

Assessment of Acid Sulfate Soil Materials in the Talwood-Mungindi Region of the Murray-Darling Basin

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Cover Photograph

Trent McIntyre collecting water samples in the irrigation channel (site 80050_1). Photograph: Dr V.N.L. Wong.

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EXECUTIVE SUMMARY

The Talwood-Mungindi region is located in the Weir River catchment, approximately 90 km south-east of St George in south-east Queensland, and close to the Queensland/New South Wales border. The Talwood-Mungindi region is primarily a cotton growing region, with water in this flat landscape being supplied by a series of storage dams and irrigation channels. Irrigation infrastructure constructed into naturally saline subsoil has often been found to provide suitable conditions for sulfide formation (Biggs and King 2008). Previous surveys have found the presence sulfidic sediments at sites within an irrigation channel in the Talwood-Mungindi region.

The Murray-Darling Basin Authority (MDBA), in partnership with its Partner Governments and scientists, instigated the Murray-Darling Basin Acid Sulfate Soil Risk Assessment Project (MDB ASSRAP), which aims to assess the spatial 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.

The MDBA Acid Sulfate Soil Risk Assessment Advisory Panel prioritised 96 wetlands throughout the Murray-Darling Basin for detailed acid sulfate soil assessment. This report provides the results of Phase 1 of a two-phased detailed acid sulfate soil assessment procedure for priority wetlands in the Talwood-Mungindi region. This Phase 1 report is aimed solely at determining whether or not acid sulfate soil materials are present in the Talwood-Mungindi region priority wetland.

Acid sulfate soils occurred at two of the eight sites examined in the Talwood-Mungindi wetland. Sulfuric materials were not observed, and although 25% 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 0.02%). Sulfidic sediments were also only present in the subsoil layers (i.e. below a depth of 10 cm). Hypersulfidic soil materials were present in one soil profile (this profile also contained a hyposulfidic material), and another soil profile contained a hyposulfidic material (with S_{CR} < 0.10%). These results indicate that minimal acidity would be produced upon oxidation of sulfides in these materials.

While monosulfidic black ooze (MBO) was not observed at the time of sampling, all sulfidic soils were identified as being monosulfidic. However, none of the soil materials contained soluble sulfate in excess of the 100 mg/kg trigger value for MBO formation potential. Other acidic soil materials were also observed at an additional three sites.

Based on the priority ranking criteria adopted by the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soil Risk Assessment Project, there were two high priority sites based on the presence of monosulfidic materials. One of these sites would also be classified as high priority based on the presence of hypersulfidic materials, and both sites contained hyposulfidic materials (S_{CR} < 0.10%) with a moderate priority. None of the sites had a high priority ranking for Phase 2 detailed assessment based on MBO formation hazard.

The potential hazards at a wetland-scale posed by acid sulfate soil materials in the priority wetland in the Talwood-Mungindi region are as below:

 Acidification: The data indicate that with low net acidities, and only four sulfidic materials (where the highest S_{CR} was only 0.02% S), that the degree of acidification hazard is low.

- Deoxygenation: The data indicate that with low soluble sulfate contents, and only four monosulfidic materials (where the highest S_{AV} was 0.02% S) at a depth of greater than 10 cm, that the degree of deoxygenation hazard is low.
- Metal mobilisation: The low acidification hazard indicates that soil acidification is not likely to increase the solubility of metals.

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1. INTRODUCTION

1.1. Region overview

The Talwood-Mungindi region is located in the Weir River catchment, approximately 90 km south-east of St George in south-east Queensland, and close to the Queensland/New South Wales border. The Talwood-Mungindi region is primarily a cotton growing region, with water in this flat landscape being supplied by a series of storage dams and irrigation channels. Irrigation infrastructure (i.e. sumps, excavations and channels) constructed into naturally saline subsoil has often been found to provide suitable conditions for sulfide formation (Biggs and King 2008). Visual evidence has indicated that greater concentrations of monosulfidic black ooze (MBO) were usually observed in sediments with gypsum, tailwater channels, low gradient channels, sumps, and below-ground structures (Biggs and King 2008). In areas where gypsum was present, organic carbon and soil moisture seemed to be the limiting factors in MBO accumulation (Biggs and King 2008). Previous surveys in 2008/09 have found the presence sulfidic sediments at sites within an irrigation channel in the Talwood-Mungindi region (Appendix 3).

In September/October 2008, a rapid assessment of acid sulfate soils in 200 inland wetland areas in the Queensland Murray-Darling Basin (MDB) was undertaken as part of the MDB Acid Sulfate Soil Risk Assessment Project (ASSRAP) (Biggs and King 2008). Wetlands were identified for acid sulfate soil assessment based on their environmental significance as well as those that may pose a risk to surrounding waters. Wetlands were also chosen to cover a variety of landscapes, climatic zones and land uses throughout the Basin. The Talwood-Mungindi region was selected for further detailed assessment based on being identified as having a high priority as result of both soil and water parameters exceeding screening trigger values (see Appendix 2), and having a risk profile. The parameters found to exceed the ASSRAP trigger values in an irrigation channel and their score priority level are shown in Table 1-1. The region has since been affected by a major flood event which occurred in March 2010.

Wetland ID	pH Soil	рH Water	EC Soil	EC Water	Sulfate Soil	Sulfate Water	Priority
80050		-				High	High
80051	Moderate	٠	High	High		High	High
80052	Moderate	٠	High	High	$\overline{}$	High	High
80053	Moderate	۰	High	High		High	High
80054		۰				Moderate	Moderate

Table 1-1: Summary of parameters exceeding the ASSRAP trigger values and score priority level.

The typical landscape and soil profile (0-40 cm) observed in the Talwood-Mungindi region is shown in Figure 1-1.

Figure 1-1. Typical landscape and soil profile (0-40 cm) in the Talwood-Mungindi priority wetland (site 80050_3).

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 $(FeS₂)$ 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).

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 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 urgent assessment.

Despite decades of scientific investigation of the ecological (e.g. Living Murray Icon Site Environmental Management Plan: MDBC 2006a,b,c), hydrological, water quality (salinity) and geological features of wetlands in the MDB, we have only recently advanced far enough to appreciate the wide spectrum of acid sulfate soil subtypes and processes that are operating in these contemporary environmental settings - especially from continued lowering of water levels (e.g. Lamontagne *et al.* 2004; Fitzpatrick *et al.* 2008a,b; Shand *et al.* 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.

