Assessment of Acid Sulfate Soil Materials in Ramsar Wetlands of the Murray-Darling Basin: NSW Central Murray State Forests

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Cover Photographs:

Wetland landscape in the NSW Central Murray State Forests Ramsar wetlands containing surface water at the time of sampling. Photograph taken at Site RSWSF 3 in the Werai State Forest.

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EXECUTIVE SUMMARY

The NSW Central Murray State Forests Ramsar wetlands comprise of three discrete areas (Millewa, Werai and Koondrook Units), all situated within 70 km of Deniliquin. These areas comprise a total of 84,000 hectares of nominated wetlands.

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 NSW Central Murray State Forests Ramsar wetlands. This Phase 1 report is aimed solely at determining whether or not acid sulfate soil materials are present in the NSW Central Murray State Forests Ramsar wetlands.

Only one sulfuric soil material was observed in these wetlands and, although one (5%) sampling site contained sulfidic materials, the reduced inorganic sulfur content of this sample was very low (i.e. only 0.01%). 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, seventeen surficial soil materials 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 high priority site based on the presence of a sulfuric material. In addition seventeen sampling sites had a high priority ranking for Phase 2 detailed assessment of MBO formation hazard.

The potential hazards posed by acid sulfate soil materials at the NSW Central Murray State Forests Ramsar wetlands are as below:

- Acidification: The pH data indicate, along with only one sulfidic material (where the highest S_{CR} was only 0.01 %S), that the degree of acidification hazard is low.

- Deoxgenation: The water soluble sulfate contents of the majority of 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 NSW Central Murray State Forests Ramsar 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 NSW Central Murray State Forests Ramsar wetlands.

1. INTRODUCTION

1.1. *Wetland overview*

The NSW Central Murray State Forests Ramsar wetlands (Figure 1-1) consists of three discrete wetland areas (Millewa, Werai and Koondrook Units), all of which were sampled in this study (Figure 1-4). These areas comprise a total of 84,000 hectares of nominated wetlands.

An overview from the Ramsar Site Information Sheet (October 2002) follows:

> *The site plays a substantial role in the functioning of the River Murray, is critically important for the retention of native biodiversity in the Riverina bioregion, and contains significant social, cultural and economic resources. It has been managed under multiple use principles including forestry for almost 150 years, making it one of the longest continuously managed natural resources in Australia.*

According to the Ramsar Site Information Sheet *"The site plays a substantial role in biodiversity retention in the Riverina bioregion as it contains high quality wetland habitats and a significant proportion of the species adapted to lowland river and floodplain environments in the Murray Darling Basin. The site is for the most part an ephemeral wetland, with permanent water restricted to rivers and deeper oxbow lagoons and channels within the floodplain. Under natural flow conditions, periods of inundation of 3-6 months duration generally occurred 6-8 times each decade between June and December."*

Figure 1-2 shows a typical wetland in this Ramsar wetland, whereas Figure 1-3 shows the only wetland that contained surface water at the time of sampling. Further information on characteristics of the NSW Central Murray State Forests from the Ramsar Site Information Sheet can be found at State Forests of NSW and NSW National Parks and Wildlife Service (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.

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).

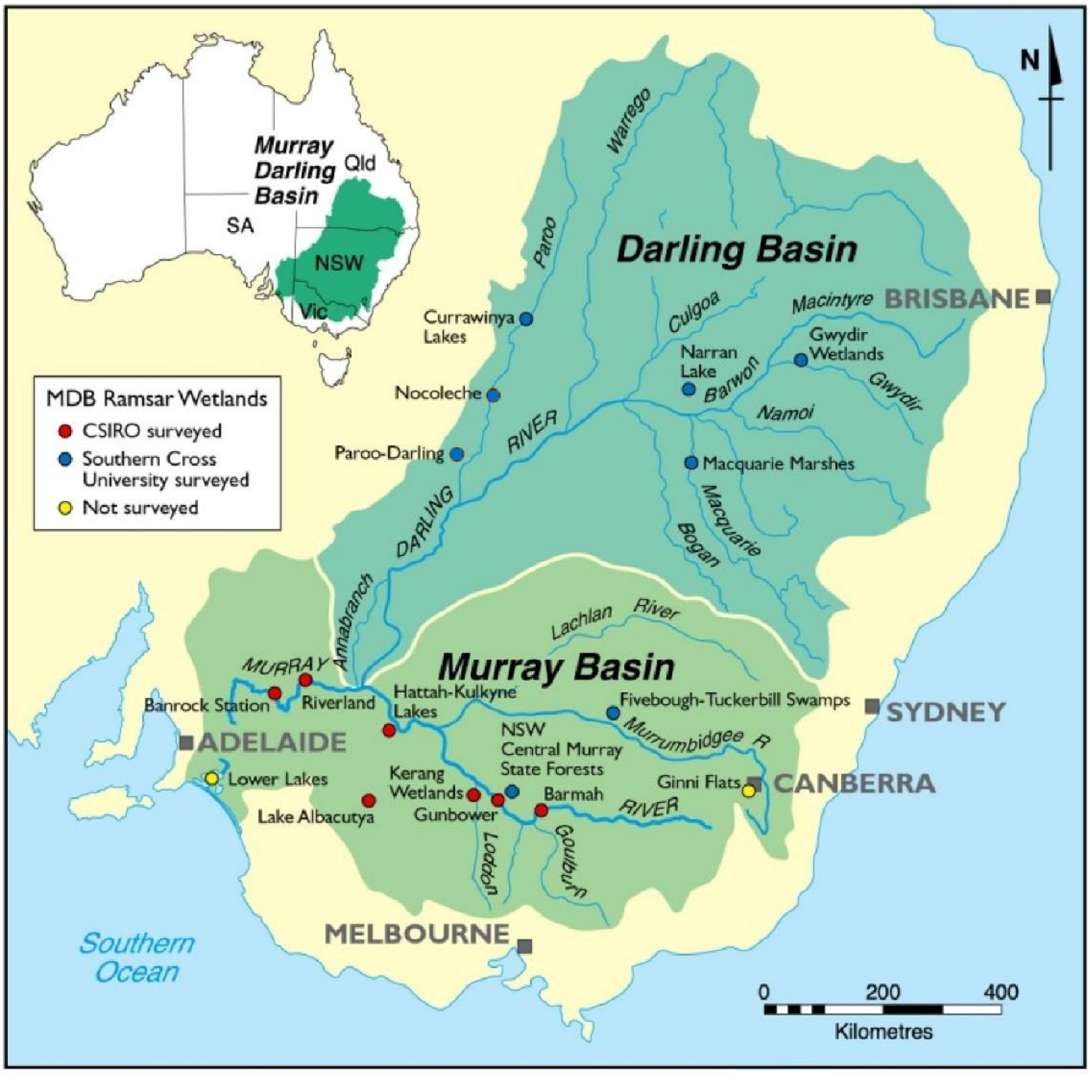

Figure 1-1 Map of Ramsar Wetlands surveyed in the Murray-Darling Basin.

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 21 representative sites within the NSW Central Murray State Forests in 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 wetland landscape in the NSW Central Murray State Forests Ramsar wetlands at the time of sampling (Site RSMIL 6).

Figure 1-3 Wetland landscape in the NSW Central Murray State Forests Ramsar wetlands containing surface water at the time of sampling (Site RSMIL 3).

