

Distribution and hazard of sulfidic sediments in a river and creek channel system of the Murray Darling Basin: Edward-Wakool channel system case study.

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Cover Photograph

Sampling in the Edward-Wakool River system.

Photographer: Mitch Tulau.

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EXECUTIVE SUMMARY

The Edward-Wakool River system is a complex network of inter-connecting rivers, creeks, flood-runners and artificial channels located north of the River Murray and west of Deniliquin (Baldwin 2009). Acid sulfate soils have been observed in the main channel of the Wakool River, Niemur River and a number of associated creek systems (e.g. Baldwin 2008, 2009; Tulau 2009; Ward *et al.* 2010b,c). However, at many sites within channels in the Edward-Wakool River system, the identification of sulfidic sediments has relied only on visual indicators.

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.

This report provides the results of Phase 1 of a two-phased detailed acid sulfate soil assessment procedure for channels in the Edward-Wakool River system. The Phase 1 component of this report is aimed solely at determining whether or not acid sulfate soil materials are present in the Edward-Wakool River system. In addition, the findings of this study were used to develop appropriate sampling strategies to assess the occurrence of sulfidic sediments in inland waterways.

This study identified the presence of acid sulfate soil materials at 76 of the 131 sites examined in the Edward-Wakool River system. Sulfuric materials were observed at two sampling sites. The reduced inorganic sulfur content of the samples was high in some channels (i.e. S_{CR} was up to 1.29% S). Hypersulfidic soil materials were present in 73 soil profiles (12 of these profiles also contained hyposulfidic materials), and another three soil profiles contained hyposulfidic materials with $S_{CR} < 0.10\%$ (one of these profiles also contained hyposulfidic materials with $S_{CR} \geq 0.10\%$). Monosulfidic soil materials were observed at 36% (i.e. 47) of the sampling sites. These results indicate that acidity would be produced upon oxidation of sulfides in many of these materials.

The surficial soil materials at 89 sites contained soluble sulfate equal to or in excess of the 100 mg/kg trigger value for monosulfidic black ooze (MBO) formation potential. The potential formation of MBO was identified in all channel systems examined except Pissen Creek. Other acidic soils, often with a pH < 5, were also observed at an additional 54 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 sulfuric material, 73 high priority sites based on hypersulfidic material, seven high priority sites based on hyposulfidic ($S_{CR} \geq 0.10\%$) material and 47 high priority sites based on monosulfidic material. There were 11 moderate priority sites based on the presence of a hyposulfidic material with $S_{CR} < 0.10\%$. In addition, 89 of the 131 sampling sites had a high priority ranking for Phase 2 detailed assessment based on MBO formation hazard. All channel systems examined in this study receive a high priority ranking on at least one of the criteria except for Pissen Creek.

The potential hazards posed by acid sulfate soil materials in the Edward-Wakool River system are as below:

- Acidification: While low-moderate net acidities were dominant in many of the channel systems examined, several channel reaches contained hypersulfidic materials with high net acidities, indicating the acidification hazard is often high.

- Deoxygenation: Monosulfidic soil materials ($S_{AV} \leq 1.03\% S$) were observed in the upper 0-10 cm layers in all channel systems containing acid sulfate soils except Yarrein Creek. These monosulfidic soil materials represent a high deoxygenation hazard. In addition, the soluble sulfate contents of 89 surface soil materials (i.e. 0-20 cm) were equal to or greater than the trigger value for MBO formation indicating the possible development of a high deoxygenation hazard at those locations after prolonged wet conditions.
- Metal mobilisation: The moderate-high acidification hazard in all channel systems containing acid sulfate soils (except Yarrein Creek) indicates that soil acidification may increase the solubility of metals. The presence of monosulfidic materials in upper soil layers and the potential for MBO formation identified at many sites may also result in a high metal release hazard. This would depend on factors such as the potential for MBO formation and the metal loading in the channel.

The findings of this study also show that for a detailed assessment of sulfidic sediment distribution in individual reaches of channels, at least one core per 250 square meters of channel reach should be used. Site selection should be done randomly within the channel system, with even spatial distribution along the study reach. In addition, ball-valve coring was the only viable way to retrieve intact and representative cores in the range of sediments and water depths. D-Section and gouge augers were found to be either ineffective or non-representative.

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1. INTRODUCTION

1.1. Overview

This study examines the occurrence and nature of reduced inorganic sulfur compounds (commonly referred to as sulfidic sediments and/or acid sulfate soils) in the Edward-Wakool channel system. The study will determine the current extent of sulfidic materials (quantifying the severity of the hazard) as well as identifying contributing factors influencing the hazard posed by these materials (e.g. disturbance).

1.2. Background on acid sulfate soils

1.2.1. Acid sulfate soils in the Murray-Darling Basin

Acid sulfate soil is the term commonly given to soil and sediment that contain iron sulfides, or the products of sulfide oxidation. Pyrite (FeS_2) is the dominant sulfide in acid sulfate soil, although other sulfides including the iron disulfide marcasite (Sullivan and Bush 1997; Bush 2000) and iron monosulfides (Bush and Sullivan 1997; Bush *et al.* 2000) can also be found.

Sulfidic sediments accumulate under waterlogged conditions where there is a supply of sulfate, the presence of metabolisable organic matter and iron-containing minerals (Dent 1986). Under reducing conditions sulfate is bacterially reduced to sulfide, which reacts with reduced iron to form iron sulfide minerals. These sulfide minerals are generally stable under reducing conditions, however, on exposure to the atmosphere the acidity produced from sulfide oxidation can impact on water quality, crop production, and corrode concrete and steel structures (Dent 1986). In addition to the acidification of both ground and surface waters, a reduction in water quality may result from low dissolved oxygen levels (Sammut *et al.* 1993; Sullivan *et al.* 2002a; Burton *et al.* 2006a), 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 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 $\text{pH} < 4$). 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.

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.

