

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

L.A. Sullivan, N.J. Ward, R.T. Bush, M. Southwell, D.M. Fyfe, P. Cheeseman, C. Sauerland, M. Bush, E. Weber and V.N.L. Wong

FINAL REPORT

Southern Cross GeoScience Report 409 Prepared for the Murray-Darling Basin Authority

Copyright and Disclaimer

© Murray-Darling Basin Authority 2009. Graphical and textual information in the work (with the exception of photographs and the MDBA logo) may be stored, retrieved and reproduced in whole or in part, provided the information is not sold or used for commercial benefit and its source is acknowledged. Reproduction for other purposes is prohibited without prior permission of the Murray-Darling Basin Authority, or the copyright holders in the case of photographs.

To the extent permitted by law, the copyright holder (including its employees and consultants) exclude all liability to any person for any consequences, including but not limited to all losses, damages, costs, expenses and any other compensation, arising directly or indirectly from using this report (in part or in whole) and any information or material contained in it.

The contents of this publication do not purport to represent the position of the Murray-Darling Basin Authority. They are presented to inform discussion for improved management of the Basin's natural resources.

Cover Photograph:

Typical uniformly flat landscape in the Gwydir Wetlands. Photograph taken at Old Dromana - West oversight paddock (Site RSGW 4).

CONTENTS

LIST OF FIGURES

LIST OF TABLES

EXECUTIVE SUMMARY

The Gwydir Wetlands (Gingham and Lower Gwydir (Big Leather) Watercourses) Ramsar site is located approximately 60 km west of Moree in northern New South Wales. This Ramsar wetland consists of four discrete wetland areas, three of which were sampled in this study. These four areas comprise a total of 832 hectares of nominated wetlands out of a total area of just over 100,000 hectares of wetlands in this region.

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 twophased detailed acid sulfate soil assessment procedure for the Gwydir Wetlands. This Phase 1 report is aimed solely at determining whether or not acid sulfate soil materials are present in the Gwydir Wetlands.

Hypersulfidic materials were identified at 23% of the sampling sites although the reduced inorganic sulfur content of these samples was low (i.e. the highest S_{CR} was only 0.07%). 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, the majority of soil materials contained water soluble sulfate in excess of the 100 mg kg^{-1} trigger value for MBO formation potential.

Sulfuric soil materials were not observed in these wetlands.

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 three high priority sites based on the presence of hypersulfidic material. In addition all 13 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 Gwydir Wetlands are as below:

 Acidification: The data indicate that with low titratable actual acidities (TAA) and only a few sulfidic materials (where the highest S_{CR} was only 0.07% S) the degree of acidification hazard is low.

- Deoxgenation: The water soluble sulfate contents for 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 Gwydir 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 Gwydir wetlands.

1. INTRODUCTION

1.1. Wetland overview

The Gwydir Wetlands Ramsar site is located approximately 60 km west of Moree in the northern region of New South Wales (Figure 1-1) and were dry when sampled in June 2008.

The formal name of this Ramsar wetland is the "Gwydir Wetlands: Gingham and Lower Gwydir (Big Leather) Watercourses" and hereafter referred to as "Gwydir Wetlands". The Ramsar wetland consists of four discrete wetland areas, three of which were sampled in this study. These four areas comprise a total of 832 hectares of nominated wetlands out of a total area of just over 100,000 hectares of wetlands in this region.

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

*The Gwydir Wetlands are one of the few terminal wetlands found within inland NSW and contain one of the largest stands of water couch (*Paspalum distichum*) and marsh club-rush (*Bolboschoenus *fluviatilis) remaining in New South Wales (Bennett and Green 1991) (McCosker and Duggin 1993). The wetlands provide breeding and feeding grounds for very large numbers of colonial water bird species (around 500,000 in 1998), habitat for many threatened species and also continues to support a viable grazing industry.*

According to the Ramsar Site Information Sheet "*the most extensive wetland areas in the Gwydir Valley are located along the watercourses, where flat, overland grades allow shallow extensive flooding over large areas of the floodplain*". The general absence of well-defined wetlands in this Ramsar wetland can be observed in Figure 1-2, and a typical soil profile is shown in Figure 1-3. Further information on characteristics of the Gwydir Wetlands from the Ramsar Site Information Sheet can be found at World Wide Fund for Nature *et al.* (1999).

