1 soil layer (RSNNR 1.3) contained titratable acidity. There was often a decrease in the TAA with depth with the Nocolèche Nature Reserve sites (Figure 3-5).

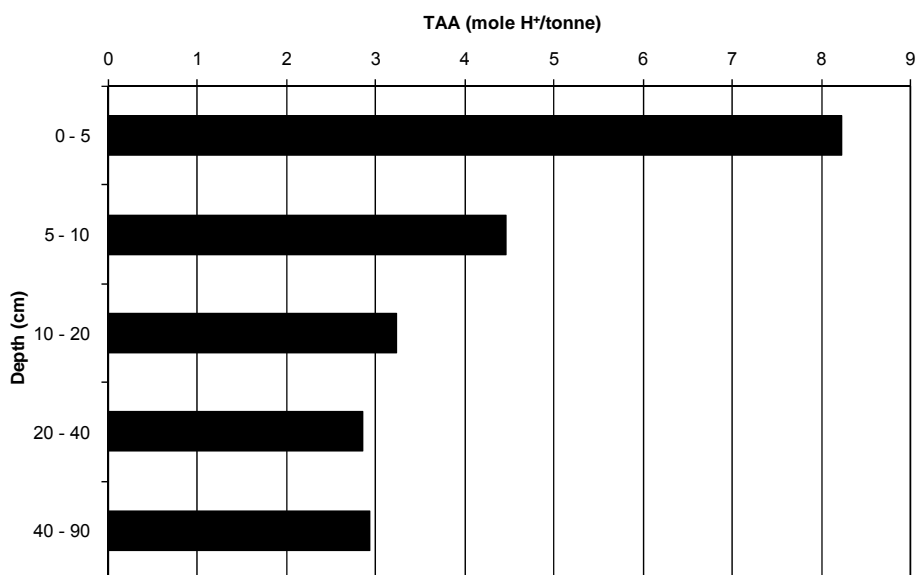


Figure 3-5 Variation in TAA (mole H⁺/tonne) with depth at site RSNNR 5.

3.2. Hydrochemistry

Surface water quality data was collected from 4 locations in the Nocolleche Nature Reserve (Sites RSNR 1, 2, 4 and 7) and 3 locations in the Paroo-Darling National Park (RSPL 1, 4 and 7). Groundwater samples were not intercepted in the non-inundated sampling sites.

A summary of the surface water characteristics measured in the field are presented 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 6.9 and 9.1 (Table 3-2) with 3 sites exceeding the most relevant ANZECC/ARMCANZ (2000) trigger value for aquatic ecosystems of 8.0 (Table 7-4, Appendix 3). The water data indicates that the surface water has not been affected by acidification. The surface water sulfate concentrations were low and ranged between 1.6 and 8.3 mg L⁻¹.

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

	pH	SEC μS cm ⁻¹	DO % sat.	Eh mV	Turbidity NTU	Alkalinity (mg L ⁻¹ as HCO ₃)
Minimum	6.90	112	85	193	155	38.8
Median	7.57	406	118	321	430	53.6
Maximum	9.06	1447	157	378	610	216
n ¹	7	7	7	7	7	7

¹ n: number of samples

4. HAZARD ASSESSMENT

4.1. Interpretation of soil and water data

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

A hypersulfidic material occurred at depth in the soil profile at only 1 of the 17 sampling locations (Table 4-1).

The acidification hazard from acid sulfate soil disturbance posed by this site is low: the single hypersulfidic material had a net acidity of only 17.5 mole H^+ /tonne.

Two hyposulfidic soil materials with $S_{CR} < 0.10\%$ were also present at the sampling sites.

The water soluble sulfate contents of three surficial soil materials sampled in the Paroo-Darling National Park (Peery Lake) exceeded the trigger value of 100 mg kg^{-1} indicating that the formation of monosulfidic materials may occur upon rewetting (Table 4-1).