1.2.2. Monosulfidic black ooze (MBO)

A class of acid sulfate soil referred to as ‘monosulfidic black ooze’ (MBO), distinctly recognisable by its black, organic, ooze-like consistency, is one of the most typical sulfidic materials known to accumulate in low energy waterways. These materials are enriched in chemically reactive iron monosulfides (Bush *et al.* 2004). Iron monosulfides are the initial product formed in the reaction between ferrous iron (Fe^{II}) and hydrogen sulfide (H_2S) under reducing conditions in sediments (Goldhaber and Kaplan 1974), and their presence is a prerequisite for sedimentary pyrite formation (Rickard and Luther III 1997). Although iron monosulfides [including mackinawite (FeS) and greigite (Fe_3S_4)] usually occur in relatively low concentrations in most sediments (Goldhaber and Kaplan 1974), iron monosulfide enriched sediments are commonly associated with acid sulfate soil landscapes (Sullivan and Bush 2000; Bush *et al.* 2004; Burton *et al.* 2006a,b; Ward *et al.* 2010a).

MBO with acid-volatile sulfide (AVS; a measure of iron monosulfide and dissolved sulfide) concentrations of $>1000 \mu\text{mol/g}$ have been reported in coastal acid sulfate soil landscapes (Bush *et al.* 2004). MBO tends to form in these environments where favourable conditions for sulfide formation occur, including a supply of reactive iron (Fe), dissolved sulfate (SO_4) and organic matter (Berner 1984). While the presence of iron monosulfides is a defining characteristic of MBO, other reduced inorganic sulfur (RIS) species including pyrite (FeS_2) and elemental sulfur (S^0), may also be present in significant quantities (Bush *et al.* 2004; Burton *et al.* 2006b; Ward *et al.* 2010a).

Trace metals are commonly associated with iron sulfides (Huerta-Diaz and Morse 1992), and the occurrence of iron monosulfide is known to control the bioavailability of many metals (Chapman *et al.* 1998). However, the mobilisation of MBO as a consequence of flooding or activities such as dredging, may result in the rapid deoxygenation and acidification of surface waters and the release of potentially toxic metals (Burton *et al.* 2006a).

Monosulfidic sediments can contain very high concentrations of AVS (Sullivan and Bush 2000). The mobilisation and subsequent oxidation of those sediments has the potential to severely affect water quality. MBOs have been shown to rapidly decrease the dissolved oxygen content of water in minutes, with acidification continuing over several days (Burton *et al.* 2006a). Concerns have been raised about the role of MBO and its known impacts on water quality when a major flood (February 2001) resulted in a large fish kill event in the Richmond River in eastern Australia (Eyre *et al.* 2006).

The two key impacts from MBO and other sulfides within channels, therefore, are extreme deoxygenation and acidification. Both are known to occur and have large impacts when MBO is suspended in floodwaters (Bush *et al.* 2004). The effects of acid discharge into aquatic environments have been reported by many authors (e.g. Sammut *et al.* 1996) and include:

- fish kills,
- onset of fish disease (e.g. epizootic ulcerative syndrome (red spot disease)),
- mass mortality of shellfish, crustacea, and worms,
- reduced growth rates and disease in crustaceans and shellfish,
- destruction of native aquatic macrophytes,

- influx of acid-tolerant vegetation (e.g. water lilies (*Nymphaea* spp)),
- loss of habitat and spawning areas,
- clarification of water, resulting in increased water temperatures, and
- smothering of benthos by iron flocs.

Monosulfides have been studied in both marine and estuarine sediments (Bush *et al.* 2004), but there is a substantial lack of knowledge about these materials in inland environments. Recent studies reveal high concentrations of monosulfides in the soils and drain/canal sediments of acid sulfate soil landscapes (e.g. Bush *et al.* 2004; Burton *et al.* 2006b; Ward *et al.* 2010a). Unlike the oxidation of pyrite, the chemical oxidation of monosulfides is rapid over a wide range of soil pH, and it is the extreme reactivity of monosulfides that poses a potential environmental threat when these sediments are mobilised and subsequently oxidised during flooding or clearing practices.

The acidic conditions in acid sulfate soil have the potential to significantly affect the chemical behaviour of heavy metals bound in sediments. In acidic conditions, metals such as Ag, Cd, Cu, Hg, Ni, and Pb can be released (Casas and Crecelius 1994). Potentially toxic metals (e.g. As, Cu, and Hg) are commonly co-precipitated with pyrite near the sediment-water interface and can be potentially bioavailable if the pyrite is oxidised (Morse and Arakaki 1993). While pyrite does not exchange trace metals as readily as monosulfides (Allen *et al.* 1993), due to its chemical stability above a pH of 4, Morse and Arakaki (1993) stated that a major portion (from 20% to over 90%) of pyrite-bound metals could be released in as little as one day if anoxic sediments were exposed to oxic seawater.

The presence of reduced inorganic sulfur compounds in the sediments of inland wetlands and lakes has recently emerged as a potentially significant hazard, particularly in the wetlands of the lower Murray and Edward-Wakool River system. This material is also known to be present in the sediments of some rivers and creeks (Baldwin 2009; Ward *et al.* 2010b). This study will examine the extent and nature of reduced inorganic sulfur compounds in the Edward-Wakool channel systems, south-west NSW (Figures 1-1 and 1-2).