Wetlands were identified for assessment based on their environmental significance as well as those that may pose a risk to surrounding waters. Through consultation with jurisdictions more than 19,000 wetlands within the MDB were identified. 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. In addition, due to the risk profile, wetlands along the Murray River between Blanchetown (Lock 1) and Wellington were also selected for immediate detailed acid sulfate soil assessment. For all other wetlands, a three tiered assessment process was developed, commencing with a desktop assessment, followed by on-ground rapid assessment and then detailed on-ground assessment at sites identified as high priority or having a risk profile. A total of 96 wetlands were identified and selected for further detailed assessment (Figure 1-2). These wetlands were divided for logistical reasons into the following seven regions:

- Murray River, Lock 1 to Lock 3, SA (21 wetlands),
- Murray River, Lock 3 to Lock 5, SA (31 wetlands),
- Mildura region, NSW and Vic (8 wetlands),
- Edward and Wakool Rivers, NSW (12 wetlands),
- Murray River, Hume to Yarrawonga, NSW and Vic (6 wetlands),
- Talwood-Mungindi region, Queensland (1 wetland), and
- Victorian Northern Flowing Rivers (17 wetlands).

Figure 1-2. Map showing priority wetlands surveyed in the Murray-Darling Basin (source: MDBA).

Southern Cross GeoScience carried out a detailed assessment at eight representative sites within one wetland in the Talwood-Mungindi region in April 2010 to determine whether acid sulfate soils were present, or if there was a potential for acid sulfate soils to form within these

wetlands (Figure 1-3). This assessment included the determination of sulfide content within the soil profile at each site. Water-soluble sulfate was used as an indicator of the potential of monosulfide black ooze (MBO) formation in these wetland sites.

Figure 1-3. Map showing the area assessed in the Talwood-Mungindi region.

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 developed by the MDB ASS Risk Assessment Project Scientific Reference Panel requires a two-phase procedure (MDBA 2010).

Phase 1 investigations determine whether or not acid sulfate soil materials are present (or absent) for the study area, and provide characterisation of the properties and types of acid sulfate soil materials.

Phase 1 activities include:

- site selection
- site and profile description
- sample collection and storage
- laboratory analysis (of soil and water)
- identification of acid sulfate soil materials
- prioritisation and selection of Phase 2 samples
- interpretation and reporting

Phase 2 investigations will only be conducted if the acid sulfate soil materials from Phase 1 are determined to be a priority concern for the study area and, based on Phase 1 recommendations, samples will undergo further investigations to determine their nature and severity and the specific risks associated with the acid sulfate soil materials.

Phase 2 activities include:

- laboratory analysis (of soil)
- risk assessment
- interpretation and reporting, including discussion on broad acid sulfate soil management options

The soil samples to be analysed for Phase 2 will have been collected as part of the Phase 1 field assessment and then put into storage. Based on the Phase 1 report recommendations the client will identify samples and the analyses to be conducted on each of the samples for Phase 2.

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 a priority wetland in the Talwood-Mungindi region.

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

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

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

- Potential Sulfidic Acidity (PSA) also known as the 'acid generation potential' (AGP) is most easily and accurately determined by assessing the Chromium reducible sulfur (S_{CR} or CRS) and then converting this to PSA (AGP) as described in Ahern *et al.* (2004).
- Titratable Actual Acidity (TAA) is a measure of the actual acidity in acid sulfate soil materials that have already oxidised. It measures the sum of both soluble and exchangeable acidity.
- Retained Acidity (RA) is the acidity 'stored' in minerals such as jarosite, schwertmannite and other hydroxy sulfate minerals. Although these minerals may be stable under acidic conditions, they can release acidity to the environment when these conditions change.
- Acid Neutralising Capacity (ANC) is measured in soils with pH_{KCl} values > 6.5 . These soils may potentially have ANC in the form of (usually) carbonate minerals, principally of calcium, magnesium and sodium. The carbonate minerals present are estimated by titration and alkalinity present expressed in $CaCO₃$ equivalents. By accepted definition (Ahern *et al.* 2004), any acid sulfate soil material with a pH_{KCl} < 6.5 has a zero ANC.

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

1.5. Classification of soil materials

Recently, the Acid Sulfate Soils Working Group of the International Union of Soil Sciences agreed to adopt in principle the following five descriptive terminology and classification definitions of acid sulfate soil materials proposed by Professor Leigh Sullivan and co-authors in a plenary lecture and Acid Sulfate Soils Working Group meeting at the $6th$ International Acid Sulfate Soil and Acid Rock Drainage Conference in September 2008 in Guangzhou, China (Sullivan *et al.* 2008b). This new classification system for acid sulfate soil materials (Sullivan *et al.* 2009) has also been recently (October 2008) adopted by the Scientific Reference Panel of the Murray–Darling Basin Acid Sulfate Soil Risk Assessment Project for use in the detailed assessment of acid sulfate soils in the Murray–Darling Basin.

The criteria to define the soil materials are as follows:

- **1. Sulfuric materials** soil materials currently defined as sulfuric by the Australian Soil Classification (Isbell 1996). Essentially, these are soil materials with a $pH_W < 4$ as a result of sulfide oxidation.
- **2. Sulfidic materials*** soil materials containing detectable sulfide minerals (defined as containing greater than or equal to 0.01% sulfidic S). The intent is for this term to be used in a descriptive context (e.g. sulfidic soil material or sulfidic sediment) and to align with general definitions applied by other scientific disciplines such as geology and ecology (e.g. sulfidic sediment). The method with the lowest detection limit is the Cr-reducible sulfide method, which currently has a detection limit of 0.01%; other methods (e.g. X-ray diffraction, visual identification, Raman spectroscopy or infra red spectroscopy) can also be used to identify sulfidic materials.

**This term differs from previously published definitions in various soil classifications (e.g. Isbell, 1996).*

- **3. Hypersulfidic material** Hypersulfidic material is a sulfidic material that (i) has a field pH of 4 or more and (ii) is identified by experiencing a substantial* drop in pH to 4 or less (1:1 by weight in water, or in a minimum of water to permit measurement) when a 2–10 mm thick layer is incubated aerobically at field capacity. The duration of the incubation is either:
	- a. until the soil pH changes by at least 0.5 pH unit to below 4; or
	- b. until a stable** pH is reached after at least 8 weeks of incubation.

**A substantial drop in pH arising from incubation is regarded as an overall decrease of at least 0.5 pH unit.*

***A stable pH is assumed to have been reached after at least 8 weeks of incubation when either the decrease in pH is < 0.1 pH unit over at least a 14 day period, or the pH begins to increase.*

4. Hyposulfidic material – Hyposulfidic material is a sulfidic material that (i) has a field pH of 4 or more and (ii) does not experience a substantial* drop in pH to 4 or less (1:1 by weight in water, or in a minimum of water to permit measurement) when a 2–10 mm thick layer is incubated aerobically at field capacity. The duration of the incubation is until a stable** pH is reached after at least 8 weeks of incubation.