The surface water data indicates that this 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 sulfuric or sulfidic materials (Total sites = 17)	Proportion of total sampling sites (%)
Sulfuric	0	0
Hypersulfidic	1	6
Hyposulfidic ($S_{CR} \geq 0.10\%$)	0	0
Monosulfidic (observed)	0	0
Monosulfidic (potential)	3	18
Hyposulfidic ($S_{CR} < 0.10\%$)	2	12
Other acidic (pH_w &/or pH_{age}) 4 – 5.5	0	0
Other soil materials	14	82

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 Paroo River Wetlands. This Phase 1 report is aimed solely at determining whether or not acid sulfate soil materials are present in the Paroo River Wetlands.

Sulfuric soil materials were not observed in these wetlands and although 12% (i.e. 2) of the sampling sites contained sulfidic materials, the reduced inorganic sulfur contents of these samples were very low (i.e. the highest S_{CR} was only 0.02%). A hypersulfidic soil material was present in one soil profile (this profile also contained a hyposulfidic material), and another soil profile contained a hyposulfidic material (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, three surficial soil materials sampled in the Paroo-Darling National Park (Peery Lake) contained soluble sulfate in excess of the 100 mg kg^{-1} 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 Soils Risk Assessment Project, there was one high priority site based on the presence of a hypersulfidic material, and one moderate priority site based on the presence of a hyposulfidic material with $S_{CR} < 0.10\%$. In addition, three sampling sites had a high priority ranking for Phase 2 detailed assessment based on MBO formation hazard.

The potential hazards posed by acid sulfate soil materials at the Paroo River Wetlands 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) the degree of acidification hazard is low.
- Deoxygenation: The water soluble sulfate contents of three of the surface soil materials were over the trigger value for MBO formation indicating the possible development of an appreciable deoxygenation hazard at those locations after prolonged wet conditions.
- Metal mobilisation: The low acidification hazard indicates that soil acidification is not likely to produce excessive metal mobilisation. 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.

While this study showed the presence of acid sulfate soil materials in the Paroo River Wetlands, when considering the wetlands as a whole there is a low priority for further assessment to determine specific acid sulfate soil risks. As such, the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soils Risk Assessment Project agreed that Phase 2 detailed assessment of acid sulfate soil materials was not required for the Paroo River wetlands.

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7. APPENDICES

APPENDIX 1. Site and sample descriptions

Table 7-1 Paroo River Wetland site and sample descriptions.

Profile	Date	Location	GPS Co-ords			Location Remarks	Profile remarks
			Zone	East.	North.		
RSNNR1	2/8/08	Nocoleche N.R.	55	222855	6682131	On the Paroo River just upstream of old weir site (weir blown up by locals). First hole dug next to water. Surface water sample taken. No surface vegetation – dry cracking clays.	Brown coloured clays. Uniform brown grey soil. Cracks in surface but no visible crust. Gravel in top layers. Very hard >40cm. Dug to 70cm.
RSNNR2	2/8/08	Nocoleche N.R.	55	222862	6682340	In main channel 200m upstream of NNR1. In between two pools of water 10x5m size. No veg, sparse iron rich gravel and cobbles on surface.	Gravel throughout profile. Uniform grey brown clay.
RSNNR3	2/8/08	Nocoleche N.R.	55	222681	6682565	Further north in channel but drier here in among the Lignum. No surface vegetation.	Grey clays with some red sand on surface. Hard to 40cm then softer grey clays. Hit rocks at 60cm.
RSNNR4	2/8/08	Nocoleche N.R.	55	226570	6693086	In southern end of Calbocaro waterhole to the east of main Paroo River channel. Sample taken under water. Surface water sample taken. Bare banks devoid of vegetation apart from sparse lignum and river cooba trees.	Dug to 40cm successfully but very hard below this. Gauge auger would not penetrate. No 4.7 sample taken.
RSNNR5	2/8/08	Nocoleche N.R.	55	226701	6693091	150m out onto flood channel. No grass cover apart from very sparse herbs. River Cooba lining slight depression 10m to the south of profile.	Uniform soil, moist at depth. Dug to 90cm.
RSNNR6	2/8/08	Nocoleche N.R.	55	226823	6693085	120m E of NNR5 on higher ground. Ground cover of sparse herbs, dead lignum and red gums.	Defined boundary from yellow brown sands to brown clay at 45cm. Dug to 90cm.
RSNNR7	3/8/08	Nocoleche N.R.	55	222151	6695870	In feeder depression adjacent to large waterhole on Paroo River near NPWS sheds at Nocoleche. No surface vegetation. Profile dug 2m from waters edge. Surface water samples taken.	Brown cracking clays on surface. Very hard >30cm. Dug to 50cm.