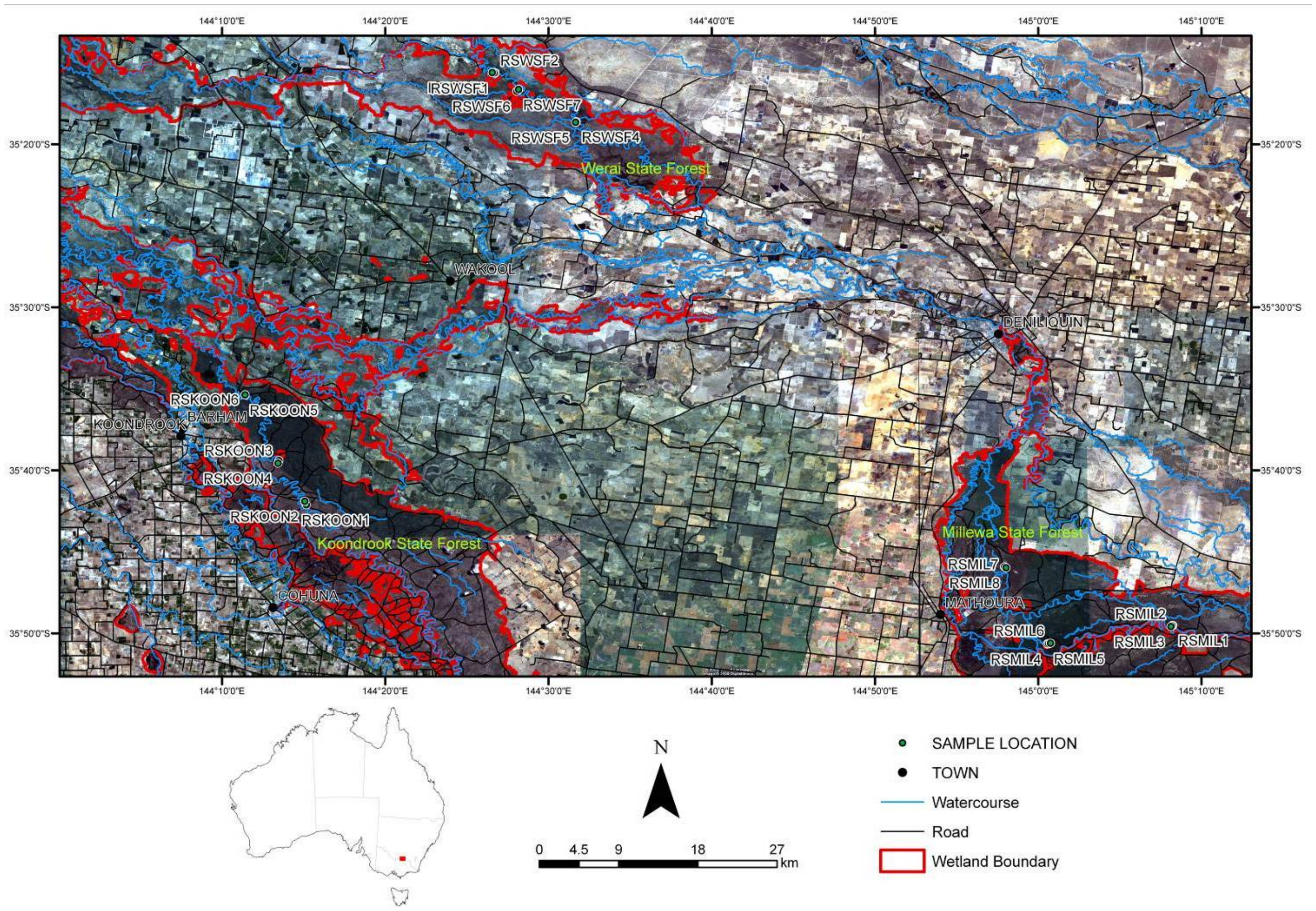

Figure 1-4 Map showing the areas assessed in the NSW Central Murray State Forests Ramsar wetlands.

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 NSW Central Murray State Forests

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: FeS_2) may occur which produce acidity, including:

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

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

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

Acid-base accounting (ABA)

Acid-base accounting (ABA) is used to assess both the potential of a soil material to produce acidity from sulfide oxidation and also its ability to neutralise any acid formed (e.g. Sullivan *et al*. 2001, Sullivan *et al*. 2002b). The standard ABA applicable to acid sulfate soil is as described in Ahern *et al*. (2004) 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 $CaCO_3$ 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^{o}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 pHw < 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 $pH_W \geq 4$ 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. NSW Central Murray State Forests site characteristics

Locations sampled in this study were uniformly flat with either a lack of vegetation cover (e.g. Figure 2-6) or more typically a vegetation cover of grasses (e.g. Figure 2-2). The textures of the soil materials sampled ranged from sandy loams to heavy clays, with a predominance of clayey-textured soil materials.

The sites were generally dry when sampled. Surface water was absent from all but one of the sampling sites and the groundwater was not intercepted in any of the other 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, the typical landscape and soil profile in each of these areas is shown below in Figures 2-1 – 2-6.

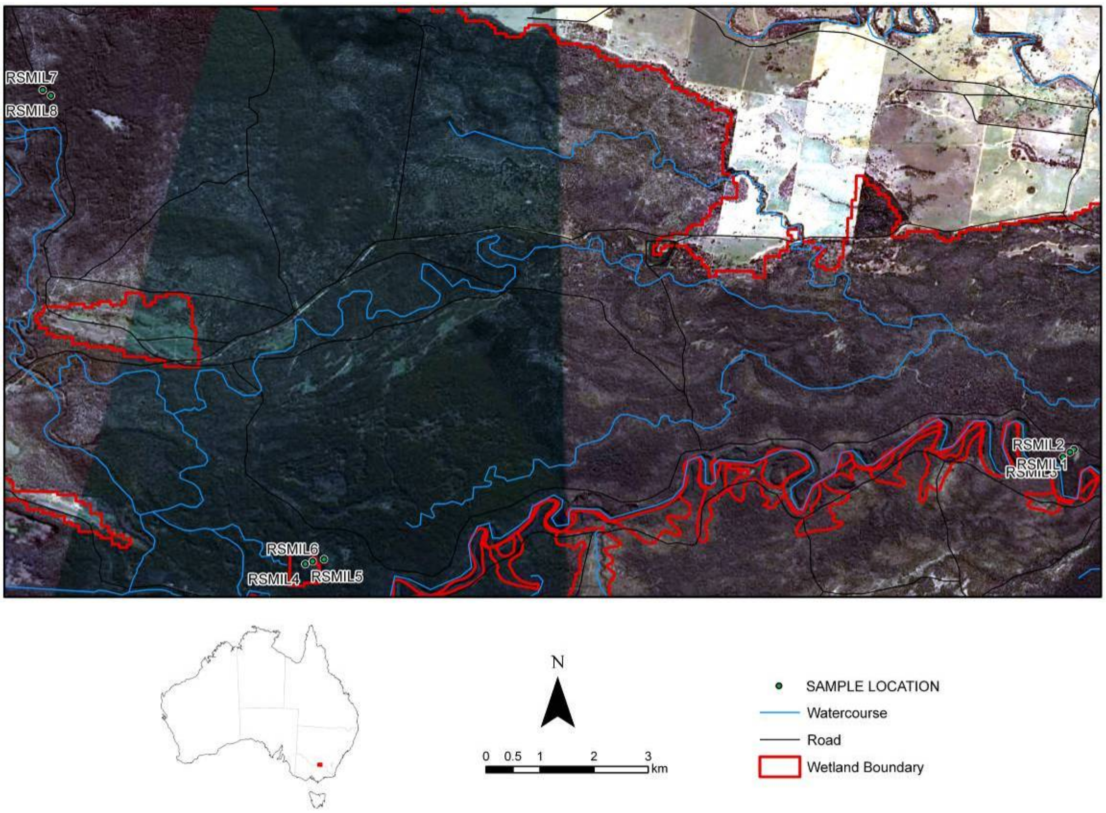

Figure 2-1 Map showing the areas assessed in the Millewa State Forest (Sites RSMIL 1-8).