**A substantial drop in pH arising from incubation is regarded as an overall decrease of at least 0.5 pH unit.*

***A stable pH is assumed to have been reached after at least 8 weeks of incubation when either the decrease in pH is < 0.1 pH unit over at least a 14 day period, or the pH begins to increase.*

5. Monosulfidic materials – soil materials with an acid volatile sulfide content of 0.01% S or more.

Non-Acid Sulfate Soil materials

In addition the Scientific Reference Panel of the Murray–Darling Basin Acid Sulfate Soil Risk Assessment Project agreed to identify the other acidic soil materials arising from the detailed assessment of wetland soils in the Murray–Darling Basin, even though these materials may not be the result of acid sulfate soil processes (e.g. the acidity developed during ageing may be the result of $Fe²⁺$ hydrolysis, which may or may not be associated with acid sulfate soil processes). The acidity present in field soils may also be due to the accumulation of acidic organic matter and/or the leaching of bases. Of course, these acidic soil materials may also pose a risk to the environment and would be identified during the present course of the Phase 1 detailed assessment. The definition of these other acidic soil materials for the detailed assessment of acid sulfate soils in the Murray–Darling Basin is as follows:

- **1. Other acidic soil materials** either:
	- a. non-sulfidic soil materials that acidify by at least a 0.5 pH_w unit to a pH_w of < 5.5 during moist aerobic incubation
	- 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. Field sampling of soils and waters

Field sampling of the Talwood-Mungindi region priority wetland was undertaken on $23rd$ April 2010. The water depth of the channel was deep for the time of the year due to flooding and water harvesting. This had an impact on sampling (i.e. could not see the bottom of the channel) and water quality (i.e. dilution).

A total of 36 soil samples were collected and analysed from eight representative soil profiles within the irrigation channel to assess the current and potential environmental hazard due to the presence of acid sulfate soils (Figure 1-3).

The number of sites sampled within the wetland was dependant on the size of the wetland (Table 2-1). A total of 8 sites were sampled in the Talwood-Mungindi priority wetland (Table 2-2). Sites were selected to ensure that the samples obtained were representative of each wetland for acid sulfate soil assessment. The rationale for site selection within each wetland is presented in Section 2.4.1 and Appendix 1.

Soil profiles were sampled along a hydro-toposequence where the profiles were chosen to represent: (i) the centre of the channel, and (ii) the channel edge. Soil samples were collected from at least five sampling depths (to a maximum depth of 90 cm) using a range of implements. Soil samples were obtained by using a bucket to grab the upper 10 cm and then a gouge auger was used to approximately 90 cm depth. Soil samples were collected in two separate plastic jars (70 mL) with a screw top lid. Additional soil samples (500 g) were packed into plastic bags in which retained air was minimised for potential future Phase 2 laboratory analysis. Monosulfides were not present at any of the sites at the time of sampling. All soil samples were maintained at $\leq 4^{\circ}$ C prior to analysis.

Soil samples from each depth at all sites were placed into two separate chip-trays. One tray was used in the determination of the pH following incubation ($pH_{\text{INCIIBATION}}$) and the other was for long term archive storage.

Site and profile descriptions including global positioning system (GPS) coordinates are presented in Appendix 1. Digital photographs were also taken to document each site and soil profile characteristics (see Appendix 1).

Surface water quality data was collected from 8 locations in the irrigation channel at a depth of 0–30 cm. 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 (Method 2320B) (APHA 2005).

Filtered (0.45 µm) water samples were collected in 125 mL polyethylene bottles. Samples analysed for metals were acidified with a couple of drops of 0.5 % v/v high grade hydrochloric acid (HCI). Samples were stored at $\leq 4^{\circ}$ C and sent to the Environmental Analysis Laboratory, Southern Cross University for laboratory analysis.

Further details on the procedures followed in collection and storage of soil and water samples are presented in MDBA (2010).

2.2. 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.

The moisture content of each soil sample was determined following oven-drying at 80° C (Ahern *et al.* 2004). 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 $pH_{\text{INCLIBATION}}$, titratable actual acidity (TAA), water soluble sulfate, chromium reducible sulfur (S_{CR}) , retained acidity (RA), acid neutralising capacity (ANC), and acid volatile sulfide (S_{AV}) .

The existing acidity of each soil layer (pH_W) was assessed by measuring the pH in a saturated paste (1:1 soil:water mixture) (Rayment and Higginson, 1992). The pH_{FOX} was determined following oxidation with 30 % hydrogen peroxide $(H₂O₂)$ (Method 4E1) (Rayment and Higginson, 1992). The KCI extractable pH (pH_{KCl}) was measured in a 1:40 1.0 M KCI 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 ($pH_{\text{INCUBATION}}$) was determined on duplicate moistened soil materials placed in chip trays (Fitzpatrick *et al*. 2008c; Sullivan *et al*. 2009). 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 conducted on surface soil samples and was prepared following the procedures described in Rayment and Higginson (1992). Water soluble sulfate was 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). The acid volatile sulfide fraction was extracted using a cold diffusion procedure (Hsieh *et al.* 2002).

Retained acidity (RA) was determined from the difference between 4M HCl extractable sulfur (S_{HCl}) and 1M KCl extractable sulfur (S_{KCl}) when the sample pH_{KCl} was < 4.5 (Method Code 20J) (Ahern *et al.* 2004). The retained acidity identifies stored soil acidity in the form of jarosite and similar relatively insoluble iron and aluminium hydroxy sulfate compounds (Ahern *et al.* 2004). Acid Neutralising Capacity, measured by the ANC_{BT} method (Method Code 19A2) (Ahern *et al.* 2004) was determined for sulfidic samples with a pH_{KCl} \geq 6.5. The Net Acidity was estimated by the Acid-Base Account method of Ahern *et al.* (2004). The objective of each method is discussed further in MDBA (2010).

2.3. Laboratory water analysis methods

The analysis of all water samples in this study was carried out by the Environmental Analysis Laboratory (EAL) at Southern Cross University. The water quality parameters measured on filter samples $(0.45 \mu m)$ in this study included:

- major cations (Na, K, Ca, Mg) and Si (APHA 3120 ICPOES) (APHA 2005),
- dissolved bromide (APHA 4500 Br) and chloride (APHA 4500 Cl) (APHA 2005),
- dissolved nitrate $(NO₃)$ (APHA 4500 $NO₃)$ (APHA 2005),
- \bullet dissolved ammonia (NH₄) (APHA 4500 NH₃-H) (APHA 2005),
- \bullet dissolved phosphate (PO₄) (APHA 4500 P-E) (APHA 2005),
- dissolved sulfate $(SO₄²)$ (APHA 3120 ICPOES) (APHA 2005),
- trace metals (Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Zn) (APHA 2005), and
- dissolved organic carbon (APHA 2005).

2.4. Quality assurance and quality control

2.4.1. Site selection and sample collection

The Senior Soil Surveyor for all the sampling undertaken in the Talwood-Mungindi priority wetland was Dr Vanessa Wong. Sampling was undertaken by Dr Vanessa Wong and Trent McIntyre on 23rd April 2010. A summary of what was done to select the site location and layers that were sampled is presented below in Table 2-3.