Table 7-1 (continued) Paroo River Wetland site and sample descriptions.

Profile	Date	Location	GPS Co-ords			Location Remarks	Profile remarks
			Zone	East.	North.		
RSNNR8	3/8/08	Nocoleche N.R.	55	222101	6695784	100m further up lignum depression to the W. bare ground surrounded by lignum clumps.	Top layer of red sands, clear boundary to brown clay (very hard) grading to pillow sandy clay at ~ 40cm. yellow SC very hard. Dug to 50cm
RSPL1	7/8/08	Paroo Darling N.P.	54	745735	6599527	On NW edge of Peery Lake. Lake about 98% full, first time in 10 yrs. First profile of transect dug in 30cm of water. Surface water sample taken.	Sandy throughout. Gravel<30cm. Brown red grading to ref >40cm. Green algae of surface. Dug to 70cm.
RSPL2	7/8/08	Paroo Darling N.P.	54	745644	6599651	Further up creek adjacent to backed up lake water. Hole dug 1m from waters edge	Soil Layers different to normal. 2.3 – 0-7cm: orange/red; 2.4 – 7-15cm: grey; 2.5 – 15-22cm: red; 2.6 – 22-40cm: grey/yellow; 2.7 – 40-75cm: grey/yellow. Very gravelly in 2.4. Large salt crystals in top of 2.7. Hit gravels and cobbles at 75cm
RSPL3	7/8/08	Paroo Darling N.P.	54	745644	6599721	75m up creek from PL2. Looks like the extent of lake water when full. In dry depression. No veg but lots of fine seed material on surface. River cooba and lignum lining creek.	Red yellow colour grading to yellow red soil. Cobbles hit at 55cm.
RSPL4	7/8/08	Paroo Darling N.P.	54	745495	6596793	Sample taken in the main lake body just north of creek mouth where transect will run. Sample taken under 30cm of water. Surface water sample taken.	Very sandy along shoreline. Very uniform sandy sediments in profile. Dug to 70cm.
RSPL5	7/8/08	Paroo Darling N.P.	54	745191	6596856	On mud flat adjacent to water in inlet. Red sands on surface with no veg.	Uniform red sandy sediments <40cm. Brown/red >40cm. Dug to 85cm.

Table 7-1 (continued) Paroo River Wetland site and sample descriptions.

Profile	Date	Location	GPS Co-ords			Location Remarks	Profile remarks
			Zone	East	North		
RSPL6	7/8/08	Paroo Darling N.P.	54	745098	6596906	Further up creek passed extent of lake water. Obvious salt crust on surface in bands on channel bar. Sample dug in one of these salt bands, thus salt crust collected (6.1)	Dark red to red /yellow <40cm Grading to brown yellow >40cm. Hit rocks at 75cm.
RSPL7	08/8/08	Paroo Darling N.P.	54	747663	6583809	Transect in southern lignum feeder channel to Peery Lake. Channel approx 1.5km wide with standing water covering most. Profile dug 120m from waters edge. Water 17cm deep.	Dug to 60cm with gouge auger.
RSPL8	08/8/08	Paroo Darling N.P.	54	747482	6583778	185m west of PL7 out of water but still muddy under foot. Adjacent to creek entrance with lush grasses and lignum. Groundcover at hole predominantly bare with some dead waterweed.	8.3 – 0-3cm; Greyer clay layer underlain by brown/red sediments. 8.4 – 3-10cm. Uniform soil under 10cm. Hole to 80cm.
RSPL9	08/8/08	Paroo Darling N.P.	54	747361	6583763	Last profile on transect. Still in grey soils but very stony on surface (cobbles >10m). Profile dug in small depression/sink hole.	Grey cracking clays with no vegetation on surface.