Figure 2-2 Typical landscape (Site RSMIL 6) and cracking clay soil surface at Site RSMIL 1 in the Millewa State Forest. Site RSMIL 6 shows groundcover of pasture grasses and Patterson's curse surrounded by red gums. Cracks approximately 10cm wide and 60cm deep at Site RSMIL 1.

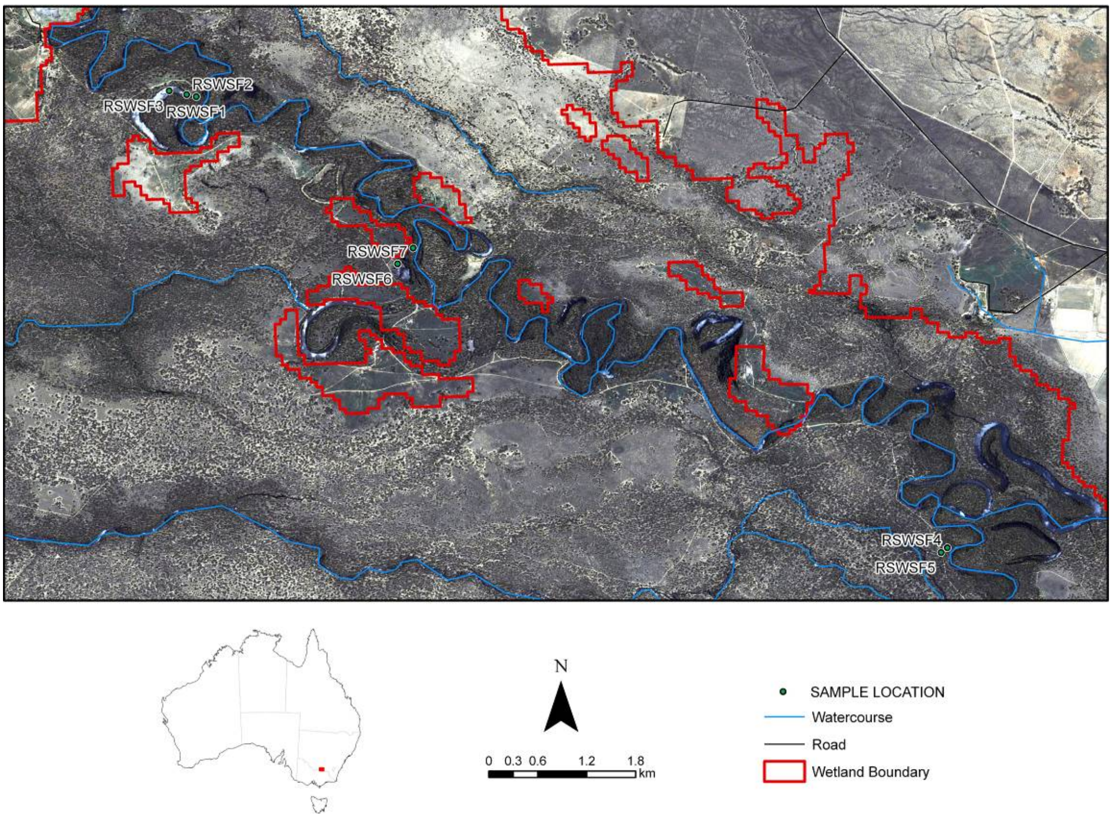

Figure 2-3 Map showing the areas assessed in the Werai State Forest (Sites RSWSF 1-7).

Figure 2-4 Typical wetland landscape (Site RSWSF 3) and forest landscape (Site RSWSF 7) in the Werai State Forest. A surface water quality sample was collected at Site RSWSF 3 for hydrochemical analyses.

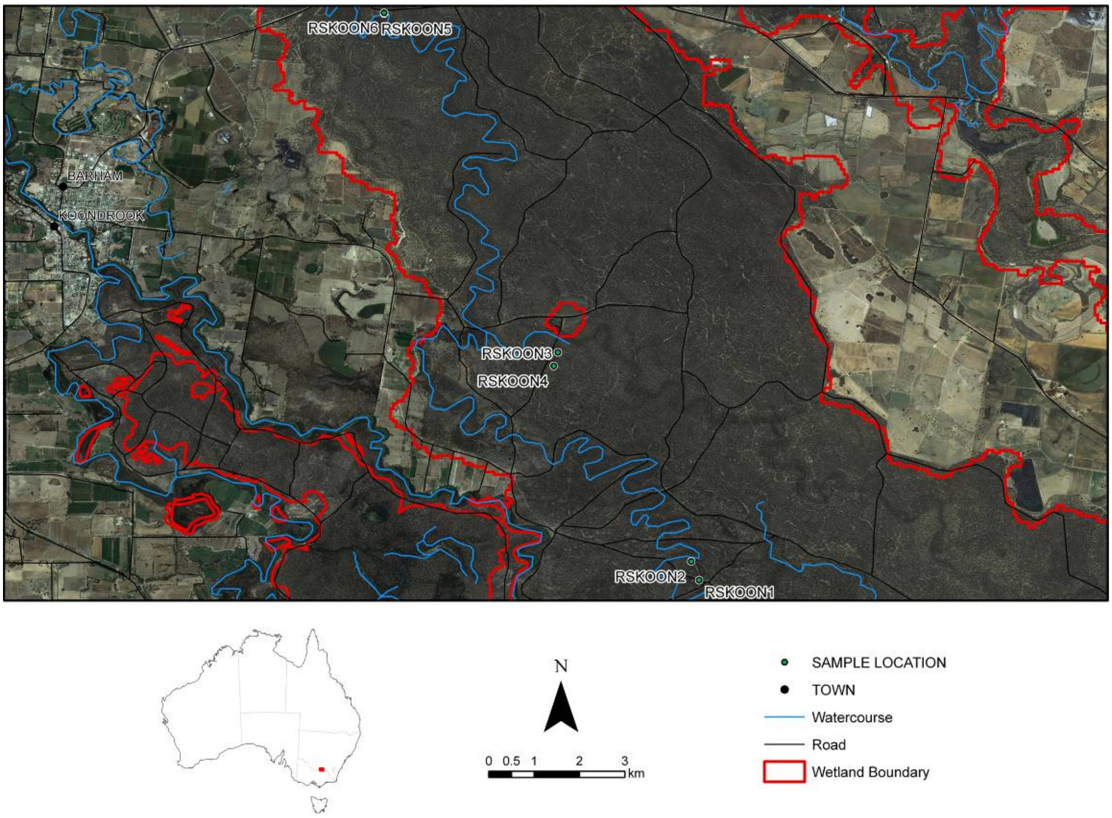

Figure 2-5 Map showing the areas assessed in the Koondrook State Forest (Sites RSKOON 1-6).

Figure 2-6 Typical landscape (Site RSKOON 2) and Cow Creek channel (Site RSKOON 5) in the Koondrook State Forest.

2.2. Field sampling of soils and waters

Field sampling of the NSW Central Murray State Forests was undertaken between 21st and 23rd July 2008. A total of 105 soil layers were collected and analysed from 21 representative soil profiles within the NSW Central Murray State Forests to assess the current and potential environmental hazard due to the presence of acid sulfate soils.