Wetland	Main Name	Date	Comments on site/layer selection
ID		Sampled	
80050	Talwood- Mungindi	23/04/2010	Sites were chosen where MBOs were previously suspected to occur. Sites were identified by Andrew Biggs (QId DERM). Layers were selected in accordance with the sampling protocols (i.e. sampled at the following depths: 0- 5 cm, 5-10 cm, 10-20 cm, 20-40 cm and 40-90 cm). At some locations samples were not collected below 40 cm due to the presence of bedrock. The water depth of the channel was deep for the time of year due to flooding and water harvesting. This had an impact on sampling (i.e. could not see the bottom of the channel) and water quality (i.e. dilution).

Table 2-3. Summary of site and layer selection for the Talwood-Mungindi priority wetland.

2.4.2. Laboratory analysis

For all tests and analyses, the Quality Assurance and Quality Control procedures were equivalent to those endorsed by NATA (National Association of Testing Authorities). The standard procedures followed included the monitoring of blanks, duplicate analysis of at least 1 in 10 samples, and the inclusion of standards in each batch.

Reagent blanks and method blanks were prepared and analysed for each method. All blanks examined here were either at, or very close to, the limits of detection. On average, the frequencies of quality control samples processed were: 8% blanks, 10% laboratory duplicates, and 6% laboratory controls. The analytical precision was ±5% for all analyses.

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

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

High Priority

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

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

The pH_W, pH_{FOX}, pH_{KCl} and pH_{INCUBATION} data for the wetland sites examined in the Talwood-Mungindi region are presented in Appendix 1 (Table 8-2) and summarised in Table 3-1. The pH_W values ranged between 4.41 and 8.11, with the majority of the samples having a $pH_W > 0$ 6.0. None of the soils in the Talwood-Mungindi region are classified as sulfuric materials as all soils had a $pH_W > 4$.

The pH_F_{OX} values ranged between 3.95 and 8.36. The majority of the soils showed a pH increase after treatment with peroxide due to the presence of carbonate and other minerals (e.g. Figure 3-1). None of the soil materials had a pH_{FOX} value < 2.5. The pH_{FOX} results indicate that one of the surface soils in the Talwood-Mungindi region (i.e. site 80050_4 (20- 40 cm)) may have the potential to acidify to pH < 4 as a result of sulfide oxidation. However, the S_{CR} data shows this layer contained no detectable sulfide (i.e. S_{CR} < 0.01% S).

The $pH_{\text{INCUBATION}}$ values ranged between 3.93 and 7.30. None of the sulfidic soil materials (i.e. $S_{CR} \ge 0.01\%$ S) acidified to pH < 4 after at least 8 weeks of incubation. However, two sulfidic soil materials (i.e. site 80050_7 (20-40 cm and 40-90 cm)) were classified as hypersulfidic as they both had positive net acidities (see Section 2.5). Other acidic soils (i.e. pH_w &/or $pH_{\text{INCUBATION}}$ 4 – 5.5) were identified at three sites (i.e. sites 80050 4 (5-40 cm), 80050_6 (20-40 cm) and 80050_8 (20-40 cm)), indicating acidity in the soil profile at levels where aluminium may mobilise. Two of these acidic soils (i.e. sites 80050_4 (20-40 cm) and 80050_8 (20-40 cm)) acidified to pH < 4 after at least 8 weeks of incubation.

Parameter	Units	Minimum	Median	Maximum	n ¹
pH_w^2		4.41	7.01	8.11	36
pH_{FOX}^3		3.95	7.42	8.36	36
pH_{KCI}^4		4.33	7.62	8.33	36
pHINCUBATION		3.93	6.86	7.30	36
TAA ⁶	mole H ⁺ /tonne	0.00	0.00	50.30	36
Soluble SO_4^7	mg/kg $SO4$	8	10	21	8
$S_{CR}^{\ \ \, 8}$	Wt. %S	< 0.01	< 0.01	0.02	36
S_{AV}^9	Wt. %S	< 0.01	< 0.01	0.02	36
RA^{10}	mole H ⁺ /tonne	0.00	0.00	0.00	36
ANC ¹¹	%CaCO ₃	0.00	0.98	7.00	36
NA ¹²	mole H ⁺ /tonne	-931.96	-129.94	50.30	36

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% 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 S_{AV} : Acid Volatile Sulfide.¹⁰ RA: Retained Acidity.¹¹ ANC: Acid Neutralising Capacity: by definition, where pH k cl < 6.5 ANC = 0.¹² NA: Net Acidity.

Figure 3-1. Depth profiles of soil pH for sites 80050 7 and 80050 8, showing soil pH (pH_w as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH (pH_{incubation} after at least 8 weeks as purple line). Critical pH_w and pH_{incubation} value of 4 (green dashed line) and critical **pH_{FOX}** value of 2.5 (red dashed line).

3.1.2. Chromium Reducible Sulfur (S_{CR})

The chromium reducible sulfur (S_{CR}) data for the wetland sites examined in the Talwood-Mungindi region are presented in Appendix 1 (Table 8-2) and summarised in Table 3-1. The S_{CR} values ranged between < 0.01 and 0.02% S. Sulfidic soil materials (i.e. $S_{CR} \ge 0.01\%$ S) were identified at two sampling sites (sites 80050_2 and 80050_7), with only four materials of the 36 samples collected equal to or greater than the sulfidic criterion. Two soil materials at sites 80050_2 (20-40 cm) and 80050_7 (10-20 cm) had a S_{CR} of 0.01% S. A S_{CR} of 0.02% S was identified in two soil materials at site 80050 7 (20-40 cm and 40-90 cm).

3.1.3. Acid volatile sulfide (SAV)

The acid volatile sulfide (S_{AV}) data for wetland sites examined in the Talwood-Mungindi region are presented in Appendix 1 (Table 8-2) and summarised in Table 3-1. The S_{AV} values ranged between < 0.01 and 0.02% S. Monosulfidic soil materials (i.e. $S_{AV} \ge 0.01\%$ S) were found at sites 80050_2 (20-40 cm) and 80050_7 (10-90 cm). No pyritic sulfur was found in the four sulfidic soil materials as the S_{AV} fraction accounted for the total S_{CR} fraction.

3.1.4. Acid Neutralising Capacity (ANC)

The acid neutralising capacity (ANC) data for the wetland sites examined in the Talwood-Mungindi region are presented in Appendix 1 (Table 8-2) and summarised in Table 3-1. The ANC ranged between zero and 7.00% CaCO₃ (see Table 3-1).

3.1.5. Net Acidity (NA)

The net acidity data for the wetland sites examined in the Talwood-Mungindi region are presented in Appendix 1 (Table 8-2) and summarised in Table 3-1. Acid-base accounting calculations showed the net acidity ranged between -931 and 50 mole H⁺/tonne, with the majority of samples (except at site 80050_8) having negative net acidities.