APPENDIX 2. Field and laboratory analytical soil data

Table 7-2 Nocoleche Nature Reserve field and laboratory analytical soil data.

Site / Sample	Depth (cm)	Texture	Colour	Mottle % / Colour	pH _w	pH _{FOX}	pH _{FOX} reaction ¹	pH _{KCl}	TAA mole H ⁺ /tonne	CRS %Scr	Net Acidity mole H ⁺ /tonne	Sulfate (mg SO ₄ /kg)
RSNNR / 1.3	0 - 5	SMC	10YR 5/2	20% 7.5YR 5/4	6.76	4.44	XXXX	7.92	-	< 0.01	-	18.71
1.4	5 - 10	SMC	10YR 5/2	40% 7.5YR 5/4	6.88	6.09	XXXX	5.25	20.17	< 0.01	20.17	23.08
1.5	10 - 20	SLMC	10YR 6/2		6.90	6.80	XXXX	5.47	5.10	< 0.01	5.10	43.40
1.6	20 - 40	SLC	10YR 6/3		7.50	7.50	XXXX	5.64	6.58	< 0.01	6.58	87.50
1.7	40 - 70	SLC	10YR 5/2		7.70	7.72	XXXX	6.73	2.67	< 0.01	2.67	283.22
RSNNR / 2.3	0 - 5	SMC	10YR 5/2	15% 7.5YR 5/3	7.03	5.60	XXXX	5.33	12.46	< 0.01	12.46	16.63
2.4	5 - 10	SMC	7.5YR 5/3	15% 10YR 5/2	6.88	6.47	XXXX	5.44	11.15	< 0.01	11.15	19.66
2.5	10 - 20	HC	10YR 5/3		6.90	6.60	XXXX	5.6	9.43	< 0.01	9.43	40.54
2.6	20 - 40	MC	10YR 5/3		6.72	6.60	XXXX	5.69	7.99	< 0.01	7.99	465.12
2.7	40 - 90	MC	10YR 5/3		6.67	6.56	XXXX	5.66	8.66	< 0.01	8.66	697.86
RSNNR / 3.3	0 - 5	CLS	2.5YR 4/4	20% 10YR 5/2	6.44	5.50	XXXX	5.26	9.72	< 0.01	9.72	19.79
3.4	5 - 10	CLS	2.5YR 4/6	20% 10YR 5/2	6.44	4.60	XXXX	5.49	9.38	< 0.01	9.38	22.71
3.5	10 - 20	SLMC	2.5YR 5/8	20% 10YR 6/2	6.45	4.90	XXXX	5.52	6.91	< 0.01	6.91	81.35
3.6	20 - 40	SLMC	2.5YR 4/6	15% 10YR 5/1	6.57	5.48	XXXX	5.49	8.56	< 0.01	8.56	249.24
3.7	40 - 60	SLMC	10YR 6/4		7.07	7.03	XXXX	6.31	6.33	< 0.01	6.33	676.69
RSNNR / 4.3	0 - 5	FSCL	10YR 6/1		7.10	6.05	XXXX	5.96	6.78	< 0.01	6.78	23.59
4.4	5 - 10	FCLC	10YR 6/1		7.10	6.38	XXXX	5.97	5.30	< 0.01	5.30	16.63
4.5	10 - 20	FSLC	10YR 6/1		7.10	6.83	XXXX	5.82	4.86	< 0.01	4.86	10.26
4.6	20 - 40	FSLMC	10YR 6/3	20% 7.5YR 5/8	6.80	6.06	XXXX	5.73	5.20	< 0.01	5.20	9.97
RSNNR / 5.3	0 - 5	FSLMC	7.5YR 5/3		6.04	4.23	XXXX	5.4	8.23	< 0.01	8.23	20.02
5.4	5 - 10	FSLMC	7.5YR 5/3		6.62	6.55	XXXX	6.04	4.47	< 0.01	4.47	60.02
5.5	10 - 20	FSLMC	10YR 5/3		6.71	6.94	XXXX	6.62	3.24	< 0.01	3.24	191.59
5.6	20 - 40	FSLMC	10YR 5/3		6.86	7.08	XXXX	6.83	2.87	< 0.01	2.87	2284.24
5.7	40 - 90	FSLMC	10YR 5/3		6.68	7.01	XXXX	6.7	2.94	< 0.01	2.94	4648.67
RSNNR / 6.3	0 - 5	FSLC	7.5YR 5/3		6.60	3.75	XXXX	4.98	11.18	< 0.01	11.18	53.96
6.4	5 - 10	FSLC	7.5YR 5/3		6.65	5.87	XXXX	5.15	8.56	< 0.01	8.56	23.03
6.5	10 - 20	FSLMC	7.5YR 6/4		6.72	6.28	XXXX	5.44	6.24	< 0.01	6.24	21.59
6.6	20 - 40	FSL	7.5YR 5/4		7.10	6.41	XXXX	5.84	2.76	< 0.01	2.76	19.50
6.7	40 - 90	MC	10YR 5/2		7.37	8.13	XXX	6.77	3.01	< 0.01	3.01	137.36
RSNNR / 7.3	0 - 5	HC	7.5YR 4/2		6.67	4.03	XXXX	5	17.14	< 0.01	17.14	14.33
7.4	5 - 10	HC	7.5YR 4/3		6.40	3.81	XXX	4.97	19.43	< 0.01	19.43	18.05
7.5	10 - 20	MHC	7.5YR 4/3		6.35	4.08	XXX	5.07	17.39	< 0.01	17.39	25.53
7.6	20 - 40	SLMC	7.5YR 4/2		6.10	4.75	XXX	5.1	13.62	< 0.01	13.62	67.21
7.7	40 - 50	SLC	10YR 5/2		6.00	3.87	XXX	5.1	10.99	< 0.01	10.99	156.63
RSNNR / 8.3	0 - 5	SL	5YR 4/4		5.94	3.09	XX	4.97	7.65	< 0.01	7.65	24.99
8.4	5 - 10	SLMC	5YR 4/4	30% 10YR 5/1	6.37	3.96	XXX	5.22	9.27	< 0.01	9.27	22.84
8.5	10 - 20	SLMC	10YR 5/3	30% 5YR 4/4	6.51	4.53	XXX	5.23	9.51	< 0.01	9.51	30.59
8.6	20 - 40	SLMC	10YR 5/4	20% 5YR 4/4	5.86	3.64	XX	4.71	13.49	< 0.01	13.49	215.11
8.7	40 - 50	SMC	10YR 6/2		6.86	5.84	XXX	5.63	3.29	< 0.01	3.29	316.93