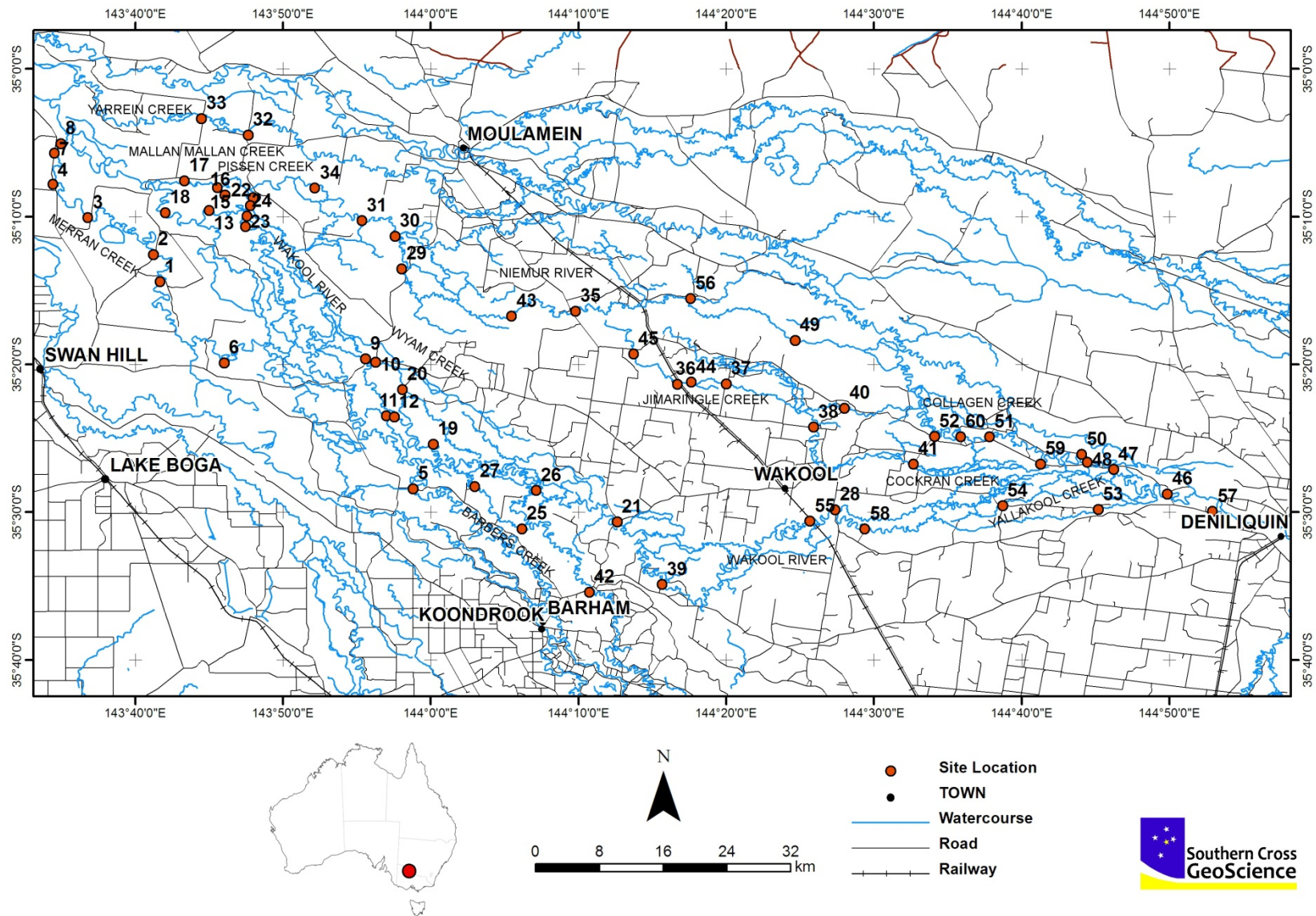


Figure 1-1. Map showing the areas assessed in the Edward-Wakool River system (Component 1).