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 $(F \in S_2)$ 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 13 representative sites within the Gwydir Wetlands in June 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 uniformly flat landscape in the Gwydir Wetlands (Site RSGW 4).

Figure 1-3 Typical grey cracking clay soil profile in the Gwydir Wetlands (Site RSGW 3).

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 $SO₄$ (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 Gwydir Wetlands Ramsar site.

1.4. Methodologies used to assess acid generation potential

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

In nature, a number of oxidation reactions of sulfide minerals (principally pyrite: $FeS₂$) may occur which produce acidity, including:

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

 $4FeS₂ + 15O₂ + 10H₂O$ ---> $4FeOOH + 8H₂SO₄$

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

Acid-base accounting (ABA)

Acid-base accounting (ABA) is used to assess both the potential of a soil material to produce acidity from sulfide oxidation and also its ability to neutralise any acid formed (e.g. Sullivan *et al*. 2001, Sullivan *et al*. 2002b). The standard ABA applicable to acid sulfate soil is as described in Ahern *et al*. (2004) as shown below:

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

*** ANC = Acid Neutralizing Capacity**

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

Potential Sulfidic Acidity

The Potential Sulfidic Acidity is most easily and accurately determined by assessing the Chromium Reducible Sulfur. This method was developed specifically for analysing acid sulfate soil materials (Sullivan *et al*. 2000) to, inter alia, assess their Potential Sulfidic Acidity (PSA) also known as the 'acid generation potential' (AGP). The method is also described in Ahern *et al*. (2004), which includes the chromium reducible sulfur $(S_{CR}$ or CRS: Method Code 22B) and its conversion to PSA.

Existing Acidity

This is the sum of the Actual Acidity and the Retained Acidity (Ahern *et al*. (2004). Titratable Actual Acidity (TAA) is a measure of the actual acidity in acid sulfate soil materials that have already oxidised. TAA measures the sum of both soluble and exchangeable acidity. The Retained Acidity is the acidity 'stored' in minerals such as jarosite, schwertmannite and other hydroxysulfate minerals. Although these minerals may be stable under acidic conditions, they can release acidity to the environment when these conditions change. The methods for determining both TAA and Retained Acidity are given by Ahern *et al*. (2004).

Acid Neutralising Capacity (ANC)

Soils with pH values > 6.5 may potentially have ANC in the form of (usually) carbonate minerals, principally of calcium, magnesium and sodium. The carbonate minerals present are estimated by titration, and alkalinity present is expressed in CaCO₃ equivalents. By accepted definition (Ahern *et al.* 2004), any acid sulfate soil material with a pH < 6.5 has a zero ANC. The methods for determining ANC are given by Ahern *et al*. (2004).

Fineness Factor (FF)

This is defined by Ahern *et al*. (2004) as "A factor applied to the acid neutralising capacity result in the acid base account to allow for the poor reactivity of coarser carbonate or other acid neutralising material. The minimum factor is 1.5 for finely divided pure agricultural lime, but may be as high as 3.0 for coarser shell material". Fine grinding of soil materials may lead to an over-estimate of ANC when carbonates are present in the form of hard nodules or shells. In the soil environment, they may provide little effective ANC when exposure to acid may result in the formation of surface crusts (iron oxides or gypsum), preventing or slowing further neutralisation reactions. For reasons including those above, the use of the "Fineness Factor" also applies to those naturally occurring alkalinity sources in soil materials as measured by the ANC methods.