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 Paroo-Darling National Park (Peery Lake) field and laboratory analytical soil data.

Site / Sample	Depth (cm)	Texture	Colour	Mottle % / Colour	pH _w	pH _{FOX}	pH _{FOX} reaction ¹	pH _{KCl}	pH _{INCUBATION}	TAA mole H ⁺ /tonne	CRS %Scr	ANC %CaCO ₃	Net Acidity mole H ⁺ /tonne	Sulfate (mg SO ₄ /kg)
RSPL / 1.3	0 - 5	FSL	5YR 5/4		7.49	5.14	XXXX	7.43		-	< 0.01	-	-	39.93
1.4	5 - 10	SL	5YR 5/4		7.78	7.15	XXXX	8.42		-	< 0.01	-	-	30.29
1.5	10 - 20	SZCL	5YR 6/3		8.13	6.10	XXXX	7.14		-	< 0.01	-	-	20.98
1.6	20 - 40	FSLC	5YR 5/4		8.02	8.76	XXXX	8.96		-	< 0.01	-	-	32.92
1.7	40 - 70	FSMC	5YR 5/6		8.85	9.08	XXXX	9.08		-	< 0.01	-	-	118.12
RSPL / 2.3	0 - 5	FSLC	5YR 4/4		7.23	4.46	XXXX	6.04		8.73	< 0.01	-	8.73	121.67
2.4	5 - 10	FSLC	7.5YR 5/3		7.96	7.11	XXXX	7.74		-	< 0.01	-	-	40.58
2.5	10 - 20	FSLC	2.5YR 4/4	40% 10YR 6/2	7.77	7.21	XXXX	7.98		-	< 0.01	-	-	21.18
2.6	20 - 40	LC	7.5YR 6/4		8.07	8.11	XXXX	8.44		-	< 0.01	-	-	33.10
2.7	40 - 75	LC	7.5YR 6/6		7.68	7.57	XXXX	8.21		-	< 0.01	-	-	9914.77
RSPL / 3.2	Crust	ZCL	10YR 4/2		7.89	6.79	XXXX		7.4	-	0.013	1.47	-187.20	466.28
3.3	0 - 5	LMC	5YR 5/6		7.92	6.95	XXXX	8.44		-	< 0.01	-	-	91.34
3.4	5 - 10	LC	5YR 5/4		7.89	7.79	XXXX	8.35		-	< 0.01	-	-	45.84
3.5	10 - 20	MHC	7.5YR 5/4		8.21	8.12	XXXX	8.34		-	< 0.01	-	-	27.49
3.6	20 - 40	LC	7.5YR 6/6		8.37	7.76	XXXX	8.48		-	< 0.01	-	-	39.79
3.7	40 - 55	LC	7.5YR 5/4		8.19	7.65	XXX	8.52		-	< 0.01	-	-	169.53
RSPL / 4.3	0 - 5	CS	5YR 5/6		8.09	6.38	XX	9.28		-	< 0.01	-	-	39.86
4.4	5 - 10	CS	5YR 5/6		8.39	6.28	X	9.39		-	< 0.01	-	-	17.64
4.5	10 - 20	LS	2.5YR 5/6		8.51	6.19	X	9.40		-	< 0.01	-	-	33.24
4.6	20 - 40	CS	5YR 5/4		8.43	6.23	X	9.70		-	< 0.01	-	-	22.45
4.7	40 - 70	FCS	5YR 5/4		9.41	6.67	X	9.60		-	< 0.01	-	-	16.84