The net acidity thresholds used to characterise the acid sulfate soil materials in this assessment include low net acidity (< 19 mole H⁺/tonne), moderate net acidity (19 - 100 mole H⁺/tonne) and high net acidity (> 100 mole H⁺/tonne). The acidification hazard from acid sulfate soil disturbance posed by the four sulfidic soil materials is low (see Figures 8-9 and 8-10, Appendix 1). The hypersulfidic soils (site 80050_7: 20-40 cm and 40-90 cm) had low net acidities of 11 and 15 mole H⁺/tonne, respectively (Table 8-2, Appendix 1). The hyposulfidic soil (S_{CR} < 0.10) materials (site 80050_2 (20-40 cm) and 80050_7 (10-20 cm)) both had negative net acidities. The positive net acidities in the non-sulfidic samples were due to the presence of some TAA and the lack of any ANC (Table 8-2, Appendix 1).

3.1.6. Water soluble SO4

The water soluble SO_4 data for the wetland sites examined in the Talwood-Mungindi region are presented in Appendix 1 (Table 8-2) and summarised in Table 3-1. The water soluble SO4 in the surface soils (i.e. 0-5 cm) in the irrigation channel ranged between 8 and 21 mg/kg. None of the surface soil layers examined had a soluble $SO₄$ content exceeding the 100 mg/kg trigger value for MBO formation potential.

3.1.7. Titratable actual acidity (TAA)

The titratable actual acidity (TAA) data for the wetland sites examined in the Talwood-Mungindi region are presented in Appendix 1 (Table 8-2) and summarised in Table 3-1. The TAA ranged between zero and 50 mole H⁺/tonne, with the majority of soil layers having a TAA $<$ 10 mole H⁺/tonne. At the two sites where a positive TAA was measured throughout the profile (i.e. sites 80050_4 and 80050_8), an increase in the TAA with depth was observed (Figure 3-2).

3.1.8. Retained acidity (RA)

The retained acidity data for wetland sites examined in the Talwood-Mungindi region are presented in Appendix 1 (Table 8-2) and summarised in Table 3-1. Retained acidity was only measured at sites 80050_4 (20-40 cm) and 80050_8 (20-40 cm), as all other soil materials in the Talwood-Mungindi region had a $pH_{KCI} > 4.5$, and therefore no retained acidity. There was also no retained acidity in the two samples analysed.

Figure 3-2. Variation in TAA (mole H⁺ /tonne) with depth at site 80050_8.

3.2. Hydrochemistry

The hydrochemical characteristics of the surface waters in the irrigation channel were measured to provide an indication of the baseline water chemistry. Some of the chemical parameters measured may show temporal variations, particularly as a result of the recent flooding in the region, and therefore the data collected only represents a snapshot of the surface water quality in the irrigation channel.

Surface water quality data was collected from each of the 8 soil sampling sites in the irrigation channel. 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 1 (Table 8-4).

The field pH of the surface waters ranged between 9.0 and 9.5 (Table 3-2) with all sites 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 $SO₄$ concentrations ranged between 26 and 54 mg/L (Table 8-4, Appendix 1). The surface water SEC at the time of sampling ranged between 621 and 1268 μ S cm⁻¹. Some nutrient (i.e. NH₄, PO₄), metal (i.e. Al, Cr, Cu, Fe, Zn) and turbidity values were found to exceed the most relevant ANZECC/ARMCANZ (2000) guideline value (Table 8-4, Appendix 1).

	pH	SEC μ S/cm	DO mg/L	Eh mV	Turbidity NTU	Alkalinity* (mg/L as $HCO3$)
Minimum	8.95	621	8.85	84	138	640
Median	9.25	710	9.67	110	277	745
Maximum	9.51	1268	9.81	244	307	770
n'	8	8	8	8	8	8

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

 $*$ HCO₃ presented as phenolphthalein alkalinity (i.e. not total alkalinity) $¹$ n: number of samples</sup>

4. DISCUSSION

A detailed assessment was undertaken in the Talwood-Mungindi region in April 2010 to determine whether acid sulfate soils were present, or if there was a potential for acid sulfate soil to form within these wetlands. This study identified the presence of acid sulfate soil materials at two of the eight sites examined. The sulfidic materials were identified as being monosulfidic materials (i.e. $S_{AV} \ge 0.01\%$). One of the acid sulfate soil profiles was classified as hypermonosulfidic, and the other was classified as hypomonosulfidic (Sullivan *et al.* 2010). The four sulfidic materials identified at the two sites had low reduced inorganic sulfur contents (i.e. $S_{CR} \le 0.02\%$) and low net acidities (i.e. ≤ 15 mole H⁺/tonne). These results indicate that minimal acidity would be produced upon oxidation of sulfides in these materials. The deoxygenation hazard is also minimal despite the presence of monosulfidic materials, as the monosulfidic materials occurred at depth of ≥ 10 cm in the soil profile. In addition, none of the surface soil layers examined had a soluble $SO₄$ content exceeding the 100 mg/kg trigger value for MBO formation potential.

Previous studies in irrigation channels in the Talwood-Mungindi priority wetland have found higher sulfide contents (up to 0.13% S_{CB}) and high soluble sulfate levels (i.e. \geq 3210 mg/kg) within surface sediments (Table 8-8, Appendix 3). In this study sulfidic sediments were only identified below a depth of 10 cm suggesting that the major flood event a month prior to sampling in March 2010 may have removed the surface sulfidic sediments. However, the sulfidic sediments previously identified also had a low acidification hazard, as all materials had negative net acidities due to sufficient ANC to neutralise the TAA and the potential acidity produced from sulfide oxidation.

5. HAZARD ASSESSMENT

5.1. Interpretation of soil and water data

Sulfuric soil materials were not encountered in any of the sampling sites (Table 5-1).

Hypersulfidic materials occurred at depth of \geq 10 cm in the soil profile at two of the eight sampling locations (Table 5-1). The acidification hazard from acid sulfate soil disturbance posed by these samples is low, as the two hypersulfidic soil materials had low net acidities (i.e. ≤ 15 mole H⁺/tonne). Two hyposulfidic soil materials with S_{CR} < 0.10% were also present at the sampling sites.

All the sulfidic materials were identified as monosulfidic materials, however, none of the soluble sulfate contents of the surficial soil materials sampled exceeded the trigger value of 100 mg/kg for potential MBO formation (Table 5-1).

Other acid soil materials were identified at three sites with a $pH_W/pH_{INCUBATION}$ of between 4 and 5.5.

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

Table 5-1 Type and prevalence of acid sulfate soil materials.

6. CONCLUSIONS AND RECOMMENDATIONS

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 priority wetlands in the Talwood-Mungindi region. This Phase 1 report is aimed solely at determining whether or not acid sulfate soil materials are present in the Talwood-Mungindi region priority wetlands.

