Assessment of Acid Sulfate Soil Materials in Ramsar Wetlands of the Murray-Darling Basin: Macquarie Marshes

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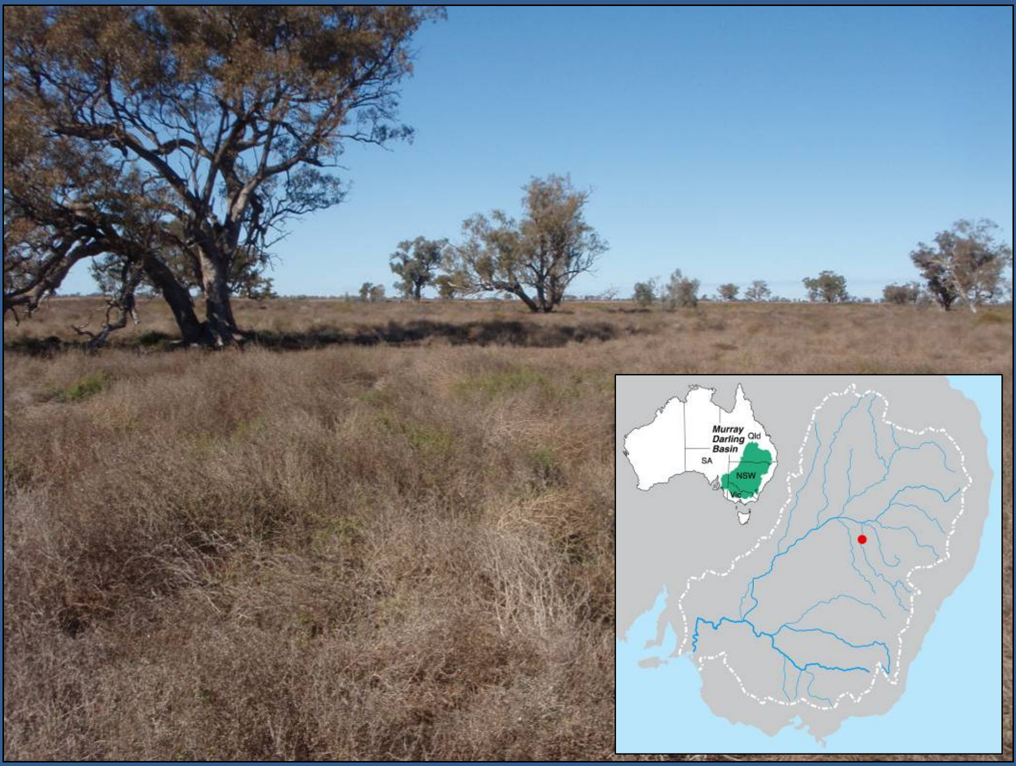
FINAL REPORT



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Cover Photographs:

Typical landscape in the Macquarie Marshes Ramsar wetlands. Photograph taken at Site RSMM 9 in the North Macquarie Marshes Nature Reserve.

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EXECUTIVE SUMMARY

The Macquarie Marshes are one of the largest remaining inland, semi-permanent wetlands in south east Australia. The Macquarie Marshes Ramsar wetland site is situated approximately 70 km north of Dubbo in the north west of New South Wales. The Macquarie Marshes Nature Reserve was listed as a Ramsar wetland in 1986. The Wilgara Wetland (583 Ha), which is on private property near the nature reserve, is also part of the 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 Macquarie Marshes Ramsar wetlands. This Phase 1 report is aimed solely at determining whether or not acid sulfate soil materials are present in the Macquarie Marshes Ramsar wetlands.

Sulfuric materials were not observed in these wetlands, and although 15% (i.e. 3) of the sampling sites contained sulfidic materials, the reduced inorganic sulfur concentrations of these samples were very low (i.e. the highest S_{CR} was only 0.01%). Hypersulfidic soil materials were present in two soil profiles (one 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, fifteen 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 were two high priority sites based on the presence of hypersulfidic material, and one moderate priority site based on the presence of a hyposulfidic material with S_{CR} < 0.10%. In addition, 15 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 Macquarie Marshes Ramsar wetland sites are as below:

- Acidification: The data indicate that with low titratable actual acidities (TAA) and only a few sulfidic materials (where the highest S_{CR} was only 0.01% S) that the degree of acidification hazard is low.

- Deoxgenation: The water soluble sulfate contents of fifteen 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 Macquarie Marshes 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 Macquarie Marshes.

1. INTRODUCTION

1.1. Wetland overview

The Macquarie Marshes are one of the largest remaining inland, semi-permanent wetlands in south east Australia (Figure 1-1). They are considered an outstanding example of the lower floodplain wetlands characteristic of the Darling Riverine Plains bioregion. They are also geomorphologically and geologically unusual as an active network of inland braided streams. They are unique in terms of both their size (approximately 200,000 hectares) and diversity. Macquarie Marshes Nature Reserve was listed as a Ramsar wetland in 1986. The Wilgara Wetland (583 Ha), which is on private property near the nature reserve, is also part of the Ramsar wetland.

The overview from the Ramsar Site Information Sheet (26th March 1999) is as follows:

> *The marshes have a variety of habitat types, and particularly diverse plants and animals - many at the limit of their range. These wetlands allow ecosystems and populations of wetland-dependent species to live in a semi-arid environment. In a catchment that has been modified by agricultural activities, the marshes have become a regionally important refuge for wildlife. In particular, they are an important drought refuge during periods when many other inland wetlands have dried out. Waterbird populations have declined in recent years. However, the wetlands of the Macquarie Marshes still regularly support more than 20,000 waterbirds - over 500,000 in large floods. When conditions are suitable, a significant proportion of the Australian population of a number of waterbird species breed here.*

The typical landscape observed in the Macquarie Marshes is shown in Figure 1-2, and a typical soil profile is given in Figure 1-3. Further information on characteristics of the Macquarie Marshes from the Ramsar Site Information Sheet can be found at NSW NPWS *et al*. (2000).

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).

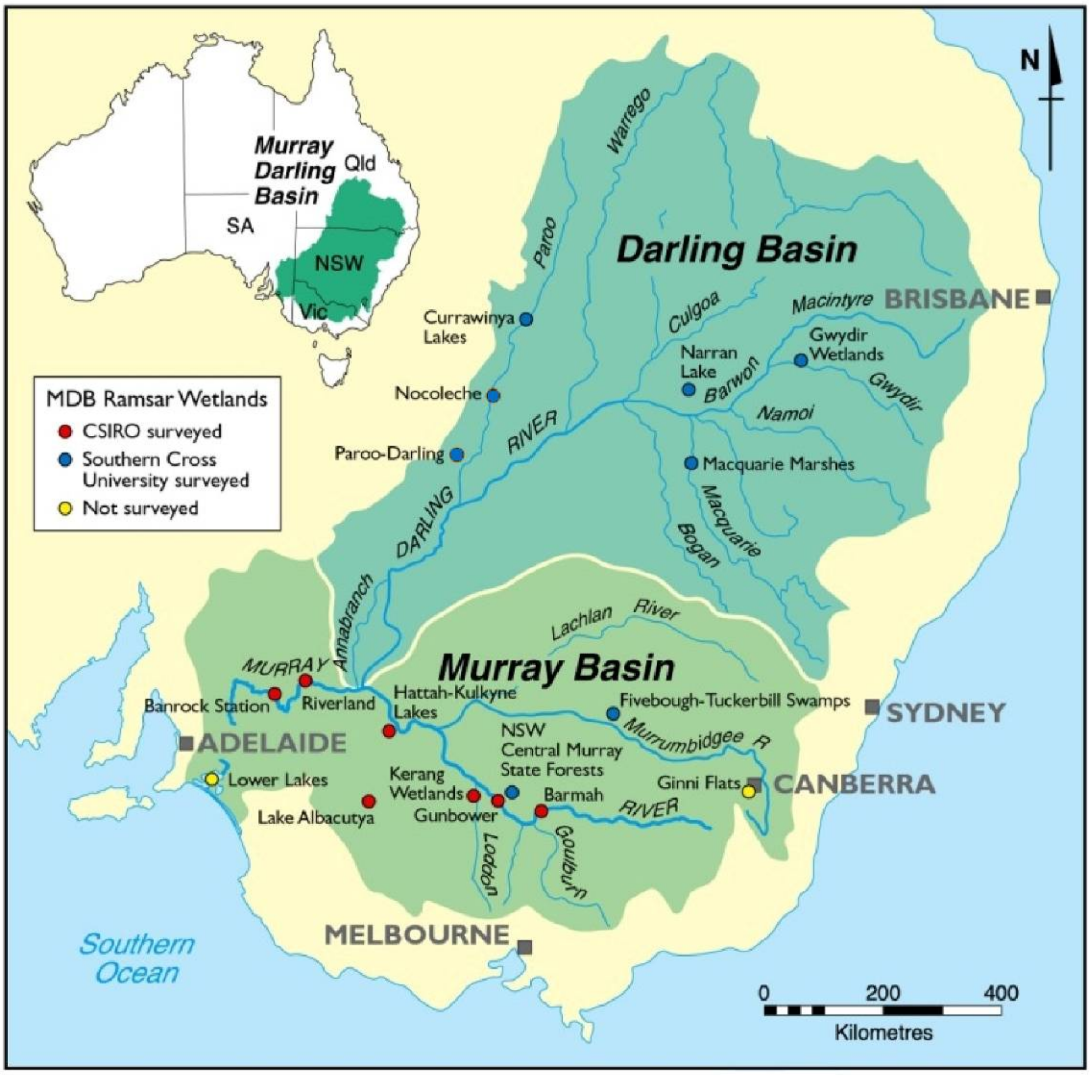

Figure 1-1 Map of Ramsar Wetlands surveyed in the Murray-Darling Basin.