RSPL / 5.3	0 - 5	SL	2.5YR 4/6		8.91	7.02	XX	8.82		-	< 0.01	-	-	21.64
5.4	5 - 10	SL	2.5YR 4/4		9.11	7.22	XX	9.00		-	< 0.01	-	-	18.24
5.5	10 - 20	SL	2.5YR 4/6		9.56	7.81	XX	9.58		-	< 0.01	-	-	17.85
5.6	20 - 40	SL	2.5YR 4/4		10.03	7.49	X	9.65		-	< 0.01	-	-	16.33
5.7	40 - 85	SL	7.5YR 5/4		10.08	7.38	X	9.66		-	< 0.01	-	-	51.06
RSPL / 6.1	Salt crust	FSL	2.5YR 4/4		9.23	7.26	XXX	9.52		-	< 0.01	-	-	7860.00
6.3	0 - 5	FCLS	2.5YR 4/4		8.80	6.04	XXXX	7.97		-	< 0.01	-	-	993.20
6.4	5 - 10	FCLS	2.5YR 3/6		9.77	5.90	XXXX	7.61		-	< 0.01	-	-	118.47
6.5	10 - 20	CLS	2.5YR 4/6		9.36	6.82	XXXX	8.29		-	< 0.01	-	-	71.12
6.6	20 - 40	CS	2.5YR 4/6		9.61	7.18	X	9.51		-	< 0.01	-	-	24.11
6.7	40 - 75	FCLS	2.5YR 5/3		10.00	8.53	X	9.58		-	< 0.01	-	-	14.97
RSPL / 7.3	0 - 5	ZCL	10YR 6/1		8.28	7.21	XXXX	7.03		-	< 0.01	-	-	77.37
7.4	5 - 10	ZLC	10YR 6/2		8.47	8.15	XXXX	7.05		-	< 0.01	-	-	34.34
7.5	10 - 20	SLMC	10YR 7/2		8.70	9.00	XXXX	8.00		-	< 0.01	-	-	132.92
7.6	20 - 40	SLMC	10YR 6/2		8.40	8.54	XXX	8.73		-	< 0.01	-	-	3810.67
7.7	40 - 60	SLMC	10YR 6/2		8.24	8.77	XXXX	8.69		-	< 0.01	-	-	3859.24
RSPL / 8.3	0 - 5	LMC	5Y 6/1		8.38	7.92	XXXX	8.44		-	< 0.01	-	-	88.32
8.4	5 - 10	MC	10YR 5/3		8.75	8.58	XXXX	8.12		-	< 0.01	-	-	23.54
8.5	10 - 20	MC	10YR 6/2		8.90	8.88	XXXX	8.47		-	< 0.01	-	-	18.44
8.6	20 - 40	LMC	10YR 5/2		8.98	9.18	XXXX	8.52		-	< 0.01	-	-	19.17
8.7	40 - 80	MC	10YR 5/2		8.95	9.32	XXXX	8.67		-	< 0.01	-	-	307.04
RSPL / 9.3	0 - 5	LMC	10YR 5/3		8.06	5.57	XXXX	6.05		9.41	< 0.01	-	9.41	70.40
9.4	5 - 10	MC	10YR 5/2		8.10	7.47	XXXX	6.17	7.4	7.65	0.016	0.00	17.53	68.28
9.5	10 - 20	MC	10YR 5/3		7.99	8.08	XXXX	6.63	7.0	-	0.011	0.50	-59.63	409.11
9.6	20 - 40	LMC	10YR 5/3		7.83	8.25	XXXX	7.81		-	< 0.01	-	-	3062.27
9.7	40 - 90	HC	10YR 4/2		7.92	8.42	XXXX	8.75		-	< 0.01	-	-	3678.00