Representative soil profiles were collected from 3 locations within each of the State Forests (Figure 1-4): Millewa State Forest (RSMIL 1-8), Werai State Forest (RSWSF 1-7) and Koondrook State Forest (RSKOON 1-6). Two or three 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. However, often only 2 profiles along a toposequence were collected at many of the locations.

Soil samples were collected from 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 ≤ 4°C prior to analysis.

Site and profile descriptions including global positioning system (GPS) coordinates are presented in Appendix 1. The soil texture and Munsell colour of each sampled soil layer is presented in Appendix 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.

A surface water quality sample was collected from 1 location in the Werai State Forest (Site RSWSF 3). No groundwater data was collected at the time of sampling as groundwater was not observed during soil pit excavation.

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°C and sent to CSIRO for analysis.

2.3. Laboratory soil analysis methods

All soil samples were oven-dried at 80^{o}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 the sulfidic sample 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 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 ≥ 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 SO_4 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 NSW Central Murray State Forests 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 NSW Central Murray State Forests wetland sites examined is presented in Table 7-2, 7-3 and 7-4 (Appendix 2) and summarised in Table 3-1. The pH_W values ranged between 3.96 and 7.89, with the majority of the samples having a $pH_W > 4.5$. Only 1 site within the Werai State Forest (Site RSWSF 6.5) with a pH_W of 3.96 would be classified as being sulfuric. None of the other soils in the NSW Central Murray State Forests wetlands would be classified as being sulfuric materials as they all had a $pH_W > 4$.

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

Parameter	Units	Minimum	Median	Maximum	[1]n
pH_W[2]		3.96	5.38	7.89	105
pH_{FOX}[3]		1.63	3.20	6.52	105
pH_{KCl}[4]		3.61	4.25	6.99	105
$pH_{INCUBATION}$[5]		4.5	4.5	4.5	1
TAA[6]	mole H^+/tonne	0.00	33.6	110.6	105
Soluble sulfate[7]	mg SO_4 kg^{-1}	17.0	68.6	451.1	105
S_{CR}[8]	Wt. %S	<0.01	<0.01	0.01	105
ANC* [9]	%$CaCO_3$	0	0	0	1
Net Acidity[10]	mole H^+/tonne	0	33.6	110.6	105

[1] n: number of samples. [2] pH_W: pH in saturated paste with water. [3] pH_{FOX}: pH after treatment with 30% H_2O_2. [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.

The pH_{FOX} values ranged between 1.63 and 6.52. All soils showed a pH drop after treatment with peroxide (e.g. Figure 3-1), with a maximum decrease of 3.6 pH units. The pH_{FOX} results also indicate that the majority of the surface soils in the NSW Central Murray State Forests wetlands may have the potential to acidify to pH < 4 as a result of sulfide oxidation. However, the S_{CR} data shows only 1 of these layers contain detectable sulfide (i.e. $S_{CR} \geq 0.01$ %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. The single sulfidic soil material (i.e. $S_{CR} \geq 0.01$ %S) did not acidify to a pH of less than 4 after at least 8 weeks of incubation.

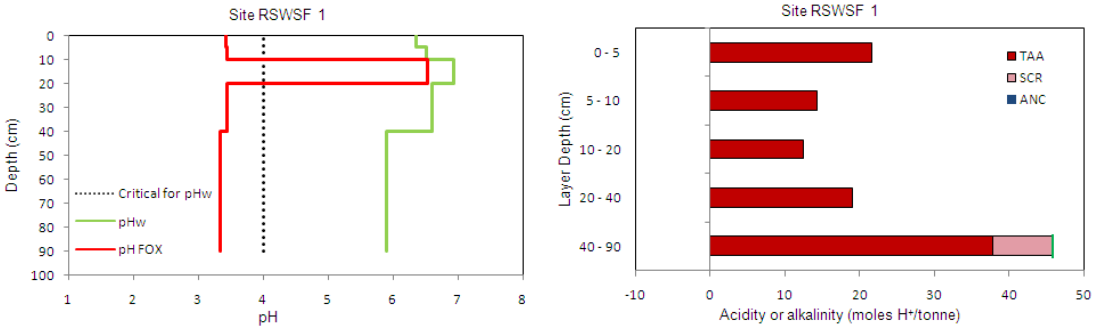

Figure 3-1 Soil pH and acid base accounting data for soil profile RSWSF 1. Left Plot: Soil (pH_W: green line) and peroxide pH (pH_{FOX}: red line). Right Plot: TAA (red bar), S_{CR} (pink bar) and Net Acidity for sulfidic layers (green line). (Note: ANC was only required to be determined for sulfidic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

3.1.2. Chromium Reducible Sulfur (S_{CR})

The S_{CR} data for the NSW Central Murray State Forests wetland sites examined is presented in Table 7-2, 7-3 and 7-4 (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 1 material of the 105 samples collected equal to the sulfidic criterion. One soil layer in the Werai State Forest (Site RSWSF 1) had a S_{CR} of 0.01 %S at depth (40–90 cm).

3.1.3. Acid Neutralising Capacity

The ANC was zero for the single sulfidic soil material (see Table 3-1).

3.1.4. Net Acidity

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 acidification hazard from acid sulfate soil disturbance posed by the single sulfidic soil material is low. The only hypersulfidic soil material (RSWSF 1.7) had a moderate net acidity of 45.9 mole H^+/tonne but was located at depth (40–90 cm) (Figure 3.1).

3.1.3. Water soluble SO_4

The water soluble SO_4 data for the NSW Central Murray State Forests wetland sites examined is presented in Table 7-2, 7-3 and 7-4 (Appendix 2) and summarised in Table 3-1. The water soluble SO_4 content in the soils in the NSW Central Murray State Forests wetlands ranged between 17.0 and 451.1 mg kg^{-1}. The water soluble SO_4 contents in 17 of the surface soil materials were greater than the trigger value of 100 mg kg^{-1} indicating that the formation of monosulfidic materials may be a potential problem upon rewetting. Only 2 of the 21 sites examined (Sites RSKOON 3 and 5) had all soil layers with a water soluble SO_4 content less than the trigger value of > 100 mg kg^{-1}. Site RSMIL 1 had water soluble SO_4 contents exceeding the trigger value in all soil layers. A decrease in water soluble SO_4 content with depth was often observed (Figure 3-2).

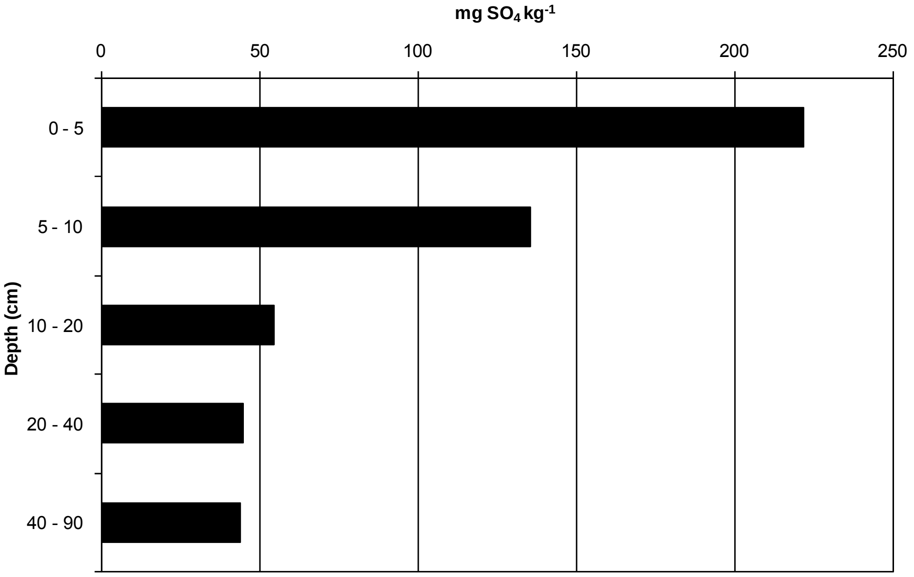

Figure 3-2 Variation in water soluble SO_4 (mg SO_4 kg^{-1}) with depth in the Koondrook State Forest (Site RSKOON 2).