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

A 1:5 soil: water extract is prepared using 5g oven dried $(80^{\circ}C)$ 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 $\geq 0.01\%$ 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 Crreducible 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 $Fe²⁺$ 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 \leq 5.5 during moist aerobic incubation; or
	- b. soil materials with a $pH_W \ge 4$ 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. Gwydir Wetlands site characteristics

Locations sampled in this study were uniformly flat with either a lack of vegetation cover (e.g. Figure 2-2) or more typically a thick vegetation cover of sedges and grasses (e.g. Figure 2-6). The soils at each site were grey cracking 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 all sampling sites and 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 – 2-8.

Figure 2-1 Map showing the areas assessed at the Moolabulla-Goddards Waterhole in the Gwydir Wetlands (Sites RSGW 1-3).

Figure 2-2 Typical landscape (Site RSGW 2) and grey cracking clay (Site RSGW 3) at the Moolabulla-Goddards Waterhole in the Gwydir Wetlands. The waterhole lacked vegetation and was surrounded by a thick ground cover of water couch interspersed with sedges. Iron segregations in the subsoil were common.

SAMPLE LOCATION Watercourse

Figure 2-3 Map showing the areas assessed in the Old Dromana-West oversight paddock in the Gwydir Wetlands (Sites RSGW 4-6).

Figure 2-4 Typical landscape (Site RSGW 6) and soil profile (Site RSGW 5) in the Old Dromana-West oversight paddock in the Gwydir Wetlands. Site RSGW 6 was covered with dead pin rush and water couch. Soil profile at site RSGW 5 is a grey cracking clay (heavy clay with organic matter, gravel and sand). Carbonate nodules common at site RSGW 4 and 6.

SAMPLE LOCATION Watercourse Ramsar Boundary

Figure 2-5 Map showing the areas assessed at Old Dromana-Big Leather in the Gwydir Wetlands (Sites RSGW 7-10).

Figure 2-6 Typical landscape (Site RSGW 7) and grey cracking clay (Site RSGW 10) at Old Dromana-Big Leather in the Gwydir Wetlands. Site RSGW 7 shows thick vegetation cover of sedges and grasses. Water quality sample collected from channel near Site RSGW 7.

Figure 2-7 Map showing the areas assessed at Crinolyn in the Gwydir Wetlands (Sites RSGW 11-13).

Figure 2-8 Typical landscape (Site RSGW 12) and surface soil (Site RSGW 13) at Crinolyn in the Gwydir Wetlands. Site RSGW 12 had a heavy cover of spike rush to 50 cm. Soil profile at site RSGW 13 was a grey cracking clay with carbonate nodules. At this site the soil surface has a crumbly condition.

2.2. Field sampling of soils and waters

Field sampling of the Gwydir Wetlands was undertaken between $18th$ and $20th$ June 2008. A total of 65 soil layers were collected and analysed from 13 representative soil profiles within the Gwydir Wetlands to assess the current and potential environmental hazard due to the presence of acid sulfate soil (Figure 1-4).

Representative soil profiles were collected from 4 locations within the Gwydir Wetlands including: Moolabulla-Goddards waterhole (Sites RSGW 1-3), Old Dromana-West oversight paddock (Sites RSGW 4-6), Old Dromana-Big Leather (Sites RSGW 7-10), and Crinolyn (Sites RSGW 11-13). At each of these locations at least 3 soil profiles were sampled along a toposequence. The profiles were chosen to represent: (i) the lowest point in the landscape, (ii) a moderately elevated site just above the observed or interpreted normal flow level, and (iii) an elevated site above the normal flow level. It should be noted that on the exceptionally flat landscape of the Gwydir Wetlands, differences in elevation along the toposequence were minimal.

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 $\leq 4^{\circ}$ 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 taken at each of the 4 transects can be found in Section 2.1.

No surface water or groundwater data was collected at the time of sampling in the Gwydir Wetlands as surface waters were absent, and groundwater was not observed during soil pit excavation. However, field water samples were collected from an artificial channel near one of the sampling sites at Old Dromana-Big Leather (Site RSGW 7).