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 20 representative sites within the Macquarie Marshes Ramsar wetlands in June and July 2008 to determine whether acid sulfate soils were present, or if there was a potential for acid sulfate soil to form within these wetlands (Figure 1-4). This assessment included the determination of sulfide content within the soil profile at each site. Water-soluble sulfate was used as an indicator of the potential of monosulfide black ooze (MBO) formation in these wetland sites.

Figure 1-2 Typical landscape in the Macquarie Marshes Ramsar wetlands (Site RSMM 9).

Figure 1-3 Typical grey clay soil profile in the Macquarie Marshes Ramsar wetlands (Site RSMM 6).

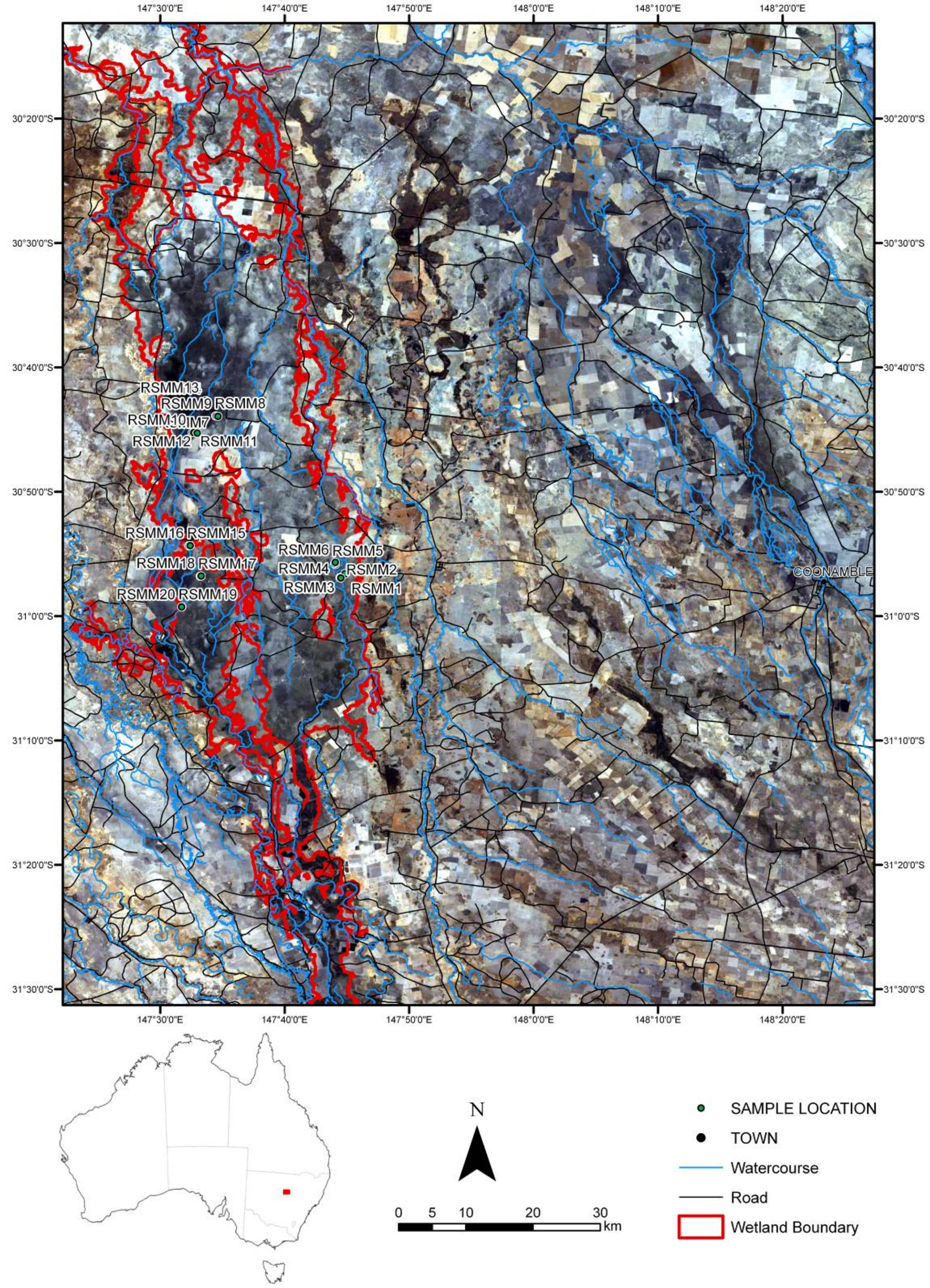

Figure 1-4 Map showing the areas assessed in the Macquarie Marshes Ramsar wetlands.

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 Macquarie Marshes 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. Macquarie Marshes site characteristics

Locations sampled in this study were uniformly flat with either a lack of vegetation cover (e.g. Figure 2-4) or more typically a vegetation cover of sedges and grasses (e.g. Figure 2-6). The soils at each site were grey clays (e.g. Figure 2-2). Accordingly, the textures of the soil materials sampled ranged from light-medium clay to heavy clay (Appendix 2).

The sites were dry when sampled. Surface water was absent from the sampling sites, although standing water was observed near to Site RSMM 7 (Figure 2-4). Groundwater was not intercepted in any of the 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.