3.1.4. Titratable actual acidity (TAA)

The TAA data for the NSW Central Murray State Forests wetland sites examined is presented in Table 7-2, 7-3 and 7-4 (Appendix 2) and summarised above in Table 3-1. The TAA ranged between 0 and 111 mole H^+/tonne, with the majority of soil layers having a TAA > 20 mole H^+/tonne. All except 2 soil layers collected from NSW Central Murray State Forests had a TAA > 0 mole H^+/tonne, as indicated by a pH_{KCl} < 6.5.

3.2. Hydrochemistry

Surface water quality data was collected from a site within the Werai State Forest (Site RSWSF 3). No groundwater data was collected from the sites sampled within the Central Murray State Forests as groundwater was not observed during soil pit excavation.

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

The field pH of the surface water collected at Site RSWSF 3 was 9.1 (Table 3-2), and exceeded the most relevant ANZECC/ARMCANZ (2000) trigger value for aquatic ecosystems of 8.0. The water data indicates that the surface water at this site has not been affected by acidification. The surface water had a sulfate concentration of 21.2 mg L^{-1}.

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

	pH	**SEC**	**DO**	**Eh**	**Turbidity**	**Alkalinity**	**n**[1]
		µS cm^{-1}	mg L^{-1}	mV	NTU	(mg L^{-1} as HCO_3)	
Surface	9.14	464	2.1	-10	158.6	72.4	1
Groundwater	n.a.[2]	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

[1] n: number of samples. [2] n.a.: not applicable

4. HAZARD ASSESSMENT

4.1. Interpretation of soil and water data

One sulfuric soil material was encountered in the NSW Central Murray State Forests (Table 4-1).

Hypersulfidic soil materials were encountered in only 1 of the 21 sampling sites and this soil material contained only the minimum reduced inorganic sulfur content of 0.01% required to classify this material as sulfidic (Table 4-1).

The acidification hazard from acid sulfate soil disturbance posed by the hypersulfidic sample is low even though it had a moderate net acidity of 45.9 mole H^+/tonne as it was the only sulfidic soil material sampled and was located at depth.

The water soluble sulfate contents of 81% of the surficial soil materials sampled greatly exceeded the trigger value of 100 mg kg^{-1} indicating that the formation of monosulfidic materials may occur upon rewetting (Table 4-1).

The water data indicates that the surface water sample analysed has not been affected by acidification and was in an anoxic and reducing condition.

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 = 21)	Proportion of total sampling sites (%)
Sulfuric	1	5
Hypersulfidic	1	5
Hyposulfidic ($S_{CR} \geq 0.10\%$)	0	0
Monosulfidic (observed)	0	0
Monosulfidic (potential)	17	81
Hyposulfidic ($S_{CR} < 0.10\%$)	0	0
Other acidic (pH_w &/or pH_{age}) 4 – 5.5	17	81
Other soil materials	1	5

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 NSW Central Murray State Forests Ramsar wetlands. This Phase 1 report is aimed solely at determining whether or not acid sulfate soil materials are present in the NSW Central Murray State Forests wetlands.

Only one sulfuric soil material was observed in these wetlands and, although one (5%) sampling site contained sulfidic materials, the reduced inorganic sulfur content of this sample was very low (i.e. only 0.01%). 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, seventeen surficial soil materials 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 high priority site based on the presence of a sulfuric material. In addition seventeen sampling sites had a high priority ranking for Phase 2 detailed assessment of MBO formation hazard.

The potential hazards posed by acid sulfate soil materials at the NSW Central Murray State Forests Ramsar wetlands are as below:

- Acidification: The pH data indicate, along with only one sulfidic material (where the highest S_{CR} was only 0.01 %S), that the degree of acidification hazard is low.

- Deoxgenation: The water soluble sulfate contents of the majority of 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 NSW Central Murray State Forests Ramsar 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 NSW Central Murray State Forests Ramsar wetlands.

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7. APPENDICES

APPENDIX 1. Site and sample descriptions

Table 7-1 NSW Central Murray State Forests site and sample descriptions.

Profile	Date	Location	GPS Co-ords *Zone*	 *East.*	 *North.*	Location Remarks	Profile remarks
RSMIL1	21/7/08	Millewa S.F.	55	331758	6033844	This is the most eastern transect in old ox bow billabong. No water present. MIL1 in base of billabong. No surface vegetation, algae covering sediments.	Deep cracking clays with cracks ~10cm wide and 60cm deep. Heavy iron coatings of voids in soil higher in profile (<40cm) Very soft grey clays at depth.
RSMIL2	21/7/08	Millewa S.F.	55	331698	6033790	South of MIL1 on edge of billabong just outside line of spike rushes (2m tall)	Sandy to 10cm then very hard yellow clays with iron coating voids. >40cm softer yellow brown soils. Salt lining cracks in 2.5.
RSMIL3	21/7/08	Millewa S.F.	55	331593	6033696	Up onto red gum floodplain in between billabong and river channel. Ground cover of short pasture grasses and sporadic tussocks.	Brown mulchy soils grading to yellow brown clays then to yellow fine sands at depth (<70cm).
RSMIL4	21/7/08	Millewa S.F.	55	320243	6031495	Middle of dry swamp to SW of forest. Bare ground in middle with fringing spike rush.	Surface cracked yellowish brown clay. Iron (?) coating cracks in soil starting at 20cm and increasing with depth. Dug to 90cm.
RSMIL5	21/7/08	Millewa S.F.	55	320353	6031548	NW of MIL4 in perimeter of spike rush (spike rush bordering swamp is 50m thick). Groundcover of dead spike rush.	Iron coatings of root holes throughout profile.
RSMIL6	21/7/08	Millewa S.F.	55	320522	6031590	Out in red gum floodplain from MIL5. Profile dug in small clearing with groundcover of pasture grasses and Patterson's curse.	Brown loamy topsoil (6.3) then extremely hard yellowish brown soil. Dug to 55cm.
RSMIL7	21/7/08	Millewa S.F.	55	316114	6040171	Up northern section of forest along the Edwards River. On dry swamp to the east of the river. Typical swamp – short grasses and herbs surrounded by spike rush.	Rich brown topsoil (7.3) abrupt boundary into yellowish brown harder clays with Iron coating root holes. 7.7 very dry and softer. Charcoal fragments from 5-80cm. Dug to 90cm.

Table 7-1 (continued) NSW Central Murray State Forests site and sample descriptions.