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.

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_{KCI} and $pH_{INCUBATION}$), titratable actual acidity (TAA), water soluble sulfate and chromium reducible sulfur (S_{CR}) .

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

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

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

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

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

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

High Priority

- 1) All sulfuric materials.
- 2) All hypersulfidic materials (as recognised by either 1) incubation of sulfidic materials or 2) a positive net acidity result with a Fineness Factor of 1.5 being used).
- 3) All hyposulfidic materials with S_{CR} contents $\geq 0.10\%$ S.
- 4) All surface soil materials (i.e. within 0-20 cm) with water soluble sulfate (1:5 soil: water) contents \geq 100 mg SO₄ 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 Gwydir Wetlands field and laboratory results

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

The pH_W, pH_{FOX}, pH_{KCl} and pH_{INCUBATION} data for the Gwydir Wetland sites examined is presented in Table 7-2 (Appendix 2) and summarised in Table 3- 1. The pH_W values ranged between 5.44 and 8.47, with the majority of the samples having a $pH_W > 6.0$. None of the soils in the Gwydir Wetlands would be classified as being sulfuric materials as all soils had a $pH_W > 4$.

The pH_{FOX} values ranged between 3.43 and 8.31. 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 3.1 pH units. The pH_{FOX} results indicate that some of the surface soils in the Gwydir Wetlands may have the potential to acidify to $pH < 4$ as a result of sulfide oxidation. However, the S_{CR} data shows only 4 of these layers contain detectable sulfide (i.e. $S_{CR} \ge 0.01\%$ S). While such decreases in pH after treatment with peroxide are often used to indicate the likely presence of iron 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. $S_{CR} \ge 0.01\%$ 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.

¹ n: number of samples. ² pH_W: pH in saturated paste with water. ³ pH_{FOX}: pH after treatment with 30% H₂O₂.⁴ pH_{KCl}: pH of 1:40 1 M KCl_extract. ⁵ pH_{INCUBATION}: pH after least 8 weeks of incubation. 6 TAA: Titratable Actual Acidity. ⁷ Soluble sulfate: in 1:5 soil:water extract. 8 S_{CR}: Chromium Reducible Sulfur. ⁹ ANC: Acid Neutralising Capacity: by definition, where pHKCl < 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 RSGW 8. 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 RSGW 9. Left Plot: Soil (pH_W: green line) and peroxide pH (pH_{FOX}: red line). Right Plot: TAA **(red bar), SCR (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 3-3 Soil pH and acid base accounting data for soil profile RSGW 13. Left Plot: Soil (pH_W: green line) and peroxide pH (pH_{FOX}: red line). Right Plot: TAA (red bar), S_{CR} (pink bar) and Net Acidity for sulfidic layers (green line). (Note: **ANC was only required to be determined for sulfidic layers and was zero at this site for these layers).**

3.1.2. Chromium Reducible Sulfur (S_{CR})

The chromium reducible sulfur (S_{CR}) data for the Gwydir Wetland sites examined is presented in Table 7-2 (Appendix 2) and summarised in Table 3- 1. Sulfidic soil materials (i.e. $S_{CR} \ge 0.01\%$ S) were largely absent from most sampling sites, with only 4 materials of the 65 samples collected being hypersulfidic. Site RSGW 13 had a S_{CR} of 0.05% S in the surface layer (0–5 cm) and 0.07% S in the soil layer immediately below (5–10 cm). Sites RSGW 8.5 (10–20 cm) and RSGW 9.4 (5–10 cm) both had a S_{CR} of 0.01% S.

3.1.3. Acid Neutralising Capacity

The ANC was zero for all sulfidic soil materials (see Table 3-1).