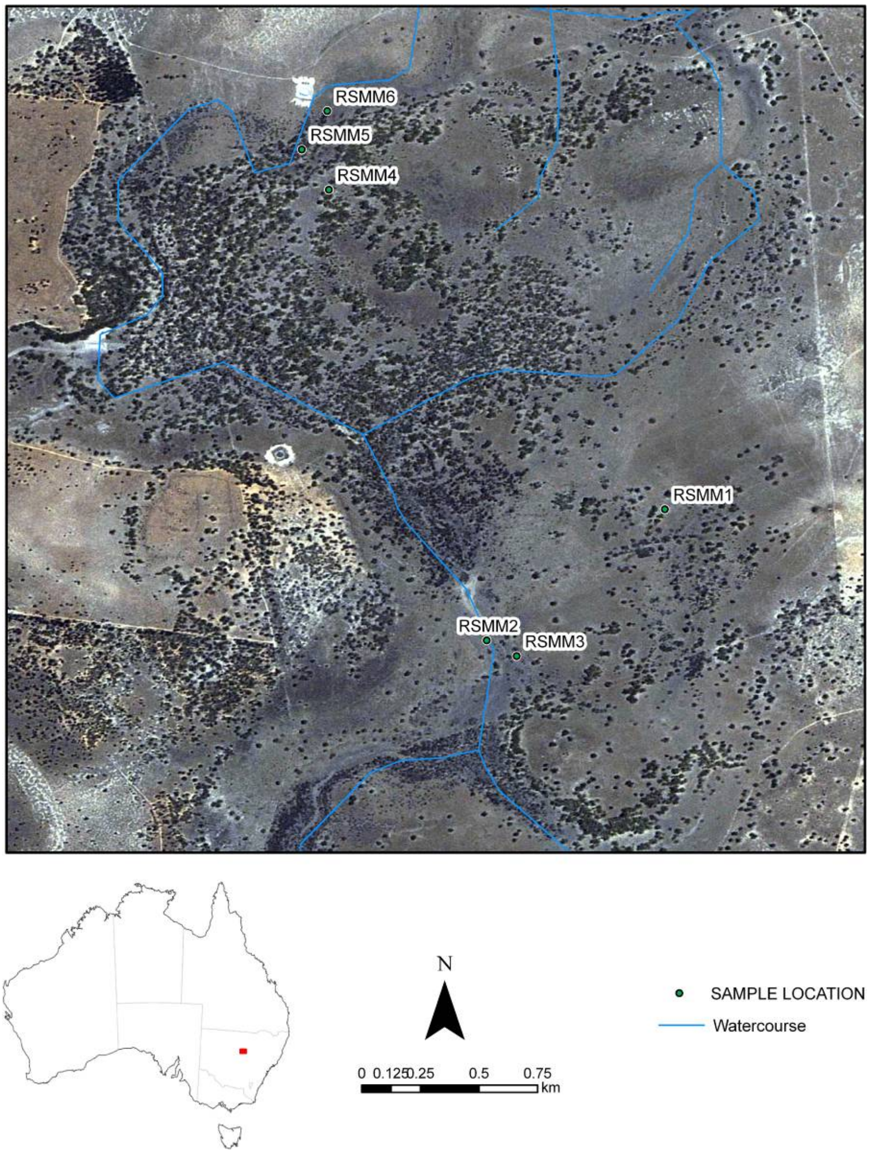

Figure 2-1 Map showing the areas assessed at Wilgara in the Macquarie Marshes Ramsar wetlands (Sites RSMM 1-6).

Figure 2-2 Typical landscape (Site RSMM 5) and grey clay (Site RSMM 6) at Wilgara in the Macquarie Marshes Ramsar wetlands. Site RSMM 6 had a groundcover of water couch and grasses next to stand of native perennial 1 m high. Carbonate nodules observed at > 40 cm in the soil profile.

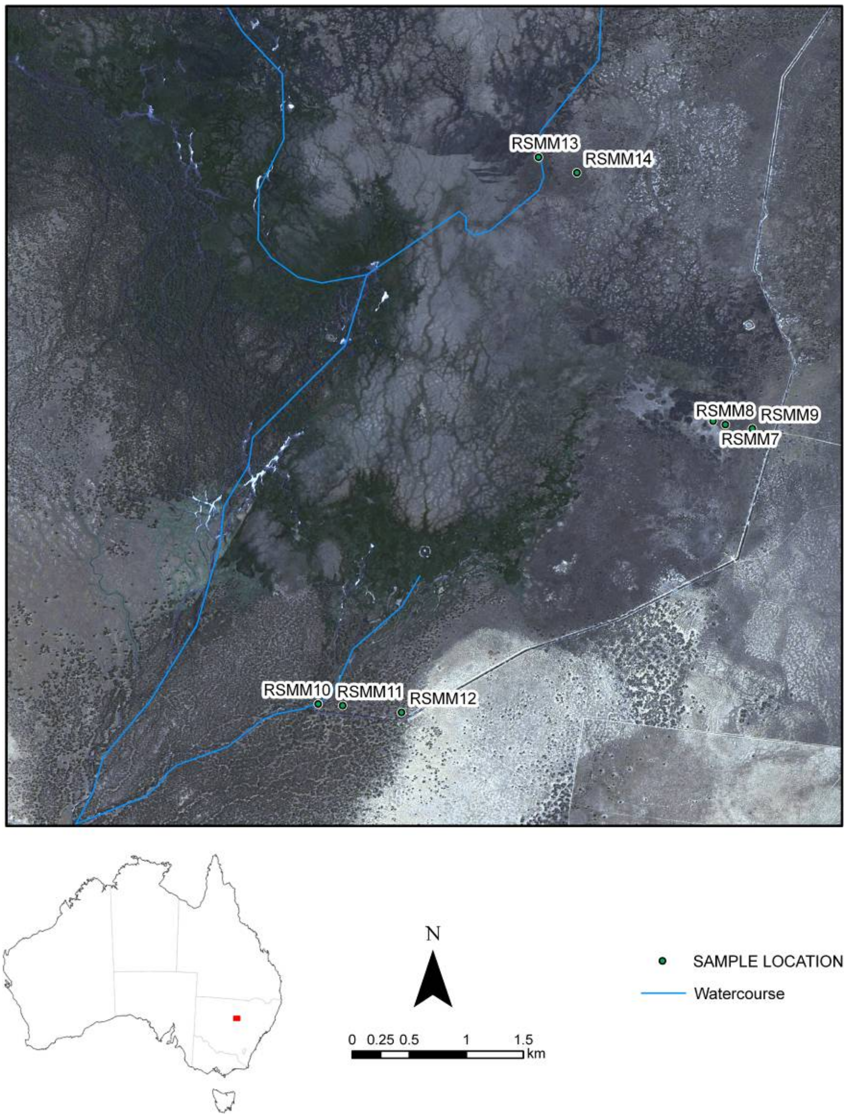

Figure 2-3 Map showing the areas assessed in the North Macquarie Marshes Nature Reserve (Sites RSMM 7-14).

Figure 2-4 Typical landscape (Site RSMM 7) and grey clay (Site RSMM 11) in the North Macquarie Marshes Nature Reserve. Water quality of standing water at Site RSMM 7 analysed. Soil profile showed brown clay grading to grey clay at 40 cm, iron coating root holes at < 40 cm, and carbonate nodules at a depth of > 60 cm.

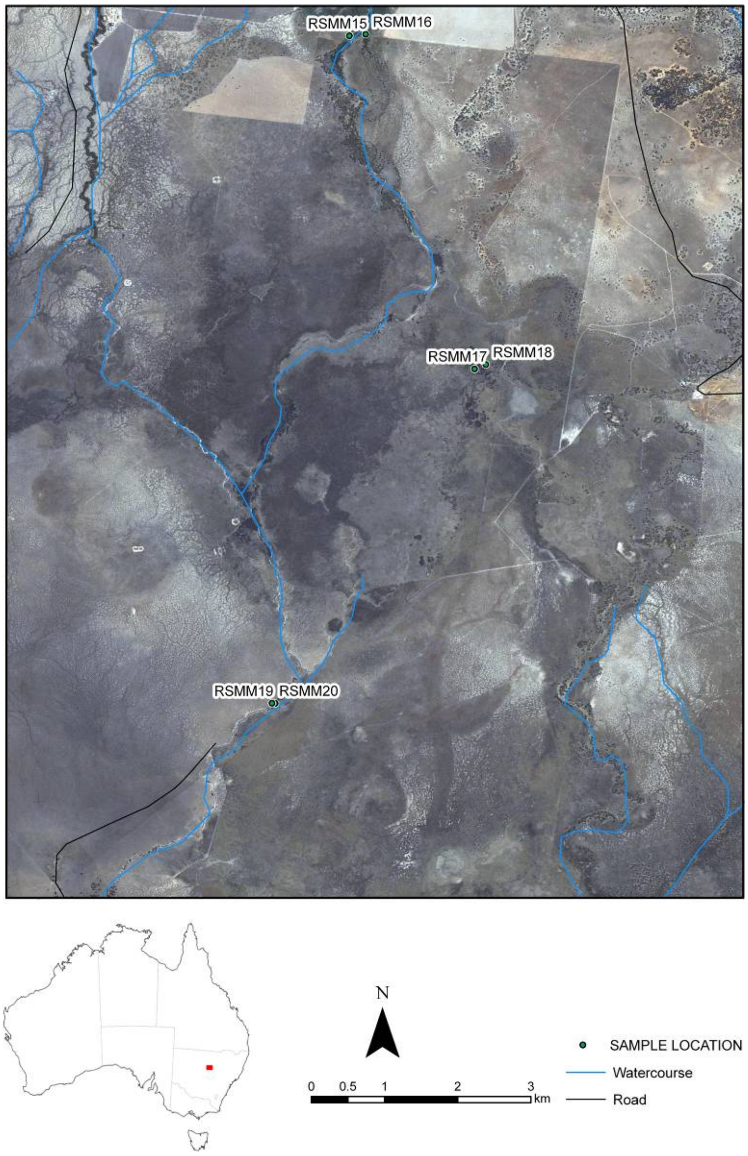

Figure 2-5 Map showing the areas assessed in the South Macquarie Marshes Nature Reserve (Sites RSMM 15-20).

Figure 2-6 Typical landscape (Site RSMM 18) and grey clay (Site RSMM 18) in the South Macquarie Marshes Nature Reserve. Site RSMM 18 located in a slight depression surrounded by dead phragmites. Carbonate nodules observed at > 50 cm in the soil profile.