Profile	Date	Location	GPS Co-ords			Location Remarks	Profile remarks
			Zone	*East.*	*North.*		
RSMIL8	21/7/08	Millewa S.F.	55	316241	6040068	Up end of 'swamp' in drainage depression to the SW. groundcover of red gum leaf litter and sporadic clumps of dead spike rush. Some algae growing on exposed sediment.	Prominent Iron coatings in 8.4-8.5. 8.7 very hard and compact yellow clay. Dug to 65cm.
RSWSF1	22/7/08	Werai S.F.	55	267619	6095060	In depression between Yadabal lagoon and River in the western end of the forest. Red gum forest with 30-50cm high tussock grasses and leaf litter as ground cover.	Reasonably uniform profile – Dark brown organic rich surface soil grading to grey clays with Iron mottling.
RSWSF2	22/7/08	Werai S.F.	55	267522	6095083	On edge of lagoon approx 40m from waterline. Profile dug in red gum seedlings.	Very prominent Iron coatings of voids from 10-40cm. Dug to 90cm.
RSWSF3	22/7/08	Werai S.F.	55	267346	6095124	In water 180 m from WSF2. Surface water sample taken.	Dug with gouge auger to approx. 55cm.
RSWSF4	22/7/08	Werai S.F.	55	275292	6089733	Further east of forest in dry red gum swamp depression behind river channel. Groundcover of herbs and red gum saplings. Soft soils, extensive Iron mottling throughout core.	Dug to 90cm.
RSWSF5	22/7/08	Werai S.F.	55	275231	6089672	Just out of swamp up on floodplain to the south. Groundcover of short herbs and some native grasses.	Iron coating of voids 5-40cm. Much darker brown colour at depth than WSF4. Dug to 90cm.
RSWSF6	22/7/08	Werai S.F.	55	269691	6093066	In dry billabong between the two other transects. Bare ground with dead red gums surrounding.	Dry and crumbly to 10cm. Iron mottling increasing with depth 10-90cm. Charcoal fragments from 50-90cm.
RSWSF7	22/7/08	Werai S.F.	55	269842	6093263	In between WSF6 and river channel. Approx 50m from river channel. Pasture grasses and tussock ground cover.	

Table 7-1 (continued) NSW Central Murray State Forests site and sample descriptions.

Profile	Date	Location	GPS Co-ords *Zone*	 *East.*	 *North.*	Location Remarks	Profile remarks
RSKOON1	23/7/08	Koondrook S.F.	55	251439	6045628	In bottom of defined dry lagoon. Vegetation of short grasses and herbs.	Loamy topsoil (3cm deep) into yellow brown cracking clays. Prominent Iron mottling >40cm.
RSKOON2	23/7/08	Koondrook S.F.	55	251287	6046032	Up NW end of lagoon out into red gum floodplain. Groundcover of scattered herbs.	Dry cracking yellow brown clays. Very hard from >30cm. Dug to 65cm.
RSKOON3	23/7/08	Koondrook S.F.	55	248763	6050568	In depression out in red gum floodplain. Sparse vegetation of weeds.	Browner soils here at depth. Dug to 90cm.
RSKOON4	23/7/08	Koondrook S.F.	55	248696	6050265	On slight rise 300m SE of BOON3. Still within red gum floodplain forest. Sparse groundcover of herbs.	Very hard from 10-40cm. Softer >40cm.
RSKOON5	23/7/08	Koondrook S.F.	55	245428	6057926	In channel of cow creek. Some rain puddles present but no water samples taken. Groundcover of red gum leaf litter and sparse grasses.	Brown loamy soils grading sharply to grey clay with Iron mottling at 20cm. Grey clay extremely hard. Dug to 50cm.
RSKOON6	23/7/08	Koondrook S.F.	55	245425	6057948	Up on floodplain surface out of Cow Creek. Sparse groundcover of grasses and leaf litter.	

APPENDIX 2. Field and laboratory analytical soil data

Table 7-2 Millewa State Forest 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)
RSMIL / 1.3	0 - 5	FSCL	10YR 5/2	25% 5YR 5/8	5.05	2.82	XX	4.00	58.69	< 0.01	58.69	164.08
1.4	5 - 10	FSCL	10YR 5/2	25% 5YR 5/8	4.72	2.54	XX	4.02	58.39	< 0.01	58.39	161.37
1.5	10 - 20	FCLS	10YR 5/2	25% 5YR 4/6	4.91	2.53	XX	4.01	54.04	< 0.01	54.04	136.78
1.6	20 - 40	FSLMC	10YR 5/1	25% 5YR 4/4	5.56	2.88	XX	4.16	62.75	< 0.01	62.75	146.34
1.7	40 - 90		10YR 4/1		5.37	2.88	XX	4.12	66.59	< 0.01	66.59	164.28
RSMIL / 2.3	0 - 5	SCL	7.5YR 3/1		5.33	2.77	XX	4.37	30.71	< 0.01	30.71	136.23
2.4	5 - 10	CS	7.5YR 4/3		5.01	1.63	XX	4.39	21.10	< 0.01	21.10	97.92
2.5	10 - 20	CL	10YR 6/1	10% 5YR 5/8	5.36	2.68	XX	4.01	56.84	< 0.01	56.84	88.02
2.6	20 - 40	CL	10YR 6/1	5% 7.5YR 5/8	4.95	3.20	XX	4.18	43.21	< 0.01	43.21	51.92
2.7	40 - 90	CL	10YR 5/1	5% 5YR 5/8	5.30	3.04	XX	4.03	46.63	< 0.01	46.63	46.52
RSMIL / 3.3	0 - 5	FCLS	7.5YR 3/2		5.69	2.52	XX	5.08	24.87	< 0.01	24.87	107.25
3.4	5 - 10	FCLS	7.5YR 3/2	3% 10YR 8/6	6.86	3.53	XXXX	5.54	10.85	< 0.01	10.85	57.12
3.5	10 - 20	FCLS	10YR 4/1	15% 10YR 8/8	7.27	3.88	XX	6.13	3.07	< 0.01	3.07	37.51
3.6	20 - 40	FCLS	10YR 4/1		7.45	5.68	X	6.08	2.59	< 0.01	2.59	29.78
3.7	40 - 90	FSCL	10YR 7/4		7.49	6.04	X	5.91	2.35	< 0.01	2.35	16.97
RSMIL / 4.3	0 - 5	CL	10YR 6/2	25% 7.5YR 6/8	5.35	3.17	XX	4.45	32.64	< 0.01	32.64	133.53
4.4	5 - 10	CL	10YR 5/2	20% 7.5YR 6/8	4.87	3.13	XX	4.10	51.65	< 0.01	51.65	96.82
4.5	10 - 20	MC	10YR 5/2	20% 7.5YR 6/8	5.01	3.58	X	4.01	56.20	< 0.01	56.20	70.59
4.6	20 - 40	MC	10YR 5/2	10% 7.5YR 6/8	5.11	3.94	X	4.06	48.29	< 0.01	48.29	40.48
4.7	40 - 90	LMC	10YR 5/1	30% 7.5YR 5/8	5.44	4.06	X	4.15	41.79	< 0.01	41.79	43.46
RSMIL / 5.3	0 - 5	FSCL	7.5YR 4/2	5% 5YR 5/8	4.63	2.59	X	3.97	79.36	< 0.01	79.36	202.35
5.4	5 - 10	FSCL	10YR 4/2	3% 7.5YR 7/8	4.70	2.49	XX	4.00	70.98	< 0.01	70.98	140.51
5.5	10 - 20	FSCL	10YR 5/2	15% 5YR 5/8	5.07	2.61	XX	4.13	48.77	< 0.01	48.77	76.73
5.6	20 - 40	LMC	10YR 4/2	15% 5YR 5/8	5.35	3.04	XX	4.13	39.60	< 0.01	39.60	49.79
5.7	40 - 90	MC	10YR 4/2	10% 5YR 5/8	5.91	3.37	XX	4.43	23.47	< 0.01	23.47	67.68
RSMIL / 6.3	0 - 5	FSL	7.5YR 3/2		6.60	3.62	XXXX	5.98	4.04	< 0.01	4.04	61.96
6.4	5 - 10	FSL	10YR 5/2		6.31	3.22	XX	5.13	6.84	< 0.01	6.84	48.95
6.5	10 - 20	FSL	10YR 4/2		6.31	4.17	XX	6.02	3.05	< 0.01	3.05	67.48
6.6	20 - 40	FSCL	10YR 4/2		7.56	5.61	X	6.57	-	< 0.01	-	235.64
6.7	40 - 55	FCLS	10YR 6/4		7.89	5.80	X	6.99	-	< 0.01	-	397.38
RSMIL / 7.3	0 - 5	FSLC	7.5YR 4/2		4.84	3.48	XXXX	4.25	33.63	< 0.01	33.63	113.71
7.4	5 - 10	FSLMC	10YR 6/1	25% 7.5YR 5/8	4.93	3.71	XXXX	4.19	35.73	< 0.01	35.73	61.37
7.5	10 - 20	LMC	10YR 5/2	15% 7.5YR 5/8	5.27	4.51	XX	4.20	29.79	< 0.01	29.79	32.58
7.6	20 - 40	LMC	10YR 6/2	10% 7.5YR 5/8	5.53	4.62	X	4.27	25.85	< 0.01	25.85	30.16
7.7	40 - 90	LC	10YR 7/2	7% 7.5YR 5/8	5.95	5.58	X	4.38	21.56	< 0.01	21.56	19.30
RSMIL / 8.3	0 - 5	FCLS	10YR 5/3	15% 5YR 5/8	4.93	3.42	XXXX	4.13	39.35	< 0.01	39.35	149.56
8.4	5 - 10	FSLC	10YR 5/3	15% 5YR 5/8	5.47	4.69	X	4.17	32.54	< 0.01	32.54	35.63
8.5	10 - 20	FSLC	10YR 5/2	20% 5YR 5/8	5.84	5.39	X	4.18	29.16	< 0.01	29.16	25.09
8.6	20 - 40	FSLC	10YR 5/3	15% 7.5YR 6/8	5.86	4.21	X	4.17	23.23	< 0.01	23.23	23.20
8.7	40 - 65	LMC	10YR 6/2	10% 7.5YR 4/6	6.13	5.65	X	4.47	16.82	< 0.01	16.82	47.85