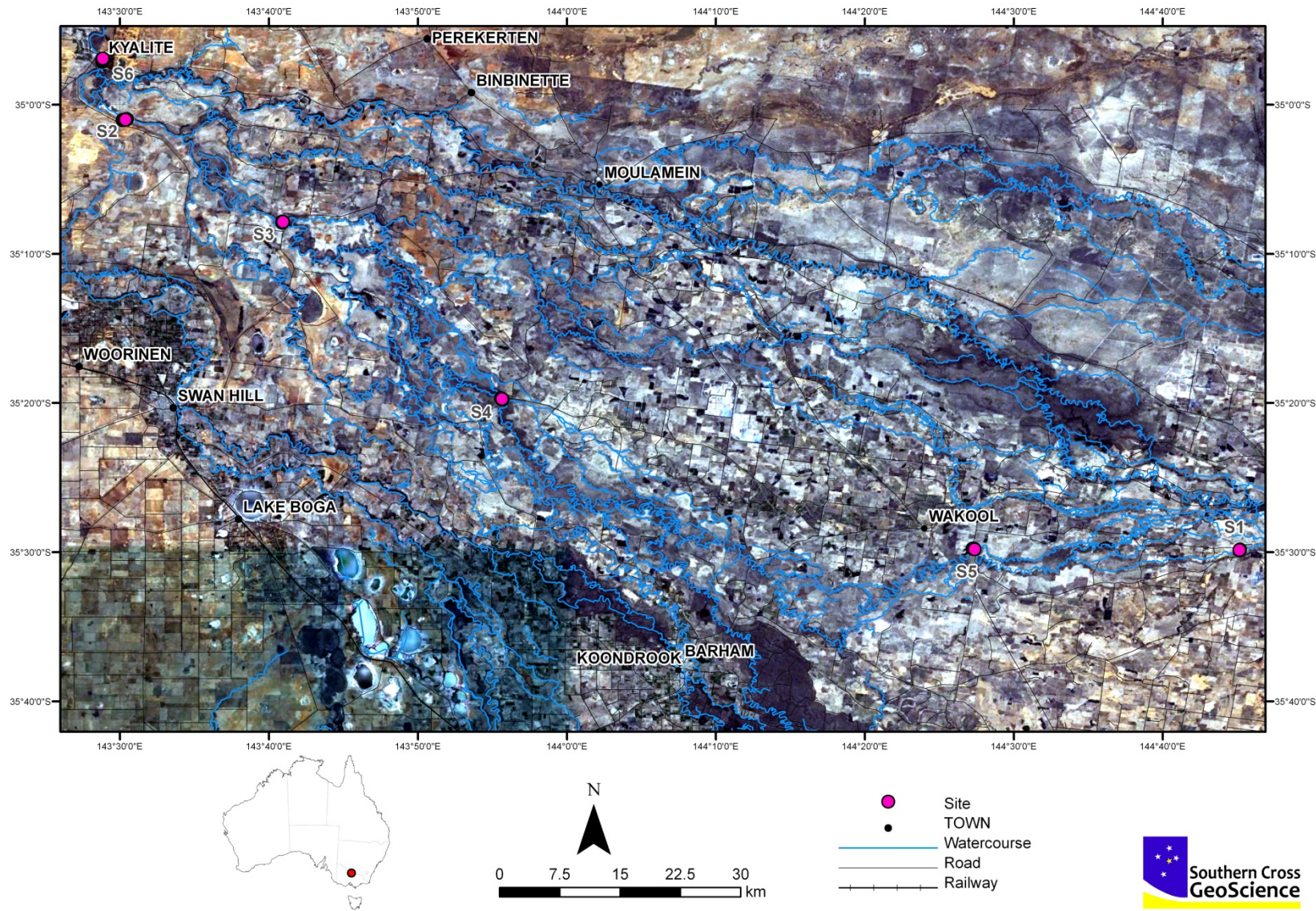


Figure 1-2. Map showing the areas assessed in the Wakool River system (Component 2).

1.3. Knowledge gaps

There are significant knowledge gaps in determining the extent and nature of sulfidic sediments in inland channelised systems. In order to address these knowledge gaps, we intend to study in detail a channelised system known to contain sulfidic sediments and use the results to quantify an appropriate sampling and risk assessment strategy for other channel systems of the Basin that may be at risk. Sulfidic sediments have been recorded previously in the main channel of the Wakool and Niemur Rivers and a number of associated creek systems (including Tuppal, Jimaringle, Cockran, Wyam and Merran Creeks) (e.g. Baldwin 2008, 2009; Tulau 2009; Ward *et al.* 2010b,c) (e.g. Figure 1-3).



Figure 1-3. Backwater of the Wakool River showing evidence of sulfidic sediments (June 2009). The pH of the water was approximately 3.

1.4. Detailed acid sulfate soil assessments using two phases

The detailed assessment stage of the Murray-Darling Basin Acid Sulfate Soils Risk Assessment Project (MDB ASSRAP) involves comprehensive analysis using a set of established and tested field and laboratory methods to determine the presence and extent of acid sulfate soil materials 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 (the subject of this report) 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:

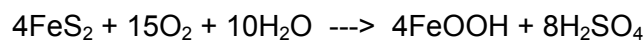
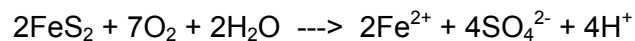
- laboratory analysis (of soil)
- risk assessment
- interpretation and reporting, including discussion on broad acid sulfate soil management options

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.

1.5. 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.* 2006a), high concentrations of aluminium and iron (Ferguson and Eyre 1999; Ward *et al.* 2002), and the release of other potentially toxic metals (Preda and Cox 2001; Sundström *et al.* 2002; Burton *et al.* 2008a; Sullivan *et al.* 2008a).

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



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

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.

1.6. 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 soils in the Murray–Darling Basin, even though these materials may not be the result of acid sulfate soil processes (e.g. the acidity developed during ageing may be the result of Fe^{2+} hydrolysis, which may or may not be associated with acid sulfate soil processes). 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 $\text{pH}_w \geq 4$ but < 5.5 in the field.
- 2. Other soil materials** – soils that do not have acid sulfate soil (or other acidic) characteristics.

2. AIMS AND OBJECTIVES

2.1. Aims

The aim of this research project is to examine the distribution and nature of sulfidic sediments in the Edward-Wakool River System in order to understand the accumulation and potential mobilisation of these materials in a channelised waterway system of the Murray-Darling Basin.

2.2. Specific objectives

This project has two specific goals:

1. Quantify the spatial occurrence of sulfidic sediments in rivers and creeks of the Edward-Wakool River system.
2. Develop appropriate sampling strategies to assess the occurrence of sulfidic sediments in inland waterways.

3. METHODS

The study includes two research components on the Edward-Wakool River System (i.e. Component 1 and 2).

3.1. Component 1 - A broad spatial assessment of the distribution of sulfidic sediments throughout the Edward-Wakool River system

This research component explores the spatial extent of sulfidic sediments (sub-aqueous acid sulfate soils) in the Edward-Wakool River system in relation to their geomorphic, hydrological and geochemical setting.

Soils material samples were taken from creeks and river systems across the whole of the study region, and site selection was weighted according to the length of the river or creek system (Table 3-1). Sixty sites were inspected and sampled during the period between the 31st May and 28th June 2010 (Figure 1-1). Sample sites were approximately evenly spaced along each river or creek channel (depending on access), and a single soil profile was sampled from the deepest part of each site. A total of 270 soil material samples were collected for laboratory analysis.

Table 3-1. Stream lengths and corresponding weighting of sites sampled in the Edward-Wakool River system.

Stream	Length	No. Sites
Wakool River	170 km	17
Niemur River - Collagen Creek	140 km	15
Yallakool Creek	40 km	2
Jimaringle – Cockran Creeks	75 km	8
Barbers Creek	30 km	3
Mallan Mallan Creek	15 km	2
Merran Creek	80 km	8
Yarrein Creek	60 km	2
Wyam Creek	22 km	2
Pissen Creek	6 km	1

Soil materials were sampled and characterised according to the procedures outlined in the protocols for the detailed assessment of acid sulfate soils in the Murray-Darling Basin (MDBA 2010). Where possible, soil profiles were collected to a depth of 90 cm using a range of implements (i.e. spades, and augers). 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. Where monosulfides were present the sample was collected into two glass jars (250 mL) with a screw top lid. All soil samples were maintained at $\leq 4^{\circ}\text{C}$ 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 ($\text{pH}_{\text{INCUBATION}}$) and the other was for long term archive storage. Soil data cards were completed for each site and entered into the NSW Soil and Land Information System. A photographic record was obtained for each

site (including photographs of site, core/profile, and chip trays). Site and profile descriptions including global positioning system (GPS) coordinates are presented for each channel system in Appendix 1. Detailed descriptions of each site and additional photographs are also presented in Tulau and Morand (2010).