2.2. Field sampling of soils and waters

Field sampling of the Macquarie Marshes Ramsar wetlands was undertaken on 28th June 2008 at Wilgara, and between 15th – 16th July 2008 at the North and South Macquarie Marshes Nature Reserve sites. A total of 101 soil layers were collected and analysed from 20 representative soil profiles within the Macquarie Marshes Ramsar wetlands to assess the current and potential environmental hazard due to the presence of acid sulfate soils (Figure 1-4).

Representative soil profiles were collected from 3 locations within the Macquarie Marshes including Wilgara (Sites RSMM 1-6), North Macquarie Marshes Nature Reserve (Sites RSMM 7-14), and South Macquarie Marshes Nature Reserve (Sites RSMM 15-20). At each of these locations soil profiles were sampled along a toposequence. Where possible the profiles were chosen to represent: (i) the lowest point in the landscape, (ii) a moderately elevated site just above the observed or interpreted normal flow level, and (iii) an elevated site above the normal flow level.

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 ≤ 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.

Surface water quality data was collected from 3 locations in the Macquarie Marshes including standing water near Site RSMM 7 (Figure 2-6), a channel near site RSMM 10, and Monkeygar Creek near Site RSMM 15. 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°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} ≥ 0.01% S) placed in chip trays using pH indicator strips. The duration of the incubation was until a stable pH was reached after at least 8 weeks of incubation.

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

Acid Neutralising Capacity, measured by the ANC_{BT} method (Method Code 19A2) (Ahern *et al.* 2004) was determined for sulfidic samples to enable Net Acidity to be estimated by the Acid Base Account method of Ahern *et al.* 2004.

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

2.4. Laboratory water analysis

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

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

The Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate 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 <u>either</u> 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 Macquarie Marshes 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 Macquarie Marshes Ramsar wetland sites examined is presented in Table 7-2 (Appendix 2) and summarised in Table 3-1. The pH$_{W}$ values ranged between 5.31 and 9.03, with the majority of the samples having a pH$_{W}$ > 6.0. None of the soils in the Macquarie Marshes would be classified as being sulfuric materials as all soils had a pH$_{W}$ > 4.

The pH$_{FOX}$ values ranged between 2.60 and 8.67. The majority of the soils showed a pH drop after treatment with peroxide (e.g. Figures 3-1 – 3-3), with a maximum decrease of 3.8 pH units. The pH$_{FOX}$ results also indicate that some of the surface soils in the Macquarie Marshes may have the potential to acidify to pH < 4 as a result of sulfide oxidation. However, the S$_{CR}$ data shows only 2 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	n[1]
pH$_{W}$[2]		5.31	7.28	9.03	101
pH$_{FOX}$[3]		2.60	5.14	8.67	101
pH$_{KCl}$[4]		3.77	6.59	8.26	101
pH$_{INCUBATION}$[5]		4.5	5.9	7.4	4
TAA[6]	mole H^{+}/tonne	0.00	9.01	79.73	101
Soluble SO$_{4}$[7]	mg SO$_{4}$ kg^{-1}	23	100	402	101
S$_{CR}$[8]	Wt. %S	<0.01	<0.01	0.013	101
ANC* [9]	%CaCO$_{3}$	0	0.28	1.61	4
Net Acidity[10]	mole H^{+}/tonne	-207.1	9.3	79.7	51

[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.

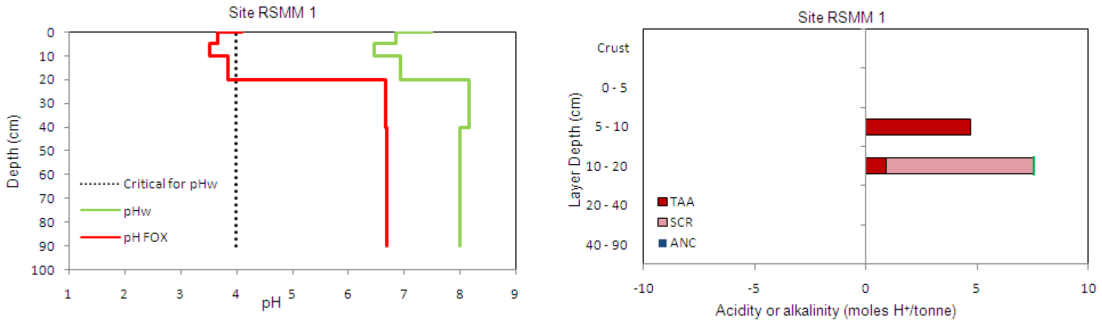

Figure 3-1 Soil pH and acid base accounting data for soil profile RSMM 1. Left Plot: Soil (pH_W: green line) and peroxide pH (pH_{FOX}: red line). Right Plot: TAA (red bar), S_{CR} (pink bar) and Net Acidity for sulfidic layers (green line). (Note: ANC was only required to be determined for sulfidic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

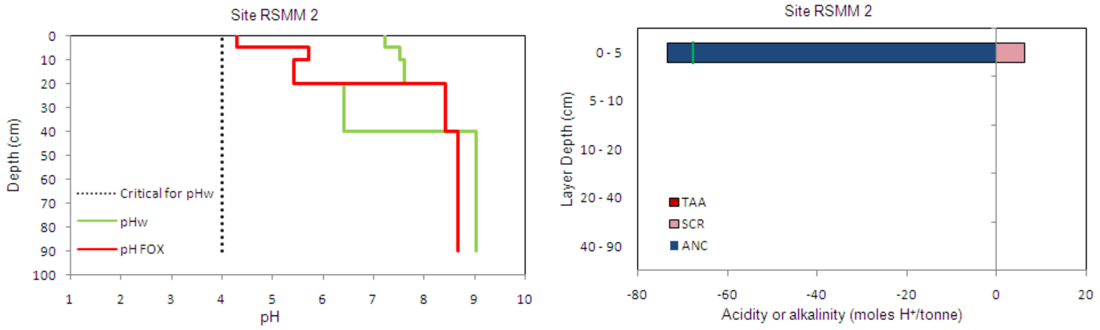

Figure 3-2 Soil pH and acid base accounting data for soil profile RSMM 2. Left Plot: Soil (pH_W: green line) and peroxide pH (pH_{FOX}: red line). Right Plot: S_{CR} (pink bar), ANC (blue bar) and Net Acidity for sulfidic layers (green line). (Note: ANC was only required to be determined for sulfidic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

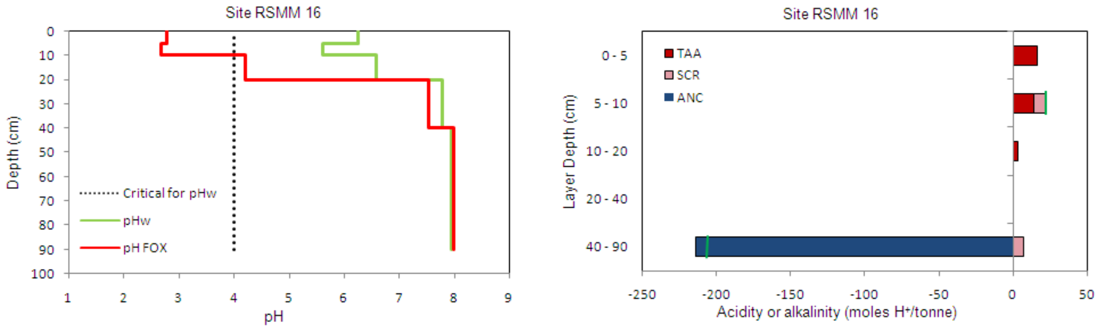

Figure 3-3 Soil pH and acid base accounting data for soil profile RSMM 16. Left Plot: Soil (pH_W: green line) and peroxide pH (pH_{FOX}: red line). Right Plot: TAA (red bar), S_{CR} (pink bar), ANC (blue bar) and Net Acidity for sulfidic layers (green line). (Note: ANC was only required to be determined 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 Macquarie Marshes Ramsar wetland sites examined is presented in Table 7-2 (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 4 materials of the 101 samples collected equal to the sulfidic criterion. Sites RSMM 1.5 (10–20 cm), RSMM 2.3 (0-5 cm), RSMM 16.4 (5-10 cm) and RSMM 16.7 (40–90 cm) all had a S_{CR} of 0.01% S.

3.1.3. Acid Neutralising Capacity

The acid neutralising capacity (ANC) ranged between zero and 1.61 %$CaCO_3$ for the 4 sulfidic soil materials (see Table 3-1).

3.1.4. Net Acidity

The acidification hazard from acid sulfate soil disturbance posed by the 4 sulfidic soil materials is low (see Figures 3-1 – 3-3). 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 2 hypersulfidic soil materials had low to moderate net acidities. The hypersulfidic soils RSMM 1.5 (10–20 cm) and RSMM 16.4 (5-10 cm) had a low net acidity of 7.6 H^+/tonne and moderate net acidity of 21.8 H^+/tonne respectively (Table 7-2, Appendix 2).