Acid sulfate soils occurred at two of the eight sites examined in the Talwood-Mungindi wetland. Sulfuric materials were not observed, and although 25% 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 0.02%). Sulfidic sediments were also only present in the subsoil layers (i.e. below a depth of 10 cm). Hypersulfidic soil materials were present in one soil profile (this profile also contained a hyposulfidic material), and another soil profile contained a hyposulfidic material (with S_{CR} < 0.10%). These results indicate that minimal acidity would be produced upon oxidation of sulfides in these materials.

While monosulfidic black ooze (MBO) was not observed at the time of sampling, all sulfidic soils were identified as being monosulfidic. However, none of the soil materials contained soluble sulfate in excess of the 100 mg/kg trigger value for MBO formation potential. Other acidic soil materials were also observed at an additional three sites.

Based on the priority ranking criteria adopted by the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soil Risk Assessment Project, there were two high priority sites based on the presence of monosulfidic materials. One of these sites would also be classified as high priority based on the presence of hypersulfidic materials, and both sites contained hyposulfidic materials (S_{CR} < 0.10%) with a moderate priority. None of the sites had a high priority ranking for Phase 2 detailed assessment based on MBO formation hazard.

The potential hazards at a wetland-scale posed by acid sulfate soil materials in the priority wetland in the Talwood-Mungindi region are as below:

- Acidification: The data indicate that with low net acidities, and only four sulfidic materials (where the highest S_{CR} was only 0.02% S), that the degree of acidification hazard is low.
- Deoxygenation: The data indicate that with low soluble sulfate contents, and only four monosulfidic materials (where the highest S_{AV} was 0.02% S) at a depth of greater than 10 cm, that the degree of deoxygenation hazard is low.
- Metal mobilisation: The low acidification hazard indicates that soil acidification is not likely to increase the solubility of metals.

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8. APPENDICES

APPENDIX 1. Wetland report

8.1. Talwood-Mungindi (Wetland ID 80050)

8.1.1. Location and setting description

The Talwood-Mungindi wetland is located approximately 32 km south-west of Talwood and approximately 10 km from the Macintyre River. The wetland is an irrigation channel approximately 20 m wide running NW-SE with a 90 degree bend at its northern edge. The wetland is bounded by cotton fields on the northern boundary and a dam on the southern boundary. The dam is approximately three metres above ground and was full at the time of sampling. There was approximately 1.0 - 1.5 m of overlying water in the channel. Salt crusts were evident in the banks and channels walls. Eight sites were sampled as shown in **Error! Reference source not found.**.

Figure 8-1. Talwood-Mungindi wetland and sample site locations.

8.1.2. Soil profile description and distribution

Eight sites were described and sampled. The soil subtype and general location description are presented in Table 8-1. Sites were sampled mid-channel and on the bank. All sites were fully submerged due to the volume of water present at the time of sampling.

Profiles 80050_1 and 80050_2 (Figure 8-3) occurred in the centre of the channel and on the edge of the channel, respectively. Profiles 80050_3 and 80050_4 (Figure 8-4) occurred in the centre of the channel and on the edge of the channel, respectively. Profiles 80050_5 and 80050 6 (Figure 8-5) occurred in the centre of the channel and on the edge of the channel, respectively. Profiles 80050_7 and 80050_8 (Figure 8-6) occurred in the centre of the channel and on the edge of the channel, respectively. Additional site and profile description data are presented in Tables 8-5 and 8-6, respectively.

Site ID	Easting UTM zone 54H	Northing UTM zone 54H	Acid sulfate soil subtype class	General location description
80050_1	714283	6829345	Subaqueous Soil	Mid-channel
80050 2	714283	6829345	Hypomonosulfidic Subaqueous Soil	Adjacent to 80050_1 on the bank of the channel
80050_3	714169	6829503	Subaqueous Soil	Approximately 100 m NW of sites 80050_1 and 80050_2; mid-channel
80050 4	714169	6829503	Subaqueous Soil	Adjacent to 80050_3 on the bank of the channel
80050 5	714083	6829626	Subaqueous Soil	Approximately 100 m NW of sites 80050_3 and 80050_4; mid-channel
80050_6	714083	6829626	Subaqueous Soil	Adjacent to 80050_5 on the bank of the channel
80050 7	714379	6829210	Hypermonosulfidic Subaqueous Soil	Approximately 100 m SE of sites 80050_1 and 80050_2; mid-channel
80050_8	714379	6829210	Subaqueous Soil	Adjacent to 80050_7 on the bank of the channel

Table 8-1. Soil identification, subtype and general location description for the irrigation channel.

Figure 8-2. Conceptual cross section diagram showing the hydro-toposequence relationship of the sediments/soil materials at sites 80050_7 and 80050_8.

Figure 8-3. Photographs of sites 80050_1 and 80050_2, showing the irrigation channel and the soil profile at site 80050_1 (0-40 cm).

Figure 8-4. Photographs of sites 80050_3 and 80050_4, showing the irrigation channel and the soil profile at site 80050_3 (0-40 cm).

Figure 8-5. Photographs of sites 80050_5 and 80050_6, showing the irrigation channel and the soil profile at site 80050_5 (0-40 cm).

Figure 8-6. Photographs of sites 80050_7 and 80050_8, showing the irrigation channel and the soil profile at site 80050_7 (0-40 cm).

8.1.3. Laboratory data assessment

Soil pH testing (pH_w, pH_{FOX}, pH_{KCI}, pH_{INCUBATION})

The pH data is provided in Table 8-2 and profiles for all the sites sampled are presented in Figures 8-7 and 8-8. The pH_W values ranged between 4.41 and 8.11, with the majority of the samples having a pH_W > 6.0. Sulfuric materials (i.e. pH_W < 4) were not present. The pH_{FOX} values ranged between 3.95 and 8.36. The pH_{FOX} results indicate that one of the surface soils may have the potential to acidify to pH < 4 as a result of sulfide oxidation. However, the S_{CR} data shows this layer contained no detectable sulfide (i.e. S_{CR} < 0.01% S). None of the sulfidic soil materials (i.e. $S_{CR} \ge 0.01\%$ S) acidified to pH < 4 after at least 8 weeks of incubation. Other acidic soil materials were identified at 3 sites, indicating acidity in the soil profile at levels where aluminium may mobilise.

Acid-base accounting

The acid-base accounting data is provided in Table 8-2 and summarised in Figures 8-9 and 8-10.

Chromium reducible sulfur

Chromium reducible sulfur (S_{CR}) values ranged between < 0.01 and 0.02% S. Sulfidic soil materials (i.e. $S_{CR} \ge 0.01\%$ S) were identified at two sampling sites (sites 80050_2 and 80050 7), with only four materials of the 36 samples collected equal to or greater than the sulfidic criterion.

Acid volatile sulfide

The acid volatile sulfide (S_{AV}) values ranged between $<$ 0.01 and 0.02% S. A total of four monosulfidic soil materials (i.e. $S_{AV} \ge 0.01\%$ S) were found at two sites (sites 80050_2 and 80050 7). No pyritic sulfur was found in the four sulfidic soil materials as the S_{AV} fraction accounted for the total S_{CR} fraction.