3.1.4. Net Acidity

The acidification hazard from acid sulfate soil disturbance posed by these 4 samples is low. The net acidity thresholds used to characterise the acid sulfate soil materials in this assessment include low net acidity (< 19 mole H⁺/tonne), moderate net acidity (19-100 mole H⁺/tonne) and high net acidity (> 100 mole H+ /tonne). All 4 hypersulfidic soil materials had moderate net acidities ranging between 21.1 and 45.6 H⁺/tonne (see Figures 3-1 – 3-3). The median net acidity was only 10.7 mole H⁺/tonne for all materials.

3.1.5. Water soluble SO4

The water soluble $SO₄$ data for the Gwydir Wetland sites examined is presented in Table 7-2 (Appendix 2) and summarised in Table 3-1. The water soluble SO4 content in the soils in the Gwydir Wetlands ranged between 39.9 and 516.6 mg kg⁻¹. All sites had at least 1 surface soil layer with 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 6 of 13 profiles had water soluble $SO₄$ contents exceeding the trigger value. A decreasing trend in water soluble $SO₄$ content with depth was often observed (Figure 3-4).

Figure 3-4 Variation in water soluble SO4 (mg SO4 kg-1) with depth at site RSGW 7.

3.1.6. Titratable actual acidity (TAA)

The TAA data for the Gwydir Wetland sites examined is presented in Table 7- 2 (Appendix 2) and summarised above in Table 3-1. The TAA ranged between 0 and 252 mole H⁺/tonne, with the majority of soil layers having a TAA < 30 mole H^{\dagger} /tonne. As observed with water soluble SO_4 data, there was often a decrease in the TAA with depth (Figure 3-5).

3.2. Hydrochemistry

Surface water was absent from the Gwydir Wetlands at the time of sampling, and groundwater was not observed during soil pit excavation. However, water quality data was collected from an artificial channel near one of the sampling sites at Old Dromana-Big Leather (Site RSGW 7) and is presented below in Table 3-2.

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

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

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).

Four samples from 3 sites were hypersulfidic (Table 4-1).

The acidification hazard from acid sulfate soil disturbance is low. While all four hypersulfidic soil materials had moderate net acidities (see Table 3-1) the median net acidity for all soil materials was only 10.7 mole H⁺/tonne.

The water soluble sulfate contents of all 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).

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

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

Hypersulfidic materials were identified at 23% of the sampling sites although the reduced inorganic sulfur content of these samples was low (i.e. the highest S_{CR} was only 0.07%). 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, the majority of soil materials contained soluble sulfate in excess of the 100 mg kq^{-1} trigger value for MBO formation potential.

Sulfuric soil materials were not observed in these wetlands.

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 three high priority sites based on the presence of hypersulfidic material. In addition all 13 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 Gwydir Wetlands are as below:

- Acidification: The data indicate that with low titratable actual acidities (TAA) and only a few sulfidic materials (where the highest S_{CR} was only 0.07% S) 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 Gwydir 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 Gwydir wetlands.

6. REFERENCES

Ahern CR, Sullivan LA, McElnea AE (2004) Laboratory methods guidelines 2004 - acid sulfate soils. In 'Queensland Acid Sulfate Soil Technical Manual'. (Department of Natural Resources, Mines and Energy: Indooroopilly, Queensland).

ANZECC/ARMCANZ (2000) 'Australian and New Zealand guidelines for fresh and marine water quality.' (Australian and New Zealand Environment and Conservation Council, Agricultural and Resource Management Council of Australia and New Zealand: Canberra).

Baldwin DS, Hall KC, Rees GN, Richardson AJ (2007) Development of a protocol for recognising sulfidic sediments (potential acid sulfate soils) in freshwater wetlands. *Ecological Management and Restoration*, 8, 56-60.

Burton ED., Bush RT, Sullivan, LA (2006) Acid-volatile sulfide oxidation in coastal floodplain drains: iron-sulfur cycling and effects on water quality. *Environmental Science & Technology* 40, 1217 –1222.