Field surface water data was collected from 54 sites in the Edward-Wakool Rivers region and are presented in Appendix 1. Six sites were dry at the time of sampling (i.e. WC_33, WC_37, WC_38, WC_40, WC_41 and WC_59). Water temperature, pH, specific electrical conductivity (SEC), dissolved oxygen (DO) and redox potential (ORP) were determined using calibrated electrodes linked to a Hach HQ40d multi-parameter meter. Turbidity was measured using a calibrated Hach 2100P Turbidity meter.

The geomorphic setting at each sampling location was described in detail for the purpose of contextualising the spatial attributes and their potential relationship with sulfidic accumulations (Tulau and Morand 2010). Integration of the site specific geomorphic data to the broader channel system was achieved by use of conventional air-photo interpretation and GIS analysis of LiDAR (Light Detection And Ranging) land elevation data held by New South Wales Department of Environment, Climate Change and Water (NSW DECCW) on a catchment scale.

3.2. Component 2 - A detailed assessment of the distribution of sulfidic sediments in individual reaches of the Wakool River

The objective of this part of the project was to determine the optimum sampling strategy for assessing the hazard posed by sulfidic sediments in channelised systems. Using data collected from Component 1 and Component 2, two specific questions were addressed:

1. How many samples are necessary to give sufficient statistical power to show that a particular river reach contains enough sulfidic sediment to cause a risk if disturbed?
2. What is the optimal way to sample channelised systems to determine the distribution of sulfidic sediments in inland creeks and rivers?

Six river reaches/pools along the main stem of the Wakool River were selected, four in areas where sulfidic sediments were known to occur and two where the presence of sulfidic sediments was not suspected (i.e. four reaches to the west and two reaches to the east of the Moulmein-Barham Road) (Figure 1-2). At each of these reaches up to 13 profiles were assessed using a ball-valve corer to a depth of up to 90 cm.

A total of 71 profiles across six sites were inspected and collected during the period between 21st June and 30th June 2010. Site descriptions and basic surveys were completed for geomorphic characterisation. As with Component 1 of this study, soil materials were sampled and characterised according to the procedures outlined in the protocols for the detailed assessment of acid sulfate soils in the Murray-Darling Basin (MDBA 2010). Profiles were collected up to a depth of 90 cm, with the majority collected from the top ~40 cm due to the presence of coarse channel gravels at depth. Soil samples were collected from at least five sampling depths where possible, with a total of 318 soil material samples collected and frozen for laboratory analysis. Redox potential (Eh) and pH of soil materials were recorded in the field using calibrated electrodes linked to a TPS 90-FLMV multi-parameter meter (Appendix 2).

Site and profile descriptions including global positioning system (GPS) coordinates are presented in Appendix 2. Digital photographs were also taken upstream and downstream to document the characteristics of each site (see Appendix 2). Additional photographs are also presented in Appendix 4.

Field surface water data was collected from up to three depths at 11 sites and are presented in Appendix 2. Water pH and SEC were determined using calibrated electrodes linked to a TPS 90-FLMV multi-parameter meter.

Different sampling devices (i.e. gouge auger, D-section and ball-valve corer) were assessed to determine their efficiency and utility for routine survey application.

Geostatistical analysis was performed using ArcGIS v10 to show the percent AVS and CRS vs depth relationships across sites 1 to 3 (Appendix 3). Kriging was used to interpolate between profiles to model the occurrence of sulfidic material across the sites. Post-hoc power analysis was subsequently applied to optimise sampling strategies in channelised systems (Baldwin and Howitt, 2007).

3.3. Laboratory soil analysis

3.3.1. 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 $pH_{INCUBATION}$), 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 (H_2O_2) (Method 4E1) (Rayment and Higginson, 1992). The KCl extractable pH (pH_{KCl}) was measured in a 1:40 1M 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 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 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).

3.3.2. Quality assurance and quality control

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: 5% blanks, $\geq 10\%$ laboratory duplicates, and 5% laboratory controls.

3.4. 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 Soil Risk Assessment Project (MDB ASSRAP) 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 SO_4 /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 channel system as a whole.

4. RESULTS

4.1. Summary of field and laboratory results (Component 1)

4.1.1. Soil pH (pH_W , pH_{FOX} , pH_{KCl} and $pH_{INCUBATION}$)

The pH_W , pH_{FOX} , pH_{KCl} and $pH_{INCUBATION}$ data for the 60 sites examined in the Edward-Wakool River system are presented in Appendix 1 and summarised in Table 4-1. The pH_W values ranged between 3.19 and 7.63. Sulfuric materials (i.e. $pH_W < 4$) were only identified in soil materials at Barbers Creek (WC_42 (5-40 cm)) and Wyam Creek (WC_10 (0-10 cm)). While two soil materials at Cockran Creek (sites WC_40 and WC_59) also had pH_W values of less than four, field pH values and limited pedological evidence of sulfide oxidation (i.e. no mottles and/or coatings with accumulations of jarosite, and no underlying sulfidic materials) indicate that these soils are not sulfuric materials. None of the other soils in the Edward-Wakool River system are classified as sulfuric materials as they all had a $pH_W > 4$.

The pH_{FOX} values ranged between 1.48 and 7.27. The majority of the soils showed a pH drop after treatment with peroxide, with a maximum decrease of 5.4 pH units (e.g. Figure 4-1). The pH_{FOX} results also indicate that many of the soils examined in the Edward-Wakool River system may have the potential to acidify to $pH < 4$ as a result of sulfide oxidation. Half of the channels examined in the Edward-Wakool River system had layers with $pH_{FOX} < 2.5$. However, the S_{CR} data shows that many of the layers which showed a substantial pH drop after treatment with peroxide contained no detectable sulfide (i.e. $S_{CR} < 0.01\%$ S). While decreases in pH after treatment with peroxide are often used to indicate the presence of sulfide minerals in coastal acid sulfate soil materials, the S_{CR} data from these studies suggest that pH decreases in inland acid sulfate soil materials after peroxide has been added are often due to non-acid sulfate soil factors such as the oxidation of organic matter.