3.1.5. Water soluble SO_4

The water soluble SO_4 data for the Macquarie Marshes Ramsar wetland sites examined is presented in Table 7-2 (Appendix 2) and summarised in Table 3-1. The water soluble SO_4 in the soils in the Macquarie Marshes Ramsar wetlands ranged between 23 and 402 mg kg^{-1}. At least 1 surface soil layer in 15 of the 20 sites examined had a water soluble SO_4 content exceeding the trigger value of > 100 mg kg^{-1} indicating that the formation of monosulfidic materials may be a potential hazard upon rewetting. All layers in 3 of 20 profiles had water soluble SO_4 contents exceeding the trigger value. A decrease in water soluble SO_4 content with depth was often observed (Figure 3-4).

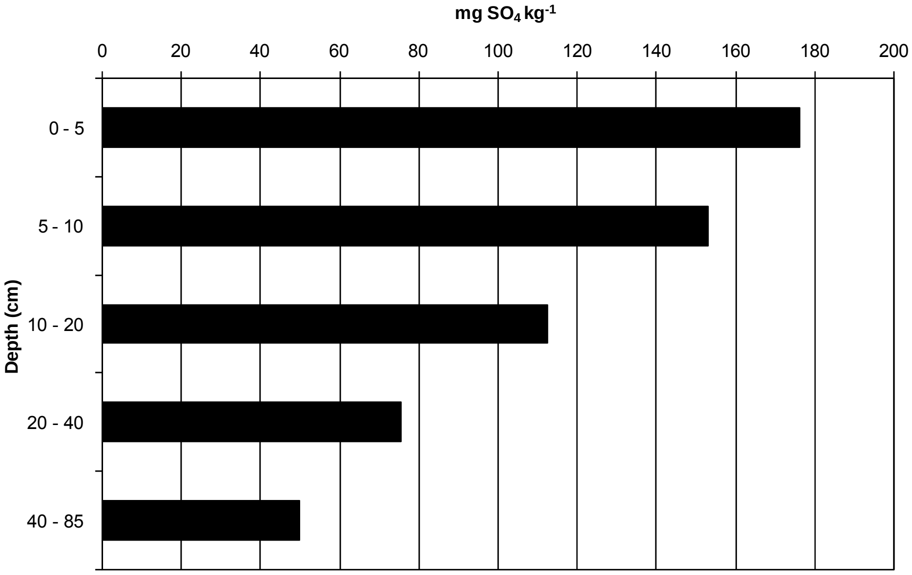

Figure 3-4 Variation in water soluble SO_4 (mg SO_4 kg^{-1}) with depth at site RSMM 18.

3.1.6. Titratable actual acidity (TAA)

The TAA data for the Macquarie Marshes Ramsar wetland sites examined is presented in Table 7-2 (Appendix 2) and summarised above in Table 3-1. The TAA ranged between 0 and 80 mole H^+/tonne, with the majority of soil layers having a TAA < 30 mole H^+/tonne. As observed with water soluble SO_4 data, there was often a decrease in the TAA with depth (Figure 3-5).

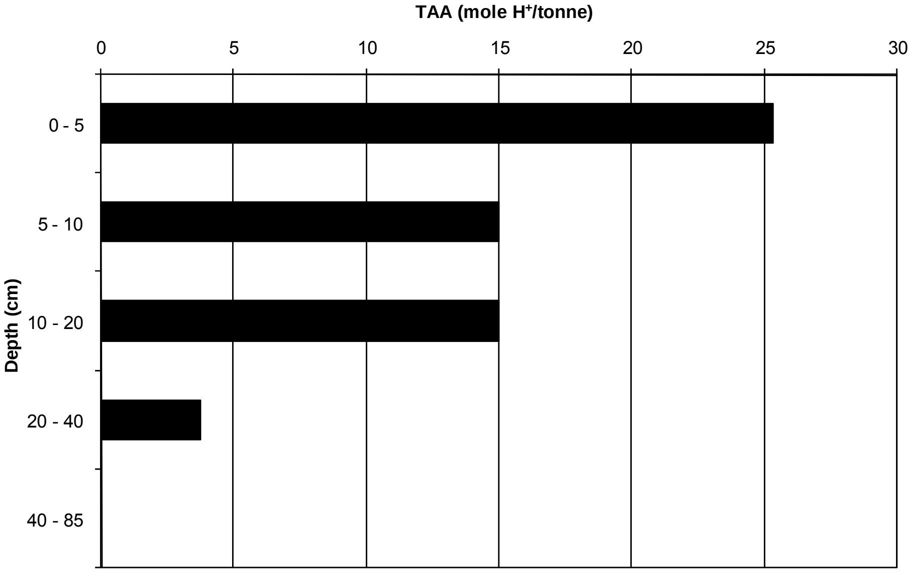

Figure 3-5 Variation in TAA (mole H^+/tonne) with depth at site RSMM 18.

3.2. Hydrochemistry

Surface water quality data was collected from 3 locations in the Macquarie Marshes Ramsar wetlands including standing water near Site RSMM 7 (Figure 2-6), a channel near site RSMM 10, and Monkeygar Creek near Site RSMM 15. No groundwater data was collected at the time of sampling 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 the results of the laboratory analyses are presented in Appendix 3.

The field pH of the surface waters ranged between 7.5 and 8.2 (Table 3-2) with only one site exceeding the most relevant ANZECC/ARMCANZ (2000) trigger value for aquatic ecosystems of 8.0. The water data indicates that the surface water has not been affected by acidification. The surface water sulfate concentrations ranged between 5.5 and 62.9 mg L^{-1} (Table 7-4, Appendix 3).

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	7.46	426	22.6	17	5.6	96
Median	7.47	449	83.7	318	68.6	112
Maximum	8.20	862	107.9	324	73.3	216
n[1]	3	3	3	3	3	3

[1] n: number of samples

4. HAZARD ASSESSMENT

4.1. Interpretation of soil and water data

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

Hypersulfidic materials occurred at depth in the soil profile at two of the 20 sampling locations (Table 4-1). Both of the sites where hypersulfidic materials occurred were in the lowest elevation drainage depressions where water-logged and reducing conditions, suitable for the formation of sulfides, occur.

The acidification hazard from acid sulfate soil disturbance posed by these samples is low: the two hypersulfidic soil materials had low to moderate net acidities (net acidities were 7.6 and 21.8 mole H^+/tonne).

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

The water soluble sulfate contents of fifteen surficial soil materials sampled 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 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 = 20)	Proportion of total sampling sites (%)
Sulfuric	0	0
Hypersulfidic	2	10
Hyposulfidic (S_{CR} ≥ 0.10%)	0	0
Monosulfidic (observed)	0	0
Monosulfidic (potential)	15	75
Hyposulfidic (S_{CR} < 0.10%)	2	10
Other acidic (pH_w &/or pH_{age}) 4 – 5.5	3	15
Other soil materials	5	25

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 Macquarie Marshes Ramsar wetlands. This Phase 1 report is aimed solely at determining whether or not acid sulfate soil materials are present in the Macquarie Marshes Ramsar wetlands.

Sulfuric materials were not observed in these wetlands, and although 15% (i.e. 3) of the sampling sites contained sulfidic materials, the reduced inorganic sulfur concentrations of these samples were very low (i.e. the highest S_{CR} was only 0.01%). Hypersulfidic soil materials were present in two soil profiles (one 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, fifteen 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 were two high priority sites based on the presence of hypersulfidic material, and one moderate priority site based on the presence of a hyposulfidic material with S_{CR} < 0.10%. In addition, 15 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 Macquarie Marshes Ramsar wetland sites are as below:

- Acidification: The data indicate that with low titratable actual acidities (TAA) and only a few sulfidic materials (where the highest S_{CR} was only 0.01% S) that the degree of acidification hazard is low.

- Deoxgenation: The water soluble sulfate contents of fifteen 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 Macquarie Marshes 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 Macquarie Marshes.

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7. APPENDICES

APPENDIX 1. Site and sample descriptions

Table 7-1 Macquarie Marshes Ramsar wetland site and sample descriptions.