Burton, ED, Bush RT, Sullivan L A, Johnston SG, Hocking, RK (2008a) Mobility of arsenic and selected metals during re-flooding of iron- and organicrich acid sulfate soil. *Chemical Geology* 253, 64 – 73.

Burton ED, Sullivan LA, Bush RT, Johnston SG, Keene AF (2008b) A simple and inexpensive chromium-reducible sulfur method for acid-sulfate soils. *Applied Geochemistry* 23, 2759-2766.

Bush RT (2000) Iron sulfide micromorphology and mineralogy in acid sulfate soils: Their formation and behaviour. Unpublished Ph.D., University of NSW.

Bush RT, Sullivan LA (1997) Morphology and behaviour of greigite from a Holocene sediment in eastern Australia. *Australian Journal of Soil Research* 35, 853-861.

Bush RT, Sullivan LA, Lin C (2000) Iron monosulfide distribution in three coastal floodplain acid sulfate soils, eastern Australia. *Pedosphere* 10, 237- 245.

Dent D (1986) 'Acid sulphate soils: a baseline for research and development.' (International Institute for Land Reclamation and Improvement ILRI, Wageningen, The Netherlands).

Ferguson A, Eyre B (1999) Behaviour of aluminium and iron in acid runoff from acid sulphate soils in the lower Richmond River catchment. *Journal of Australian Geology & Geophysics* 17, 193-201.

Fitzpatrick RW, Marvanek S, Shand P, Merry RH, Thomas, M (2008a) Acid sulfate soil maps of the River Murray below Blanchetown (Lock 1) and Lakes Alexandrina and Albert when water levels were at pre-drought and current drought conditions. CSIRO Land and Water Science Report 12/08.

Fitzpatrick RW, Merry RH, Raven MD, Shand P (2008b) Acid sulfate soil materials and salt efflorescences in subaqueous and wetland soil environments at Tareena Billabong and Salt Creek, NSW: Properties, risks and management. CSIRO Land and Water Science Report 07/08.

Isbell RF (1996) 'The Australian Soil Classification.' (CSIRO Publishing, Melbourne, Vic).

Lamontagne S, Hicks WS, Fitzpatrick RW, Rogers S (2004) Survey and description of sulfidic materials in wetlands of the Lower River Murray floodplains: Implications for floodplain salinity management Technical Report 28/04. CSIRO Land and Water. Adelaide, Australia.

MDBC (2006a) The Barmah-Millewa Forest Icon Site Environmental Management Plan 2006-2007. MDBC Publication No. 30/06. http://thelivingmurray.mdbc.gov.au/__data/page/195/BM_EMP_2006-07.pdf (last accessed 15/04/2009).

MDBC (2006b) The Hattah Lakes Icon Site Environmental Management Plan 2006–2007. MDBC Publication No. 31/06. http://thelivingmurray.mdbc.gov.au/__data/page/1327/HL_EMP_2006-07.pdf (last accessed 15/04/2009).

MDBC (2006c) The Gunbower-Koondrook-Perricoota Forest Icon Site Environmental Management Plan 2006–2007. MDBC Publication No. 32/06. http://thelivingmurray.mdbc.gov.au/__data/page/195/GKP_EMP_2006-07.pdf (last accessed 15/04/2009).

Preda M, Cox ME (2001) Trace metals in acid sediments and waters, Pimpama catchment, southeast Queensland, Australia. *Environmental Geology* 40, 755-768.

Rayment GE, Higginson FR (1992) 'Australian laboratory handbook of soil and water chemical methods.' (Inkata Press: Melbourne, Vic).

Sammut J, Callinan RB, Fraser GC (1993) The impact of acidified water on freshwater and estuarine fish populations in acid sulphate soil environments. In 'Proceedings National Conference on Acid Sulphate Soils'. Coolangatta, NSW. 24-25 June 1993. (Ed. RT Bush) pp. 26-40. (CSIRO, NSW Agriculture, Tweed Shire Council).