Acid neutralising capacity

The acid neutralising capacity (ANC) ranged between zero and 7.00% CaCO₃.

Titratable actual acidity

The titratable actual acidity (TAA) ranged between zero and 50 mole H⁺/tonne, with the majority of soil layers having a TAA $<$ 10 mole H⁺/tonne. At the two sites where a positive TAA was measured throughout the profile, an increase in the TAA with depth was observed.

Figure 8-7. Depth profiles of soil pH in the irrigation channel (80050_1 – 80050_4), showing soil pH (pH_w as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH (pH_{incubation} after at least 8 weeks as purple line). Critical pH_w and pH_{incubation} value of 4 (green dashed line) and critical pH_{FOX} value of 2.5 (red dashed line).

Figure 8-8. Depth profiles of soil pH in the irrigation channel (80050_5 – 80050_8), showing soil pH (pH_w as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH (pH_{incubation} after at least 8 weeks as purple line). Critical pH_w and pH_{incubation} value of 4 (green dashed line) and critical pH_{FOX} value of 2.5 (red dashed line).

Retained acidity

Retained acidity was not present in any of the soil materials.

Net acidity

Net acidity ranged between -931 and 50 mole H⁺/tonne, with the majority of samples having negative net acidities. The two hypersulfidic soils had low net acidities of 11 and 15 mole H+ /tonne.

Water Soluble Sulfate

The water soluble sulfate in the surface soils (i.e. 0-5 cm) ranged between 8 and 21 mg/kg. None of the surface soil layers examined had a soluble sulfate content exceeding the 100 mg/kg trigger value for MBO formation potential.

Water Data

The surface water data measured in the field and in the laboratory are presented in Tables 8-3 and 8-4, respectively. The field pH of the surface waters ranged between 9.0 and 9.5 with all sites 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 26 and 54 mg/L (Table 8-4, Appendix 1). Some nutrient (i.e. $NH₄$, PO₄), metal (i.e. Al, Cr, Cu, Fe, Zn) and turbidity values were found to exceed the most relevant ANZECC/ARMCANZ (2000) guideline value.

Figure 8-9. Acid-base accounting depth profiles in the irrigation channel (80050_1 – 80050_4). Left side shows the components: titratable actual acidity (TAA - red bar), acid generating potential (AGP as S_{CR} -pink bar), acid neutralising capacity (ANC - blue bar), retained acidity **(RA - yellow bar), and right side shows net acidity.**

Figure 8-10. Acid-base accounting depth profiles in the irrigation channel (80050_5 – 80050_8). Left side shows the components: titratable actual acidity (TAA - red bar), acid generating potential (AGP as S_{CR}-pink bar), acid neutralising capacity (ANC - blue bar), retained acidity **(RA - yellow bar), and right side shows net acidity.**

8.1.4. Discussion

Acid sulfate soils occurred at two of the eight sites examined in the Talwood-Mungindi wetland. Sulfidic sediments were only present in the subsoil layers (i.e. below a depth of 10 cm) at site 80050_7 (10-90 cm) and in one layer at site 80050_2 (20-40 cm).

Sulfuric materials were not observed in this wetland, and although 25% 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 0.02%). Hypersulfidic soil materials were present in one soil profile (this profile also contained a hyposulfidic material), and another soil profile contained a hyposulfidic material (with S_{CR} < 0.10%). These results indicate that minimal acidity would be produced upon oxidation of sulfides in these materials.

While monosulfidic black ooze (MBO) was not observed at the time of sampling, all sulfidic soils were identified as being monosulfidic. However, none of the soil materials contained soluble sulfate in excess of the 100 mg/kg trigger value for MBO formation potential. Other acidic soil materials were also observed at an additional three sites.

Based on the priority ranking criteria adopted by the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soil Risk Assessment Project, there were two high priority sites based on the presence of monosulfidic materials. One of these sites would also be classified as high priority based on the presence of hypersulfidic materials, and both sites contained hyposulfidic materials (S_{CR} < 0.10%) with a moderate priority. None of the sites had a high priority ranking for Phase 2 detailed assessment based on MBO formation hazard.

The potential hazards at a wetland-scale posed by acid sulfate soil materials in the priority wetland in the Talwood-Mungindi region are as below:

- Acidification: The data indicate that with low net acidities, and only four sulfidic materials (where the highest S_{CR} was only 0.02% S), that the degree of acidification hazard is low.
- Deoxygenation: The data indicate that with low soluble sulfate contents, and only four monosulfidic materials (where the highest S_{AV} was 0.02% S) at a depth of greater than 10 cm, that the degree of deoxygenation hazard is low.
- Metal mobilisation: The low acidification hazard indicates that soil acidification is not likely to increase the solubility of metals.

Summary of key findings for the Talwood-Mungindi priority wetland:

Table 8-2. Laboratory analytical data for acid sulfate soil assessment of the irrigation channel (Wetland ID 80050).

(red printed values indicate data results of potential concern)

* Indicates that a stable pH has not been reached after 11 weeks of incubation for this sample.

Waiting for additional incubation data to determine if this sample is stable.

Table 8-2 (continued). Laboratory analytical data for acid sulfate soil assessment of the irrigation channel (Wetland ID 80050).

(red printed values indicate data results of potential concern)

Classified as hypersulfidic based on positive net acidity.

Table 8-3. Field hydrochemistry data for acid sulfate soil assessment of the irrigation channel (Wetland ID 80050).

 1 HCO₃ presented as phenolphthalein alkalinity (i.e. not total alkalinity).

* ANZECC water quality guidelines for lowland rivers and freshwater lakes/reservoirs in South-east Australia are provided for relevant parameters (there are currently no trigger values defined for 'Wetlands') (ANZECC/ARMCANZ, 2000). Surface water values outside the ranges defined in the ANZECC guidelines are indicated with red text. (SW) and (PW) indicate whether the sample was taken from surface water or pore-water, respectively.