Profile	Date	Location	GPS Co-ords			Location Remarks	Profile remarks
			Zone	*East.*	*North.*		
RSMM1	28/6/08	Wilgara	55	571409	6576440	Base of dry watercourse. Adjacent to photo point. Ground cover of clover, lippia and dead grasses. Watercourse bordered by red gums and lignum.	Dry soil. Carbonate nodules 20-90cm. Possible crust
RSMM2	28/6/08	Wilgara	55	570753	6575890	90% cover of lippia, nardoo, clover and water couch. Hoof prints common.	Carbonate nodules present.
RSMM3	28/6/08	Wilgara	55	570862	6575823	200m east of MM2. In band of red gums and lignum. 50% cover of grasses and herbs.	Iron mottling <20cm. Iron lining root holes 20-80cm. Carbonate nodules 40-70cm. Dug to 80cm.
RSMM4	28/6/08	Wilgara	55	570187	6577801	Transect through bird nesting site. MM4 in 80% cover of water couch and herbs. Surrounded by red gum floodplain forest. In base of low depression.	Mottling at 5cm. Iron staining 20-30cm. Soil dryer >40cm than at surface.
RSMM5	28/6/08	Wilgara	55	570089	6577972	100% groundcover of water couch and grasses next to stand of native perennial 1m high.	Iron stained carbonate nodules 20-30cm. Carbonate nodules >40cm.
RSMM6	28/6/08	Wilgara	55	570183	6578134	65% cover of grasses, lippia, clover and leaf litter. Red gum and river cooba tree's surrounding. NE of dry water course.	Carbonate nodules >40cm. Dug to 90cm.
RSMM7	15/7/08	North Mac Marshes N.R.	55	554971	6599981	Eastern side of north marsh. This profile close to standing water – deepest profile in transect. Surface water taken. No vegetation cover.	Very sticky grey clay. Dug to 80cm.
RSMM8	15/7/08	North Mac Marshes N.R.	55	555063	6599950	90m east of MM7. Higher with cover of herbs, clumps and Noogoora Bur and phragmites.	Dug to 85cm.
RSMM9	15/7/08	North Mac Marshes N.R.	55	555267	6599914	Further out onto floodplain in roly-poly and herbs. Rolypoly mostly dead.	Very hard brown grey clays. Dug to 50cm.

Table 7-1 (continued) Macquarie Marshes Ramsar wetland site and sample descriptions.

Profile	Date	Location	GPS Co-ords			Location Remarks	Profile remarks
			Zone	*East.*	*North.*		
RSMM10	15/7/08	North Mac Marshes N.R.	55	551979	6597525	Junction of North marsh bypass channel and Macquarie River channel. Some salt crust evident on waters edge of bypass channel. 100% lippia ground cover. Surface water sample taken.	Iron coating root holes <50cm. Carbonate nodules at depth ~ 80cm. Dug to 90cm.
RSMM11	15/7/08	North Mac Marshes N.R.	55	552164	6597509	200m E of MM10 out onto floodplain. Groundcover of Lippia and dead pin rush. Surrounded by Noogoora bur and Red gums.	Brown grading to grey clay at 40cm. Iron coating root holes <40cm. Carbonate nodules >60cm.
RSMM12	15/7/08	North Mac Marshes N.R.	55	552607	6597448	Further E. In among young stand of red gums. Sparse lippia, roly poly and other herbs.	Soil very hard at depth. Dug to 60cm.
RSMM13	15/7/08	North Mac Marshes N.R.	55	553665	6602294	Northern end of North NR. Groundcover of low herbs surrounded by stands of dead phragmites.	Nice loamy brown soil grading to sticky grey clays with significant carbonate nodules at depth (>60cm).
RSMM14	15/7/08	North Mac Marshes N.R.	55	553954	6602157	200m E of MM13. Out in roly poly and short herbs.	Carbonate nodules throughout profile. Extremely hard grey clays at depth. Dug to 55cm.
RSMM15	15/7/08	South Mac Marshes N.R.	55	551430	6580713	Northern end of South NR. On bank of Monkeygar Creek. Sparse herbs <2cm on bank of standing water with large stand of phragmites (3m tall).	Dug to 90cm.
RSMM16	15/7/08	South Mac Marshes N.R.	55	551621	6580734	In secondary channel E of MM15. Sparse cover of dead noogoora bur and water couch.	Distinct change from sands to grey clays at 20cm. Carbonate nodules throughout. Iron staining in top 20cm.

Table 7-1 (continued) Macquarie Marshes Ramsar wetland site and sample descriptions.

Profile	Date	Location	GPS Co-ords *Zone*	 *East.*	 *North.*	Location Remarks	Profile remarks
RSMM17	16/7/08	South Mac Marshes N.R.	55	552877	6576168	Site within minor channel on Eastern side of South NR. Surrounded by dead phragmites with groundcover of small herbs – 50% cover.	Loamy brown soil grading to hard grey clay. Some carbonate nodules at depth. Dug to 80cm.
RSMM18	16/7/08	South Mac Marshes N.R.	55	553009	6576225	Further east of MM17. In slight depression surrounded by dead phragmites. Groundcover of dead phragmites pieces.	Softer soil than MM17 with more moisture. Carbonates at depth (>50cm). Dug to 85cm.
RSMM19	16/7/08	South Mac Marshes N.R.	55	550515	6571622	At southern end of South NR. In minor channel among phragmites and willows. No water present.	Distinct boundary between clays and sands at 30cm. Clay above sands. Dug to 90cm.
RSMM20	16/7/08	South Mac Marshes N.R.	55	550477	6571624	In close proximity to MM19 but out of channel on floodplain surface. Sparse Groundcover of herbs in roly-poly plain.	Very hard clays at depth. Dug to 60cm.