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 Paroo River Wetlands field hydrochemistry data.

Water Type	Site	Units	Site RSNR 1	Site RSNR 2	Site RSNR 4	Site RSNR 7	Site RSPL 1	Site RSPL 4	Site RSPL 7	Minimum	Median	Maximum	Range	n
			Surface	Surface	Surface	Surface	Surface	Surface	Surface					
pH			7.50	7.57	7.45	6.90	9.06	8.64	8.50	6.90	7.57	9.06	6.90 - 9.06	7
SEC		$\mu\text{S cm}^{-1}$	116	1447	157	112	420	406	514	112	406	1447	112 - 1447	7
DO		% sat	101.0	117.9	91.3	85.0	157.0	121.0	125.0	85.0	117.9	157.0	85.0 - 157.0	7
Eh		mV	277	332	378	337	281	321	193	193	321	378	193 - 378	7
Turbidity		NTU	520	610	430	450	170	155	170	155	430	610	155 - 610	7
Alkalinity		(mg L^{-1} as HCO_3)	44.8	42.4	53.6	38.8	164.0	158.0	216.0	38.8	53.6	216.0	38.8 - 216.0	7
Temperature		$^{\circ}\text{C}$	12.3	14.7	15.0	6.6	10.1	12.3	10.6	6.6	12.3	15.0	6.6 - 15.0	7

Table 7 - 5 Paroo River Wetlands laboratory analytical hydrochemistry data.