The $pH_{INCUBATION}$ values ranged between 1.76 and 7.79. Twenty-three of the 84 sulfidic soil materials (i.e. $S_{CR} \geq 0.01\%$ S) acidified to $pH < 4$ after at least 8 weeks of incubation. In addition, five non-sulfidic soils (i.e. other acidic) acidified to $pH < 4$ over the 8 week incubation period (Appendix 1). Several sulfidic soil materials that did not acidify to $pH < 4$ after at least 8 weeks of incubation were classified as hypersulfidic as they had positive net acidities (see Section 3.4).

Table 4-1. Summary soil data for pH testing and sulfur suite (Component 1).

Parameter	Units	Minimum	Median	Maximum	n ¹
pH_W ²		3.19	5.92	7.63	270
pH_{FOX} ³		1.48	3.25	7.27	270
pH_{KCl} ⁴		3.57	4.77	8.93	270
$pH_{INCUBATION}$ ⁵		1.76	4.62	7.79	270
TAA ⁶	mole H ⁺ /tonne	0.00	6.57	63.00	270
Soluble SO ₄ ⁷	mg/kg SO ₄	8.7	98.6	24,150	270
S_{CR} ⁸	Wt. %S	<0.01	<0.01	1.16	270
S_{AV} ⁹	Wt. %S	<0.01	<0.01	0.54	270
RA ¹⁰	mole H ⁺ /tonne	0.00	0.00	201	270
ANC ¹¹	%CaCO ₃	0.00	0.00	5.22	270
NA ¹²	mole H ⁺ /tonne	-559	11	602	270

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 S_{AV} : Acid Volatile Sulfide. ¹⁰ RA: Retained Acidity. ¹¹ ANC: Acid Neutralising Capacity: by definition, where $pH_{KCl} < 6.5$ ANC = 0. ¹² NA: Net Acidity.

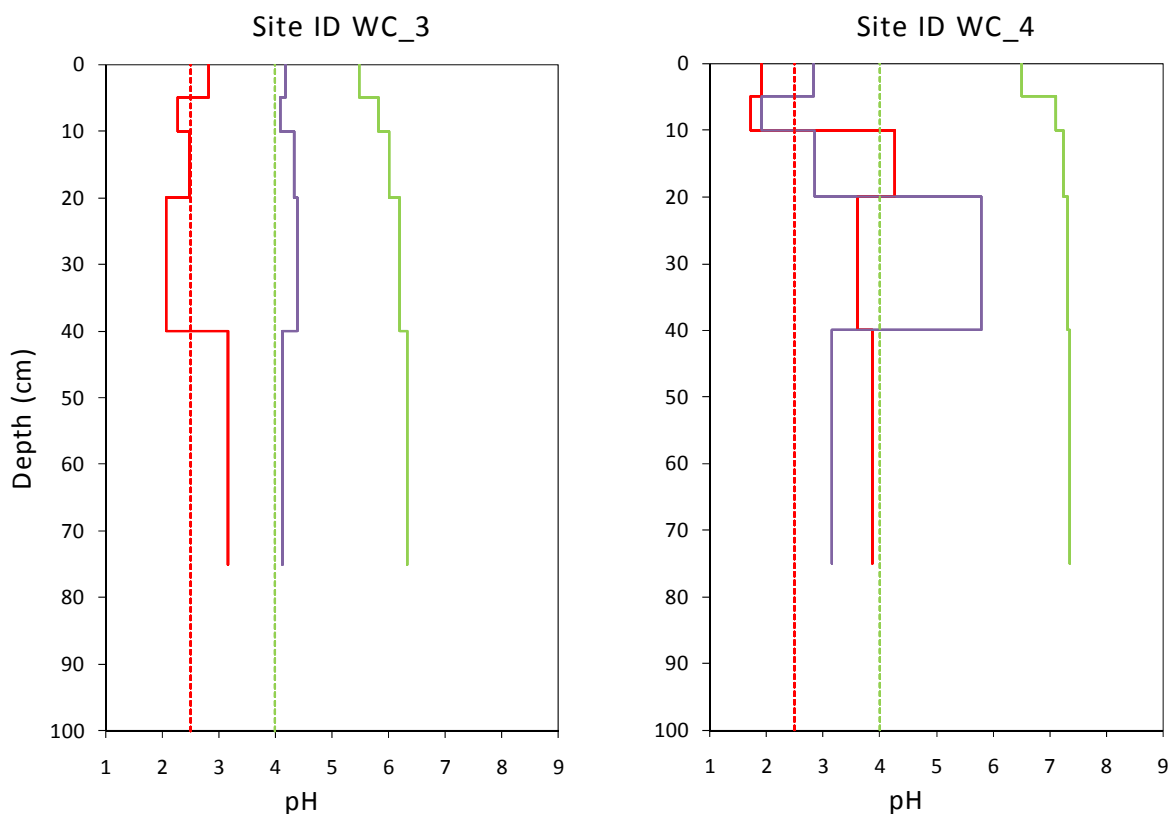


Figure 4-1. Depth profiles of soil pH for sites WC_3 and WC_4, showing soil pH (pH_W as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH ($pH_{incubation}$ after at least 8 weeks as purple line). Critical pH_W and $pH_{incubation}$ value of 4 (green dashed line) and critical pH_{FOX} value of 2.5 (red dashed line).

4.1.2. Chromium Reducible Sulfur (S_{CR})

The chromium reducible sulfur (S_{CR}) data for the 60 sites examined in the Edward-Wakool River system are presented in Appendix 1 and summarised in Table 4-1. The S_{CR} values ranged between < 0.01 and 1.16% S. Sulfidic soil materials (i.e. $S_{CR} \geq 0.01\%$ S) were only absent from two of the ten channel systems examined (i.e. Yallakool and Pissen Creeks), with 84 materials of the 270 samples collected equal to or greater than the sulfidic criterion.

A summary of the S_{CR} content and number of sulfidic soil materials observed in each channel system is given in Table 4-2. Mallan Mallan and Wyam Creeks had the highest percentage of sites containing sulfidic soil materials (i.e. 100%). Mallan Mallan Creek also had the highest percentage of layers examined containing sulfidic soil materials (i.e. 100%). Further information on the distribution of sulfidic sediments within each river system is given in Appendix 1.