APPENDIX 2. Field and laboratory analytical soil data

Table 7-2 Macquarie Marshes 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)
RSMM / 1.2	Crust	-	2.5Y 4/1		7.48	4.09	XXXX	6.91		-	<0.01	-		111.90
1.3	0 - 5	LMC	10YR 4/1		6.85	3.65	XXXX	6.51		-	<0.01	-		211.65
1.4	5 - 10	LMC	2.5Y 3/2		6.47	3.51	XXXX	6.28		4.74	<0.01	-	4.74	200.70
1.5	10 - 20	MC	2.5Y 3/1		6.93	3.83	XXXX	6.24	5.9	0.95	0.011	0.00	7.56	140.25
1.6	20 - 40	LMC	10YR 4/1		8.16	6.67	XXXX	6.79		-	<0.01	-	-	46.65
1.7	40 - 90	LMC	2.5Y 5/2		7.99	6.69	X	7.18		-	<0.01	-	-	58.20
RSMM / 2.3	0 - 5	LMC	10YR 4/2		7.23	4.30	XXXX	6.83	5.8	-	0.010	0.55	-66.94	178.80
2.4	5 - 10	LMC	10YR 4/2		7.51	5.72	XXXX	7.53		-	<0.01	-	-	114.00
2.5	10 - 20	LMC	2.5Y 4/1		7.60	5.43	XXXX	7.78		-	<0.01	-	-	82.20
2.6	20 - 40	KSLMC	2.5Y 4/1		6.41	8.43	XXXX	7.85		-	<0.01	-	-	46.35
2.7	40 - 90	KSLMC	10YR 5/1		9.03	8.67	XXXX	8.05		-	<0.01	-	-	100.20
RSMM / 3.3	0 - 5	LMC	10YR 4/2		6.42	3.68	XX	6.26		3.79	<0.01	-	3.79	74.25
3.4	5 - 10	LC	10YR 4/2	7.5YR 5/8	7.76	5.14	XXX	6.55		-	<0.01	-	-	79.95
3.5	10 - 20	LMC	2.5Y 4/1		8.10	6.93	XXXX	8.02		-	<0.01	-	-	80.25
3.6	20 - 40	KSLMC	2.5Y 4/1		8.30	7.27	XXXX	8.14		-	<0.01	-	-	48.00
3.7	40 - 80	KSLMC	2.5Y 5/1		8.51	8.33	XXX	8.26		-	<0.01	-	-	105.75
RSMM / 4.3	0 - 5	SiC	10YR 3/2		5.58	3.49	XX	5.90		9.01	<0.01	-	9.01	77.55
4.4	5 - 10	SC	10YR 3/2		5.87	3.61	XX	5.88		5.69	<0.01	-	5.69	45.15
4.5	10 - 20	SC	10YR 3/2		6.46	4.16	XX	6.29		2.37	<0.01	-	2.37	33.30
4.6	20 - 40	SC	2.5Y 3/1		7.13	4.95	XXX	6.37		1.90	<0.01	-	1.90	34.80
4.7	40 - 90	LMC	2.5Y 4/1		7.15	5.57	XXX	6.40		1.42	<0.01	-	1.42	102.15
RSMM / 5.3	0 - 5	LC	10YR 4/3		6.45	3.52	XXX	6.14		6.64	<0.01	-	6.64	125.25
5.4	5 - 10	LMC	2.5Y 4/1		7.00	4.08	XXX	6.35		1.90	<0.01	-	1.90	72.00
5.5	10 - 20	LMC	2.5Y 3/1		7.64	5.76	XXX	6.41		0.95	<0.01	-	0.95	51.90
5.6	20 - 40	LC	2.5Y 4/1		8.23	5.69	XXX	7.42		-	<0.01	-	-	39.90
5.7	40 - 90	KSLC	10YR 4/1		8.43	6.93	XXX	8.08		-	<0.01	-	-	45.15
RSMM / 6.3	0 - 5	SiCL	10YR 4/2		5.43	2.83	XXX	5.92		12.80	<0.01	-	12.80	140.70
6.4	5 - 10	LC	2.5Y 4/2		5.50	2.91	XXXX	5.86		9.95	<0.01	-	9.95	113.55
6.5	10 - 20	LC	10YR 4/1		6.02	3.70	XXXX	5.95		6.64	<0.01	-	6.64	63.60
6.6	20 - 40	LC	10YR 4/2		7.67	5.31	XXX	6.59		-	<0.01	-	-	39.15
6.7	40 - 90	LC	2.5Y 3/1		7.94	7.46	XXX	8.02		-	<0.01	-	-	76.35
RSMM / 7.3	0 - 5	LC	10YR 3/1		7.35	3.53	XXXX	6.92		-	<0.01	-	-	240.45
7.4	5 - 10	LC	2.5Y 2.5/1		7.03	3.62	XXXX	6.43		1.90	<0.01	-	1.90	97.20
7.5	10 - 20	LMC	2.5Y 2.5/1		7.24	4.36	XXXX	6.39		2.37	<0.01	-	2.37	74.25
7.6	20 - 40	LMC	2.5Y 2.5/1		7.74	6.52	XXX	6.61		-	<0.01	-	-	88.95
7.7	40 - 80	MC	10YR 4/1		8.39	7.49	XXX	8.02		-	<0.01	-	-	169.35
RSMM / 8.3	0 - 5	LC	7.5YR 3/1		6.31	3.03	XXX	6.34		4.74	<0.01	-	4.74	198.45
8.4	5 - 10	LMC	10YR 3/1	10% 2.5YR 5/8	6.38	3.24	XXXX	6.37		2.37	<0.01	-	2.37	163.80
8.5	10 - 20	LMC	10YR 3/1		6.92	3.75	XXXX	6.77		-	<0.01	-	-	141.30
8.6	20 - 40	MC	10YR 3/1	3% 2.5YR 4/8	7.96	7.08	XXXX	8.03		-	<0.01	-	-	95.85
8.7	40 - 85	SMC	10YR 5/1		8.13	8.26	XXX	8.17		-	<0.01	-	-	191.40
RSMM / 9.3	0 - 5	LMC	7.5YR 4/1		7.96	5.68	XXXX	7.75		-	<0.01	-	-	72.60
9.4	5 - 10	MC	7.5YR 4/2	5% 5YR 5/8	8.08	6.23	XXXX	8.06		-	<0.01	-	-	51.90
9.5	10 - 20	MC	7.5YR 4/1		8.20	7.51	XXXX	8.15		-	<0.01	-	-	49.65
9.6	20 - 40	SMHC	7.5YR 5/1		8.43	7.78	XXXX	8.20		-	<0.01	-	-	70.35
9.7	40 - 50	-	10YR 5/1		8.38	7.76	XXXX	8.23		-	<0.01	-	-	84.60
RSMM / 10.3	0 - 5	LMC	7.5YR 3/1	15% 2.5YR 5/8	6.03	3.04	XXXX	6.15		8.06	<0.01	-	8.06	251.25
10.4	5 - 10	HC	7.5YR 2.5/1	30% 2.5YR 5/8	5.92	3.31	XXXX	5.77		13.27	<0.01	-	13.27	124.80
10.5	10 - 20	HC	10YR 3/1	20% 2.5YR 4/8	6.00	3.67	XXXX	5.77		11.38	<0.01	-	11.38	81.45
10.6	20 - 40	HC	10YR 3/1		6.87	4.40	XXXX	7.37		-	<0.01	-	-	46.95
10.7	40 - 90	HC	10YR 4/1	15% 5YR 5/8	7.77	7.80	XXX	6.87		-	<0.01	-	-	184.50

[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 7-2 (continued) Macquarie Marshes 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)
RSMM / 11.3	0 - 5	LMC	10YR 3/1	7% 5YR 5/8	6.87	3.10	XXX	6.12		7.58	<0.01	-	7.58	145.80
11.4	5 - 10	MC	10YR 3/1	12% 2.5YR 4/8	6.79	3.22	XXX	4.63		31.42	<0.01	-	31.42	135.15
11.5	10 - 20	MHC	10YR 4/1	20% 2.5YR 4/6	6.93	4.05	XXXX	5.08		9.85	<0.01	-	9.85	91.20
11.6	20 - 40	HC	10YR 4/1	15% 5YR 5/8	7.66	7.44	XXXX	5.20		12.66	<0.01	-	12.66	113.70
11.7	40 - 90	HC	10YR 4/1	5% 2.5YR 6/8	8.23	6.97	XXXX	7.25		-	<0.01	-	-	169.35
RSMM / 12.3	0 - 5	LC	7.5YR 4/1	5% 2.5YR 5/8	6.18	3.49	XXX	5.32		14.07	<0.01	-	14.07	91.05
12.4	5 - 10	LC	10YR 4/2	5% 5YR 5/8	6.83	4.32	XXXX	6.51		-	<0.01	-	-	72.00
12.5	10 - 20	MC	5YR 4/1	2% 7.5YR 5/8	7.81	6.91	XXXX	7.38		-	<0.01	-	-	86.70
12.6	20 - 40	MC	5YR 4/1	2% 2.5YR 4/8	8.00	6.92	XXXX	7.54		-	<0.01	-	-	64.95
12.7	40 - 60	MC	2.5YR 4/1		7.99	7.26	XXXX	7.49		-	<0.01	-	-	35.85
RSMM / 13.3	0 - 5	SLC	10YR 3/2		5.75	2.62	XXX	5.11		30.49	<0.01	-	30.49	325.65
13.4	5 - 10	SLC	10YR 3/1	5% 7.5YR 6/8	5.97	2.60	XXX	4.92		22.51	<0.01	-	22.51	152.25
13.5	10 - 20	SLMC	7.5YR 2.5/1		6.33	3.07	XXXX	4.86		29.08	<0.01	-	29.08	125.70
13.6	20 - 40	MC	7.5YR 2.5/1		6.65	4.21	XXXX	4.74		26.73	<0.01	-	26.73	136.65
13.7	40 - 90	SMC	7.5YR 2.5/1	5% 10YR 6/8	7.51	6.97	XXX	3.77		79.73	<0.01	-	79.73	213.30
RSMM / 14.3	0 - 5	LC	7.5YR 3/1	3% 5YR 5/8	6.71	3.69	XXXX	5.72		13.13	<0.01	-	13.13	123.45
14.4	5 - 10	LMC	7.5YR 3/1		6.61	4.16	XXXX	5.80		6.57	<0.01	-	6.57	84.90
14.5	10 - 20	MC	7.5YR 3/1		7.28	6.12	XXXX	6.64		-	<0.01	-	-	55.35
14.6	20 - 40	MC	10YR 4/1		8.02	7.07	XXXX	7.82		-	<0.01	-	-	78.15
14.7	40 - 55	MC	10YR 4/1		8.01	8.16	XXXX	7.98		-	<0.01	-	-	137.55
RSMM / 15.3	0 - 5	SLMC	7.5YR4/2	7% 7.5YR 5/8	7.73	7.33	XXXX	7.79		-	<0.01	-	-	39.45
15.4	5 - 10	SMC	2.5Y 5/1		7.90	8.15	XXX	7.96		-	<0.01	-	-	22.80
15.5	10 - 20	SMC	2.5Y 5/1	12% 10YR 6/8	7.99	8.15	XXX	7.98		-	<0.01	-	-	31.35
15.6	20 - 40	SMHC	2.5Y 5/2	25% 2.5Y 7/8	8.05	8.06	XXX	8.04		-	<0.01	-	-	35.85
15.7	40 - 90	SMHC	2.5Y 5/2	25% 2.5Y 7/6	8.05	8.36	XXX	8.12		-	<0.01	-	-	29.70
RSMM / 16.3	0 - 5	ICL	7.5YR 4/2		6.25	2.79	XXX	5.65		16.42	<0.01	-	16.42	402.45
16.4	5 - 10	SLC	7.5YR 4/2	15% 7.5YR 5/6	5.61	2.68	XXX	5.47	4.5	13.60	0.013	0.00	21.84	343.35
16.5	10 - 20	SLC	10YR 4/2	50% 5YR 5/8	6.58	4.20	XXXX	5.99		3.28	<0.01	-	3.28	145.95
16.6	20 - 40	SMC	10YR 4/1		7.78	7.53	XXX	7.83		-	<0.01	-	-	104.10
16.7	40 - 90	SMHC	10YR 4/1		7.95	7.98	XXX	7.94	7.4	-	0.012	1.61	-207.13	187.20
RSMM / 17.3	0 - 5	ICL	10YR 2/1		5.31	2.74	XX	5.04		44.09	<0.01	-	44.09	212.25
17.4	5 - 10	MC	7.5YR 3/2	10% 2.5YR 5/8	5.35	2.96	XX	4.96		25.33	<0.01	-	25.33	287.40
17.5	10 - 20	MC	10YR 3/1	15% 2.5YR 5/8	5.86	3.05	XXX	5.26		17.35	<0.01	-	17.35	129.45
17.6	20 - 40	MC	10YR 3/1		7.77	6.97	XXXX	7.74		-	<0.01	-	-	53.55
17.7	40 - 80	MC	7.5YR 4/1		7.96	7.04	XX	7.91		-	<0.01	-	-	46.95
RSMM / 18.3	0 - 5	ICL	7.5YR 3/1		5.92	3.24	XXX	5.27		25.33	<0.01	-	25.33	176.25
18.4	5 - 10	LC	7.5YR 3/1	15% 2.5YR 4/8	6.04	3.44	XXX	5.41		15.01	<0.01	-	15.01	153.15
18.5	10 - 20	LMC	10YR 4/1	30% 2.5YR 4/8	6.50	3.45	XXXX	5.36		15.01	<0.01	-	15.01	112.65
18.6	20 - 40	MC	10YR 4/1		7.21	6.66	XXXX	5.99		3.75	<0.01	-	3.75	75.75
18.7	40 - 85	MC	10YR 4/1		7.73	6.97	XXX	7.85		-	<0.01	-	-	50.10
RSMM / 19.3	0 - 5	MHC	7.5YR 3/1	40% 7.5YR 5/8	6.77	3.75	XXXX	6.29		1.88	<0.01	-	1.88	345.60
19.4	5 - 10	LMC	7.5YR 3/1	20% 7.5YR 5/8	7.49	4.16	XXXX	6.59		-	<0.01	-	-	204.30
19.5	10 - 20	LMC	10YR 3/1	10% 7.5YR 6/8	8.00	6.53	XXXX	7.91		-	<0.01	-	-	208.65
19.6	20 - 40	SCL	10YR 4/1	15% 5YR 5/8	7.98	6.76	XXXX	8.02		-	<0.01	-	-	168.90
19.7	40 - 90	SCL	10YR 4/4		8.08	6.60	XXX	8.09		-	<0.01	-	-	172.35
RSMM / 20.3	0 - 5	LMC	7.5YR4/2		6.23	3.86	XXX	5.88		6.57	<0.01	-	6.57	169.20
20.4	5 - 10	MC	10YR 3/1	10% 2.5YR 4/8	6.41	3.69	XXX	5.59		9.38	<0.01	-	9.38	136.65
20.5	10 - 20	LMC	10YR 3/2		6.88	3.75	XXXX	5.90		5.16	<0.01	-	5.16	75.75
20.6	20 - 40	LMC	10YR 3/1	15% 2.5YR 4/8	7.85	5.98	XXXX	7.73		-	<0.01	-	-	56.55
20.7	40 - 60	MC	2.5Y 5/2	30% 10YR 7/8	7.96	6.30	XXXX	8.02		-	<0.01	-	-	119.10