Parameter	Units	Site RSNR 1	Site RSNR 2	Site RSNR 4	Site RSNR 7	Site RSPL 1	Site RSPL 4	Site RSPL 7	Minimum	Median	Maximum	Range	n
pH		6.82	6.93	7.14	6.83	i.s.	8.16	8.04	6.82	7.04	8.16	6.82 - 8.16	6
E.C.	$\mu\text{S cm}^{-1}$	97	129	133	97	i.s.	368	549	97	131	549	97 - 549	6
Alkalinity	meq/L	0.42	0.54	0.75	0.46	i.s.	2.39	3.29	0.42	0.65	3.29	0.42 - 3.29	6
Ammonium (NH ₄ -N)	mg/L	0.101	0.180	< 0.005	< 0.005	0.042	0.036	0.034	< 0.005	0.036	0.180	< 0.005 - 0.180	7
Oxides of Nitrogen (NO _x -N)	mg/L	0.630	0.058	0.915	0.643	0.316	0.681	0.028	0.028	0.630	0.915	0.028 - 0.915	7
Nitrate (NO ₃ -N)	mg/L	0.609	0.011	0.898	0.630	0.293	0.681	0.028	0.011	0.609	0.898	0.011 - 0.898	7
Nitrite (NO ₂ -N)	mg/L	0.022	0.047	0.017	0.013	0.023	< 0.005	< 0.005	0.013	0.017	0.047	0.013 - 0.047	7
Phosphate (PO ₄ -P)	mg/L	0.032	0.056	0.019	0.024	1.430	0.155	0.017	0.017	0.032	1.430	0.017 - 1.430	7
Chloride (Cl)	mg/L	7.06	12.93	8.35	6.74	28.81	27.48	59.30	6.74	12.93	59.30	6.74 - 59.30	7
Bromide (Br)	mg/L	0.02	0.04	0.03	0.02	< 0.05	0.03	0.13	0.02	0.03	0.13	0.02 - 0.13	7
Sulfate (SO ₄ ²⁻)	mg/L	6.19	8.31	4.02	5.81	3.79	3.77	1.55	1.55	4.02	8.31	1.55 - 8.31	7
Calcium (Ca)	mg/L	3.57	4.31	5.41	4.28	15.37	15.53	17.33	3.57	5.41	17.33	3.57 - 17.33	7
Potassium (K)	mg/L	3.87	4.64	5.12	4.11	7.26	7.53	7.66	3.87	5.12	7.66	3.87 - 7.66	7
Magnesium (Mg)	mg/L	1.49	2.08	2.32	1.86	5.49	5.65	7.20	1.49	2.32	7.20	1.49 - 7.20	7
Sodium (Na)	mg/L	12.36	19.79	16.60	12.01	65.28	64.26	103.03	12.01	19.79	103.03	12.01 - 103.03	7
Sulfur (S)	mg/L	2.44	3.30	1.68	2.33	1.92	1.88	1.25	1.25	1.92	3.30	1.25 - 3.30	7
Total Organic Carbon (NPOC)	mg/L	8.86	12.48	9.06	8.38	12.51	13.36	19.75	8.38	12.48	19.75	8.38 - 19.75	7
Total Nitrogen (TN)	mg/L	1.48	1.90	1.77	1.65	0.85	1.31	0.91	0.85	1.48	1.90	0.85 - 1.90	7
Aluminium (Al)	mg/L	0.292	2.182	0.616	1.737	1.355	2.342	0.168	0.168	1.355	2.342	0.168 - 2.342	7
Boron (B)	mg/L	0.040	0.055	0.063	0.038	0.165	0.166	0.104	0.038	0.055	0.166	0.038 - 0.166	7
Copper (Cu)	mg/L	0.006	0.008	< 0.005	0.008	0.005	0.005	< 0.005	< 0.005	0.005	0.008	< 0.005 - 0.008	7
Iron (Fe)	mg/L	0.433	3.049	0.895	2.813	1.553	2.781	0.146	0.146	1.553	3.049	0.146 - 3.049	7
Manganese (Mn)	mg/L	< 0.006	0.023	0.014	0.031	0.014	0.017	< 0.006	< 0.006	0.014	0.031	< 0.006 - 0.031	7
Phosphorus (P)	mg/L	0.038	0.111	0.076	0.092	0.220	0.217	0.062	0.038	0.092	0.220	0.038 - 0.220	7
Zinc (Zn)	mg/L	0.050	< 0.003	< 0.003	0.039	0.007	0.005	0.005	< 0.003	0.005	0.050	< 0.003 - 0.050	7
Molybdenum (Mo)	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	7
Cobalt (Co)	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	7
Nickel (Ni)	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	7
Cadmium (Cd)	mg/L	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	7
Lead (Pb)	mg/L	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	7
Selenium (Se)	mg/L	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	7