Shand P, Edmunds WM (2008a) The baseline inorganic chemistry of European groundwaters. In, WM Edmunds & P Shand (Eds.), Natural Groundwater Quality, 21-58. Blackwell Publishing, Oxford.

Shand P, Merry RH, Fitzpatrick, RW (2008b) Acid sulfate soil assessment of wetlands associated with Lock 8 and Lock 9 weir pools. CSIRO Land and Water Science Report 40/08.

Simpson S, Angel B, Spadarol D, Fitzpatrick RW, Shand P, Merry RH, Thomas M. (2008) Acid and Metal Mobilisation Following Rewetting of Acid Sulfate Soils in the River Murray, South Australia. CSIRO Land and Water Science Report 27/08.

Sullivan LA, Burton ED, Bush RT, Watling K, Bush M (2008a) Acid, metal and nutrient mobilisation dynamics in response to suspension of MBOs in freshwater and to freshwater inundation of dried MBO and sulfuric soil materials. Southern Cross GeoScience, Report Number 108.

Sullivan LA, Bush RT (1997) Quantitative elemental microanalysis of roughsurfaced soil specimens in the scanning electron microscope using a peak-tobackground method. Soil Science 162, 749-757.

Sullivan LA, Bush RT, Fyfe D (2002a) Acid sulfate soil drain ooze: distribution, behaviour and implications for acidification and deoxygenation of waterways. In 'Acid sulfate soils in Australia and China.' (Eds C. Lin, M. Melville and L.A. Sullivan) (Science Press, Beijing.) pp. 91-99.

Sullivan LA, Bush RT, McConchie D (2000) A modified chromium reducible sulfur method for reduced inorganic sulfur: optimum reaction time in acid sulfate soil. *Australian Journal of Soil Research*, 38, 729-34.

Sullivan LA, Fitzpatrick RW, Burton ED, Bush RT, Shand P (2008b) Assessing environmental hazards posed by acid sulfate soil materials and other inorganic sulfide-containing soil materials: classification issues. Plenary Paper, Joint Conference of the $6th$ International Symposium in Acid Sulfate Soils and the Acid Rock Drainage Symposium. Guangzhou, China, 16-20 September 2008.

Sullivan LA, Ward NJ, Bush RT (2001) Chemical analysis for acid sulfate soil management. *In* 'Proceedings of the 2nd Australia and New Zealand Conference on Environmental Geotechnics - Geoenvironment 2001. Newcastle, November 28-30 2001) (Australian Geomechanics Society Inc. Newcastle) pp. 109-120. (Australian Geomechanics Society Inc. Newcastle).

Sullivan LA, Ward NJ, Bush RT, Lin, C (2002b) Evaluation of approaches to the chemical analysis of acid sulfate soil. *In* 'Acid sulfate soils in Australia and China.' (Eds C. Lin, M. Melville and L.A Sullivan) pp. 72-82. (Science Press, Beijing).

Sundström R, Aström M, Österholm P (2002) Comparison of metal content in acid sulfate soil runoff and industrial effluents in Finland. *Environmental Science & Technology* 36, 4269-4272.

Ward NJ, Sullivan LA, Bush RT (2002) Sulfide oxidation and acidification of acid sulfate soil materials treated with $CaCO₃$ and seawater-neutralised bauxite refinery residue. *Australian Journal of Soil Research* 40, 1057-1067.

World Wide Fund for Nature & National Parks Association, and National Parks and Wildlife Service (1999) Information Sheet on Ramsar Wetlands (RIS) – Gwydir Wetlands: Gingham and Lower Gwydir (Big Leather) Watercourses. http://www.wetlands.org/reports/ris/5AU051en.pdf (last accessed 21/04/2009).

7. APPENDICES

Table 7-1 Gwydir site and sample descriptions.

APPENDIX 2. Field and laboratory analytical soil data

Table 7-2 Gwydir field and laboratory analytical soil data.

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).