[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 Werai State Forest 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	Net Acidity mole H^+/tonne	Sulfate (mg SO_4 /kg)
RSWSF / 1.3	0 - 5	FCLS	7.5YR 4/2		6.34	3.41	XXX	5.20		21.55	< 0.01	21.55	105.07
1.4	5 - 10	LC	7.5YR 4/2	10% 2.5YR 4/4	6.51	3.44	XXXX	5.11		14.33	< 0.01	14.33	51.44
1.5	10 - 20	LMC	7.5YR 4/2	10% 2.5YR 4/3	6.93	6.52	XXXX	5.11		12.44	< 0.01	12.44	39.91
1.6	20 - 40	LMC	10YR 5/2	25% 5YR 5/8	6.60	3.44	XX	4.53		18.94	< 0.01	18.94	37.66
1.7	40 - 90	MC	10YR 6/2		5.89	3.33	XX	4.03	4.5	37.72	0.013	45.90	45.09
RSWSF / 2.3	0 - 5	SCL	10YR 4/2	5% 7.5YR 6/8	5.99	3.06	XX	5.06		24.48	< 0.01	24.48	374.90
2.4	5 - 10	LMC	10YR 5/2	30% 7.5YR 5/8	6.00	2.72	XX	4.78		22.90	< 0.01	22.90	127.90
2.5	10 - 20	MC	10YR 4/2	15% 10YR 7/8	6.07	3.00	XX	4.37		22.23	< 0.01	22.23	51.88
2.6	20 - 40	MC	10YR 4/1	30% 5YR 5/8	6.03	2.85	X	4.20		30.79	< 0.01	30.79	44.81
2.7	40 - 90	MC	10YR 5/1	10% 5YR 5/8	6.25	3.11	X	4.48		19.72	< 0.01	19.72	28.73
RSWSF / 3.3	0 - 5	ZCL	10YR 3/2		6.23	2.67	XXXX	5.59		6.93	< 0.01	6.93	178.26
3.4	5 - 10	ZCL	10YR 3/2		5.83	2.31	XXXX	5.14		15.54	< 0.01	15.54	145.73
3.5	10 - 20	ZCL	10YR 3/2		5.47	2.24	XX	4.92		18.41	< 0.01	18.41	127.38
3.6	20 - 40	MC	10YR 4/2		5.40	2.36	XX	4.42		28.85	< 0.01	28.85	84.54
3.7	40 - 55	MC	10YR 5/2	10% 10YR 7/8	4.96	2.91	X	4.04		48.74	< 0.01	48.74	43.43
RSWSF / 4.3	0 - 5	ZCL	10YR 5/2	10% 7.5YR 6/8	5.00	2.22	XX	3.85		69.97	< 0.01	69.97	209.45
4.4	5 - 10	CL	10YR 5/2	15% 7.5YR 6/8	4.73	1.92	XX	3.61		106.93	< 0.01	106.93	181.92
4.5	10 - 20	LC	10YR 6/2	15% 7.5YR 7/8	4.70	2.27	XX	3.66		110.58	< 0.01	110.58	117.89
4.6	20 - 40	MC	10YR 5/2	20% 7.5YR 6/8	4.46	2.59	XX	3.70		100.06	< 0.01	100.06	75.07
4.7	40 - 90	MHC	10YR 5/2	25% 5YR 5/8	4.59	3.14	X	3.86		75.30	< 0.01	75.30	47.53
RSWSF / 5.3	0 - 5	CLS	10YR 5/3	7% 5YR 5/8	5.11	2.46	XX	4.48		34.61	< 0.01	34.61	147.26
5.4	5 - 10	LC	10YR 5/3	7% 5YR 5/8	5.38	2.49	XX	4.46		38.90	< 0.01	38.90	92.00
5.5	10 - 20	LC	10YR 4/3	7% 5YR 3/3	5.60	2.81	XX	4.10		42.22	< 0.01	42.22	44.33
5.6	20 - 40	LMC	7.5YR 4/2		5.74	2.97	XX	4.03		41.78	< 0.01	41.78	54.23
5.7	40 - 90	LMC	7.5YR 4/2		5.39	3.57	X	4.16		29.26	< 0.01	29.26	364.92
RSWSF / 6.3	0 - 5	CL	10YR 4/2	15% 7.5YR 4/6	4.81	2.57	XX	4.27		35.88	< 0.01	35.88	208.91
6.4	5 - 10	CL	10YR 5/2	15% 7.5YR 7/8	4.46	2.37	XX	4.15		42.24	< 0.01	42.24	190.26
6.5	10 - 20	LC	10YR 4/2	10% 7.5YR 6/8	3.96	2.18	XX	3.93		58.98	< 0.01	58.98	154.99
6.6	20 - 40	LC	10YR 4/2	25% 7.5YR 5/8	4.05	2.10	XX	3.91		67.42	< 0.01	67.42	98.15
6.7	40 - 90	LMC	10YR 6/2	35% 5YR 5/8	4.34	2.58	X	3.98		56.34	< 0.01	56.34	46.17
RSWSF / 7.3	0 - 5	LC	10YR 4/2		5.67	2.46	XXX	4.70		30.22	< 0.01	30.22	131.88
7.4	5 - 10	LC	10YR 4/2	3% 7.5YR 5/8	6.09	2.66	XXX	4.48		25.26	< 0.01	25.26	69.31
7.5	10 - 20	LC	10YR 4/2		6.02	3.23	XX	4.45		22.16	< 0.01	22.16	45.07
7.6	20 - 40	LMC	10YR 4/2	3% 7.5YR 5/8	5.24	3.30	XX	4.18		31.48	< 0.01	31.48	59.35
7.7	40 - 90	LMC	10YR 5/3	3% 7.5YR 5/8	4.99	3.49	XX	4.21		24.68	< 0.01	24.68	79.40