[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 7-3 Macquarie Marshes field hydrochemistry data.

Site	Units	Site RSMM7	Site RSMM10	Site RSMM15	Minimum	Median	Maximum	Range	n
Water type		surface	surface	surface					
pH		8.20	7.46	7.47	7.46	7.47	8.20	7.46 -8.20	3
SEC	μS cm^{-1}	862	426	449	426	449	862	426 - 862	3
DO	% sat	22.6	83.7	107.9	22.6	83.7	107.9	22.6 -107.9	3
Eh	mV	17	324	318	17	318	324	17 - 324	3
Turbidity	NTU	68.6	73.3	5.6	5.6	68.6	73.3	5.6 - 73.3	3
Alkalinity	(mg L^{-1} as HCO_3)	216	112	96	96	112	216	96- 216	3
Temperature	°C	12.8	11.7	10.6	10.6	11.7	12.8	10.6 - 12.8	3

Table 7-4 Macquarie Marshes laboratory analytical hydrochemistry data.

Parameter	Units	Site RSMM7	Site RSMM10	Site RSMM15	Minimum	Median	Maximum	Range	n
pH		7.96	7.98	7.70	7.70	7.96	7.98	7.70 - 7.98	3
E.C.	μS cm^{-1}	720	344	386	344	386	720	340 - 720	3
Alkalinity	meq/L	2.23	1.25	1.11	1.11	1.25	2.23	1.11 - 2.23	3
Ammonium (NH_4-N)	mg/L	0.532	0.040	0.053	0.040	0.053	0.532	0.040 - 0.532	3
Oxides of Nitrogen (NO_x-N)	mg/L	1.137	0.009	0.098	0.009	0.098	1.137	0.009 - 1.137	3
Nitrate (NO_3-N)	mg/L	1.131	0.001	0.050	0.001	0.050	1.131	0.001 - 1.131	3
Nitrite (NO_2-N)	mg/L	0.006	0.008	0.047	0.006	0.008	0.047	0.006 - 0.047	3
Phosphate (PO_4-P)	mg/L	0.028	0.003	0.008	0.003	0.008	0.028	0.003 - 0.028	3
Fluoride (F^-)	mg/L	0.14	0.10	0.07	0.07	0.10	0.14	0.07 - 0.14	3
Chloride (Cl^-)	mg/L	145.09	40.39	39.74	39.74	40.39	145.09	39.74 - 145.09	3
Bromide (Br^-)	mg/L	0.64	0.07	0.05	0.05	0.07	0.64	0.05 - 0.64	3
Sulfate (SO_4^{2-})	mg/L	5.48	32.94	62.86	5.48	32.94	62.86	5.48 - 62.86	3
Calcium (Ca)	mg/L	50.51	27.19	32.18	27.19	32.18	50.51	27.19 - 50.51	3
Potassium (K)	mg/L	15.38	4.06	8.69	4.06	8.69	15.38	4.06 - 15.38	3
Magnesium (Mg)	mg/L	27.24	13.56	14.95	13.56	14.95	27.24	13.56 - 27.24	3
Sodium (Na)	mg/L	89.15	31.44	34.63	31.44	34.63	89.15	31.44 - 89.15	3
Sulfur (S)	mg/L	4.11	11.12	22.46	4.11	11.12	22.46	4.11 - 22.46	3
Total Organic Carbon (NPOC)	mg/L	54.12	5.81	8.12	5.81	8.12	54.12	5.81 - 54.12	3
Total Nitrogen (TN)	mg/L	4.74	0.54	0.78	0.54	0.78	4.74	0.54 - 4.74	3
Aluminium (Al)	mg/L	0.029	0.024	0.023	0.023	0.024	0.029	0.023 - 0.029	3
Boron (B)	mg/L	0.018	0.017	0.027	0.017	0.018	0.027	0.017 - 0.027	3
Copper (Cu)	mg/L	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	3
Iron (Fe)	mg/L	0.066	0.030	0.046	0.030	0.046	0.066	0.030 - 0.066	3
Manganese (Mn)	mg/L	0.844	0.024	0.040	0.024	0.040	0.844	0.024 - 0.844	3
Phosphorus (P)	mg/L	0.181	< 0.03	< 0.03	<0.03	0.181	0.181	<0.03 - 0.181	3
Zinc (Zn)	mg/L	0.034	0.013	0.066	0.013	0.013	0.066	0.013 - 0.066	3
Molybdenum (Mo)	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	3
Cobalt (Co)	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	3
Nickel (Ni)	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	3
Chromium (Cr)	mg/L	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008	3
Cadmium (Cd)	mg/L	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	< 0.003	3
Lead (Pb)	mg/L	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	3
Selenium (Se)	mg/L	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	3

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