Parameter	units	ANZECC Guidelines	Site 1 (SW)	Site 2 (SW)	Site 3 (SW)	Site 4 (SW)	Site 5 (SW)	Site 6 (SW)	Site 7 (SW)	Site 8 (SW)
depth	cm									
Na	mg I^{-1}		113.3	69.3	87.5	91.5	80.5	85.1	106.6	100.7
Κ	$mgI-1$		9.1	6.3	8.2	9.4	7.2	8.3	11.3	7.9
Ca	$mgI-1$		33.6	18.6	26.3	25.7	23.8	25.3	31.9	30.1
Mg	$mgI-1$		18.2	11.4	13.4	13.6	13.1	12.8	16.8	15.6
Si	mg I^1		1.39	2.70	5.82	5.27	3.66	4.39	1.28	4.35
Br	mg Γ^1		0.619	0.353	0.458	0.456	0.447	0.429	0.589	0.542
CI	mgI^1		824	911	2,279	2,691	942	862	732	1,033
NO ₃	mgI^1	0.7	0.007	0.011	0.028	0.013	0.014	< 0.005	0.016	0.043
NH_4-N	$mgI-1$	0.01	0.021	0.067	0.059	0.023	0.052	0.032	0.066	0.056
PO_4 - P^E	mgI^1	0.005	0.007	0.030	0.028	0.012	0.022	0.011	0.037	0.023
SO ₄	$mgI-1$		54	$26\,$	38	34	32	35	50	45
Ag	μ g l ⁻¹	0.05	<1	$<$ 1	$<1\,$	$<$ 1	$<$ 1	$<$ 1	$<$ 1	$<$ 1
AI^A	μ g l $^{-1}$	55	48	260	141	166	304	309	89	261
As^{B}	μ g Γ^1	13	$\boldsymbol{2}$	$\mathbf{1}$	\overline{c}	\overline{c}	\overline{c}	$\overline{2}$	$\overline{\mathbf{c}}$	$\overline{2}$
Cd	μ g l ⁻¹	0.2	<1	$<$ 1	<1	<1	<1	$<$ 1	<1	$<1\,$
$\rm Co$	$\mu g \mid^{-1}$	2.8	$<$ 1	$<$ 1	$<$ 1	$<$ 1	$<$ 1	$<$ 1	$<$ 1	$<1\,$
Cr^C	$\mu g \mid^{-1}$	$\mathbf{1}$	$\mathbf{1}$	$\mathbf{1}$	$\overline{2}$	$\overline{2}$	$\overline{2}$	$\mathbf{1}$	$\mathbf{1}$	$\mathbf{1}$
Cu ^H	$\mu g \mid^{-1}$	1.4	25	11	$\overline{7}$	9	$\bf 6$	10	14	66
Fe	$\mu g \mid^{-1}$	300	50	280	156	178	334	348	70	278
Mn	μ g l ⁻¹	1700	7	33	17	17	50	41	12	38
Ni ^H	μ g l ⁻¹	11	$\,$ 5 $\,$	$\overline{\mathbf{4}}$	6	6	4	$\mathbf 5$	$\mathbf 5$	$\,$ 5 $\,$
Pb^H	μ g Γ^1	3.4	$<$ 1	$<$ 1	$<$ 1	$<$ 1	<1	$<$ 1	<1	$<$ 1
Se	μ g l ⁻¹	11	2	$\mathbf{1}$	2	$\sqrt{2}$	$\overline{2}$	2	\overline{c}	$\mathbf 2$
Zn^{H}	μ g l ⁻¹	$\bf 8$	37	33	36	171	76	26	41	59
DOC	mgI^1		31.7	31.9	36.9	23.3	28.8	21.7	34.7	51.5

Table 8-4. Laboratory hydrochemistry data for acid sulfate soil assessment of the irrigation channel (Wetland ID 80050).

Notes.

The ANZECC guideline values for toxicants refer to the Ecosystem Protection – Freshwater Guideline for protection of 95% of biota in 'slightly-moderately disturbed' systems, as outlined in the Australian Water Quality Guidelines for Fresh and Marine Water Quality (ANZECC/ARMCANZ, 2000). For the nutrients NH4 and PO4, guideline values are provided for Freshwater Lakes and Reservoirs. Surface water values outside the ranges defined in the ANZECC guidelines are indicated with red text. (SW) and (PW) indicate whether the sample was taken from surface water or pit-water (groundwater that entered an excavated pit), *respectively.*

- ^A*Guideline is for Aluminium in freshwater where pH > 6.5.*
- B Guideline assumes As in solution as Arsenic (AsV).
- ^C*Guideline is for Chromium is applicable to Chromium (CrVI) only.*
- ^E*Guideline is for filterable reactive phosphorous (FRP).*
- H *Hardness affected (refer to Guidelines).*

Table 8-6. Profile description data for acid sulfate soil assessment of the irrigation channel (Wetland ID 80050).

Table 8-6 (continued). Profile description data for acid sulfate soil assessment of the irrigation channel (Wetland ID 80050).

APPENDIX 2. ASSRAP screening criteria

Table 8-7. Screening criteria for selecting detailed acid sulfate soil assessment study areas developed by the Scientific Reference Panel of the Acid Sulfate Soils Risk Assessment Project (source: MDBA 2010).

* As determined by both in-field measurements and subsequent analysis of samples collected in chiptrays.

APPENDIX 3. Additional data

Wetland	Date	Depth	1 EC	2 pH _w	3 pH _{KCI}	4TAA	5 CRS	⁶ ANC	Net Acidity	⁸ AVS	Total Carbon	$^{9}SO_4$
ID	Sampled	(m)	(dS/m)			(mole H^+ /t)	$(*SCR)$	$(\%$ CaCO ₃)	(mole H^{\dagger}/t)	$(*S_{AV})$	$(\%C)$	(mg SO_4/kg)
80051	23-Sep-08	$0.00 - 0.05$	6.53	7.9	7.70	0	0.03	.50	-181	< 0.005	1.33	3810
80052	23-Sep-08	$0.03 - 0.11$	3.66	7.8	6.80	0	< 0.02	0.80		< 0.005	0.62	3210
80053	23-Sep-08	$0.10 - 0.30$	4.89	7.8	7.10	Ω	< 0.02	0.90		< 0.005	0.45	3900
	30-Jul-07	$0.00 - 0.02$	36.30	7.7	7.6	0	< 0.02	0.80			0.46	
	30-Jul-07	$0.02 - 0.10$	6.88	6.2	5.5	$<$ 10	<0.02	< 0.5	٠	۰	0.35	
	30-Jul-07	$0.02 - 0.10$	14.00	7.5	7.4	0	0.03	0.90	-101	۰	0.71	
	30-Jul-07	$0.10 - 0.20$	17.40	7.2	6.9	0	0.07	0.80	-63	۰	0.69	
	14-Mar-07	$0.00 - 0.10$	7.56	7.7	7.6	0	0.13	1.00	-52	۰	0.80	$\overline{}$
	14-Mar-07	$0.00 - 0.10$	6.76	7.6	7.4	0	0.03	0.90	-101	۰	0.64	$\overline{}$

Table 8-8. Summary of additional laboratory data for the irrigation channel (source: Qld DERM unpublished data).

¹EC: electrical conductivity (1:5 soil:water). ²pH_w: pH water (1:5 soil:water). ³pH_{KCl}: pH in KCl. ⁴TAA: titratable actual acidity. ⁵CRS: chromium reducible sulfur. ⁶ANC: acid neutralising capacity. ⁷Net acidity does not include retained acidity. ⁸AVS: acid volatile sulfide. ⁹ SO₄: soluble sulfate: in 1:5 soil:water extract.