[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 7-4 Koondrook State Forest 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)
RSKOON / 1.3	0 - 5	FSLMC	10YR 5/3	2% 7.5YR 7/8	5.03	2.38	XX	4.29	41.98	< 0.01	41.98	192.68
1.4	5 - 10	FSMC	10YR 5/3	7% 7.5YR 6/8	5.08	2.80	XX	4.12	57.58	<0.01	57.58	86.67
1.5	10 - 20	FSMC	10YR 5/2	10% 5YR 4/6	5.16	3.60	XX	4.08	52.56	< 0.01	52.56	57.09
1.6	20 - 40	FSMC	10YR 5/2	5% 5YR 5/8	5.32	3.89	XX	4.14	40.96	< 0.01	40.96	49.07
1.7	40 - 90	FSLC	10YR 5/3	15% 5YR 5/8	5.42	3.95	XX	4.18	47.92	< 0.01	47.92	45.72
RSKOON / 2.3	0 - 5	FSCL	10YR 4/3		5.35	2.17	XXX	4.59	42.80	< 0.01	42.80	221.57
2.4	5 - 10	LC	10YR 5/3	5% 5YR 5/8	5.15	2.89	XX	4.39	32.39	< 0.01	32.39	135.54
2.5	10 - 20	LMC	10YR 5/3	15% 7.5YR 6/8	5.32	3.41	XX	4.19	38.79	< 0.01	38.79	54.55
2.6	20 - 40	LMC	10YR 5/3	15% 5YR 5/8	5.35	2.94	X	3.94	50.72	< 0.01	50.72	44.89
2.7	40 - 65	LMC	10YR 5/3	15% 7.5YR 6/8	5.41	3.61	X	3.92	56.53	<0.01	56.53	44.01
RSKOON / 3.3	0 - 5	LC	10YR 4/3		5.16	3.27	XXX	4.55	28.40	< 0.01	28.40	94.51
3.4	5 - 10	MC	10YR 4/3		5.23	3.36	XX	4.35	33.83	< 0.01	33.83	42.86
3.5	10 - 20	MC	10YR 4/3	15% 5YR 5/6	5.59	3.37	XX	4.39	32.23	< 0.01	32.23	36.52
3.6	20 - 40	MC	10YR 3/2		5.89	3.61	X	4.37	28.37	< 0.01	28.37	37.44
3.7	40 - 90	MC	10YR 4/2	7% 7.5YR 5/8	5.79	3.99	X	4.31	30.04	< 0.01	30.04	50.93
RSKOON / 4.3	0 - 5	CL	10YR 4/2		5.60	3.03	XXX	4.81	45.41	< 0.01	45.41	188.46
4.4	5 - 10	LMC	10YR 3/1		6.00	4.02	XXXX	5.32	16.33	< 0.01	16.33	52.16
4.5	10 - 20	LMC	10YR 3/1	15% 7.5YR 6/8	6.56	4.16	XXXX	5.54	11.65	< 0.01	11.65	37.52
4.6	20 - 40	MHC	10YR 4/2	25% 7.5YR 6/8	5.86	3.73	XX	4.52	27.73	< 0.01	27.73	88.38
4.7	40 - 90	MHC	10YR 4/2	20% 7.5YR 6/8	5.21	3.44	X	3.93	79.21	< 0.01	79.21	190.44
RSKOON / 5.3	0 - 5	FCLS	10YR 4/3		5.09	2.62	XX	4.67	21.04	< 0.01	21.04	46.44
5.4	5 - 10	FSLMC	10YR 5/3	7% 5YR 5/8	5.29	2.98	XX	4.07	72.67	< 0.01	72.67	53.80
5.5	10 - 20	SLMC	7.5YR 5/8	15% 10YR 6/2	5.43	3.76	XX	4.23	44.11	< 0.01	44.11	54.94
5.6	20 - 40	FSLMC	10YR 7/2	7% 7.5YR 6/8	6.23	5.24	X	5.47	4.26	<0.01	4.26	69.18
5.7	40 - 50	FSLMC	10YR 8/1	10% 10YR 7/6	6.50	6.17	X	5.66	4.16	< 0.01	4.16	68.57
RSKOON / 6.3	0 - 5	LMC	7.5YR 3/3		5.91	3.58	XXXX	4.70	21.04	< 0.01	21.04	59.03
6.4	5 - 10	LMC	10YR 3/2		5.34	4.58	XXX	4.65	22.67	< 0.01	22.67	65.81
6.5	10 - 20	MC	10YR 4/3	15% 10YR 5/8	5.17	3.46	X	4.22	41.61	<0.01	41.61	69.55
6.6	20 - 40	MHC	10YR 5/4	25% 10YR 5/8	4.94	3.09	X	4.02	67.46	<0.01	67.46	105.52
6.7	40 - 90	MHC	10YR 5/3	15% 10R 5/8	4.61	3.12	X	3.99	59.61	< 0.01	59.61	451.13

[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 7-5 NSW Central Murray State Forests field hydrochemistry data.

Site	Units	Site RSWSF 3	n
Water type		surface	
pH		9.14	1
SEC	µS cm^{-1}	464	1
DO	% sat	17.8	1
Eh	mV	-10	1
Turbidity	NTU	158.6	1
Alkalinity	(mg L^{-1} as HCO_3)	72.4	1
Temperature	^{o}C	8.9	1

Table 7-6 NSW Central Murray State Forests laboratory analytical hydrochemistry data.

Parameter	Units	Site RSWSF 3	n
pH		7.30	1
E.C.	µS cm^{-1}	457	1
Alkalinity	meq/L	0.83	1
Ammonium (NH_4-N)	mg/L	0.032	1
Oxides of Nitrogen (NO_x-N)	mg/L	0.196	1
Nitrate (NO_3-N)	mg/L	0.19	1
Nitrite (NO_2-N)	mg/L	< 0.005	1
Phosphate (PO_4-P)	mg/L	0.003	1
Floride (F^-)	mg/L	0.15	1
Chloride (Cl^-)	mg/L	86.35	1
Bromide (Br^-)	mg/L	0.26	1
Sulfate (SO_4^{2-})	mg/L	21.17	1
Calcium (Ca)	mg/L	15.04	1
Potassium (K)	mg/L	8.47	1
Magnesium (Mg)	mg/L	8.57	1
Sodium (Na)	mg/L	62.27	1
Sulfur (S)	mg/L	8.56	1
Total Organic Carbon (NPOC)	mg/L	53.70	1
Total Nitrogen (TN)	mg/L	4.02	1
Aluminium (Al)	mg/L	0.200	1
Boron (B)	mg/L	0.029	1
Copper (Cu)	mg/L	< 0.005	1
Iron (Fe)	mg/L	0.126	1
Manganese (Mn)	mg/L	0.014	1
Phosphorus (P)	mg/L	0.074	1
Zinc (Zn)	mg/L	0.234	1
Molybdenum (Mo)	mg/L	< 0.01	1
Cobalt (Co)	mg/L	< 0.01	1
Nickel (Ni)	mg/L	< 0.01	1
Chromium (Cr)	mg/L	< 0.008	1
Cadmium (Cd)	mg/L	< 0.003	1
Lead (Pb)	mg/L	< 0.03	1
Selenium (Se)	mg/L	< 0.1	1

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