Table 4-2. Summary of the S_{CR} content and number of sulfidic soil materials (i.e. $S_{CR} \geq 0.01\%$ S) observed in each channel examined in the Edward-Wakool River system (Component 1).

Channel Name	S_{CR} Range (%S)	No. of sulfidic sites	No. of sulfidic layers
Wakool River	< 0.01 – 0.34	7 (41%)	20 (26%)
Niemur River – Collagen Creek	< 0.01 – 0.11	5 (33%)	11 (17%)
Yallakool Creek	< 0.01	0 (0%)	0 (0%)
Jimaringle – Cockran Creek	< 0.01 – 0.49	3 (38%)	9 (26%)
Barbers Creek	< 0.01 – 0.08	2 (67%)	6 (46%)
Mallan Mallan Creek	< 0.01 – 0.27	2 (100%)	9 (100%)
Merran Creek	< 0.01 – 1.16	6 (75%)	19 (49%)
Yarrein Creek	< 0.01 – 0.09	1 (50%)	1 (10%)
Wyam Creek	< 0.01 – 0.85	2 (100%)	9 (90%)
Pissen Creek	< 0.01	0 (0%)	0 (0%)

4.1.3. Acid volatile sulfide (S_{AV})

The acid volatile sulfide (S_{AV}) data for 60 sites examined in the Edward-Wakool River system are presented in Appendix 1 and summarised in Table 4-1. The S_{AV} values ranged between < 0.01 and 0.54% S. Monosulfidic soil materials (i.e. $S_{AV} \geq 0.01\%$ S) were only absent from two of the ten channel systems examined (i.e. Yallakool and Pissen Creeks), with 39 materials of the 270 samples analysed equal to or greater than the monosulfidic criterion. Further information on the distribution of monosulfidic sediments within each channel system is given in Appendix 1

4.1.4. Acid Neutralising Capacity (ANC)

The acid neutralising capacity (ANC) data for the 60 sites examined in the Edward-Wakool River system are presented in Appendix 1 and summarised in Table 4-1. The ANC ranged between zero and 5.22% $CaCO_3$. A total of 36 samples (i.e. 13% of samples collected) had an ANC, and only five sites had an ANC throughout the soil profile (i.e. WC_4, WC_15, WC_17, WC_19 and WC_20).

4.1.5. Net Acidity (NA)

The net acidity data for the 60 sites examined in the Edward-Wakool River system are presented in Appendix 1 and summarised in Table 4-1. Acid-base accounting calculations showed the net acidity ranged between -559 and 602 mole H^+ /tonne, with a median net acidity of 11 mole H^+ /tonne. 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). A summary of the net acidity data for each channel system is given in Table 4-3, and shows the presence of soil materials with moderate to high net acidities in seven of the ten channel systems. The three channel systems which only contained materials with low net acidities included Yallakool Creek, Yarrein Creek and Pissen Creek; of these Yarrein Creek was the only channel system to contain sulfidic materials (see Table 4-2). A total of 18 hypersulfidic soil materials had high net acidities (i.e. 7% of samples). In addition to the three channels only containing materials with low net acidities, the Niemur River – Collagen Creek channel system did not contain hypersulfidic soil materials with high net acidities. The sulfuric materials identified at Barbers Creek (WC_42 (5-40 cm)) and Wyam Creek (WC_10 (0-10 cm)) all had moderate net acidities, ranging between 54 and 94 mole H^+ /tonne.

Table 4-3. Summary of the net acidity data for all soil materials in each channel examined in the Edward-Wakool River system (Component 1).

Channel Name	Net Acidity (mole H ⁺ /tonne)		
	Minimum	Median	Maximum
Wakool River	-559	12	245
Niemur River – Collagen Creek	-16	10	75
Yallakool Creek	-179	6	12
Jimaringle – Cockran Creek	-391	10	297
Barbers Creek	4	29	291
Mallan Mallan Creek	-78	-35	101
Merran Creek	-5	20	602
Yarrein Creek	-194	3	9
Wyam Creek	-165	79	574
Pissen Creek	5	7	9

The positive net acidities in the non-sulfidic samples were due to the presence of some TAA and the lack of any ANC, although a few layers also contained some retained acidity (i.e. iron and aluminium hydroxy-sulfate compounds) (Appendix 1).

4.1.6. Water soluble SO₄

The water soluble SO₄ data for the 60 sites examined in the Edward-Wakool River system are presented in Appendix 1 and summarised in Table 4-1. The water soluble SO₄ in the surface soils (i.e. 0-20 cm) in the Edward-Wakool River system ranged between 9 and 24,150 mg/kg. The surface soil layers at 33 of the 60 sites examined had a water soluble SO₄ content exceeding the trigger value of 100 mg/kg indicating the potential formation of monosulfidic materials. Except for Pissen Creek, at least one site in each of the channel systems examined had a water soluble SO₄ content exceeding the trigger value.

4.1.7. Titratable actual acidity (TAA)

The titratable actual acidity (TAA) data for the 60 sites examined in the Edward-Wakool River system are presented in Appendix 1 and summarised in Table 4-1. The TAA ranged between zero and 63 mole H⁺/tonne, with a median TAA of 7 mole H⁺/tonne. Both an increase and decrease in the TAA with depth was observed at the sites examined.

4.1.8. Retained acidity (RA)

The retained acidity data for the 60 sites examined in the Edward-Wakool River system are presented in Appendix 1 and summarised in Table 4-1. The retained acidity ranged between zero and 201 mole H⁺/tonne, with the majority of soil layers having no retained acidity. Retained acidity was only detected in 39 layers (i.e. 14% of samples collected).

4.2. Summary of field and laboratory results (Component 2)

4.2.1. Soil pH (pH_W , pH_{FOX} , pH_{KCl} and $pH_{INCUBATION}$)

The pH_W , pH_{FOX} , pH_{KCl} and $pH_{INCUBATION}$ data for the six locations examined in the Wakool River are presented in Appendix 2 and summarised in Table 4-4. The pH_W values ranged between 4.61 and 8.08, with the majority of the samples having a $pH_W > 5.5$. None of the soils in the Edward-Wakool River system are classified as sulfuric materials as all soils had a $pH_W > 4$.

The pH_{FOX} values ranged between 1.13 and 5.89. All of the soils showed a pH drop after treatment with peroxide, with a maximum decrease of 6.4 pH units (e.g. Figure 4-2). The pH_{FOX} results also indicate that many of the surface soils (i.e. 0-20 cm) examined in the Wakool River may have the potential to acidify to $pH < 4$ as a result of sulfide oxidation. All six sites examined had layers with $pH_{FOX} < 2.5$. However, the S_{CR} data shows that some of the layers which showed a substantial pH drop after treatment with peroxide contained no detectable sulfide (i.e. $S_{CR} < 0.01\%$ S). As mentioned earlier, while decreases in pH after treatment with peroxide are often used to indicate the presence of sulfide minerals in coastal acid sulfate soil materials, the S_{CR} data from these studies suggest that pH decreases in inland acid sulfate soil materials after peroxide has been added are often due to non-acid sulfate soil factors (such as the oxidation of organic matter).

The $pH_{INCUBATION}$ values ranged between 1.94 and 7.16. Sixty-nine of the 144 sulfidic soil materials (i.e. $S_{CR} \geq 0.01\%$ S) acidified to $pH < 4$ after at least 8 weeks of incubation. In addition, a number of non-sulfidic soils (i.e. other acidic) acidified to $pH < 4$ over the 8 week incubation period (Appendix 2). Several sulfidic soil materials that did not acidify to $pH < 4$ after at least 8 weeks of incubation were classified as hypersulfidic as they had positive net acidities (see Section 3.4).

Table 4-4. Summary soil data for pH testing and sulfur suite (Component 2).

Parameter	Units	Minimum	Median	Maximum	n ¹
pH_W ²		4.61	6.22	8.08	318
pH_{FOX} ³		1.13	2.31	5.89	318
pH_{KCl} ⁴		3.93	5.79	8.57	314
$pH_{INCUBATION}$ ⁵		1.94	4.19	7.16	317
TAA ⁶	mole H ⁺ /tonne	0.00	6.22	74.86	314
Soluble SO ₄ ⁷	mg/kg SO ₄	20.3	104.0	8,565	309
S_{CR} ⁸	Wt. %S	<0.01	<0.01	1.29	318
S_{AV} ⁹	Wt. %S	<0.01	<0.01	1.03	315
RA ¹⁰	mole H ⁺ /tonne	0.00	0.00	5.00	312
ANC ¹¹	%CaCO ₃	0.00	0.00	5.18	314
NA ¹²	mole H ⁺ /tonne	-690	24	590	314

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 S_{AV} : Acid Volatile Sulfide. ¹⁰ RA: Retained Acidity. ¹¹ ANC: Acid Neutralising Capacity: by definition, where $pH_{KCl} < 6.5$ ANC = 0. ¹² NA: Net Acidity.

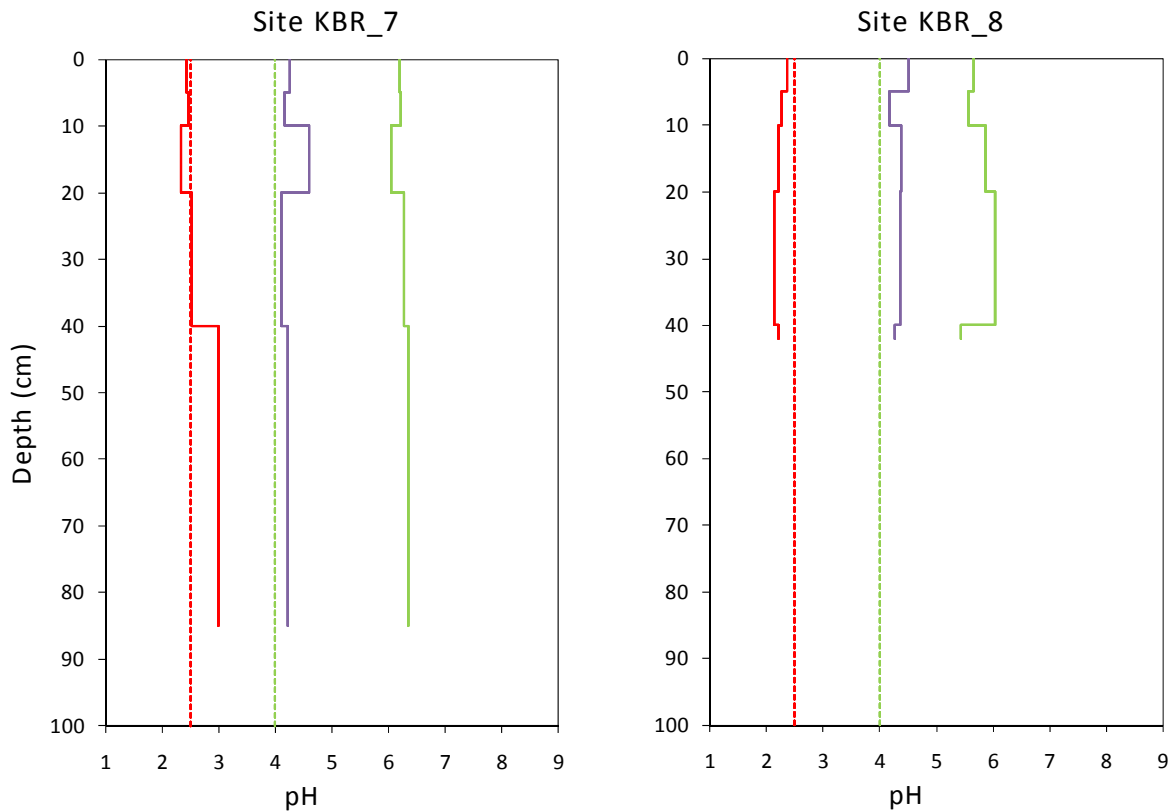


Figure 4-2. Depth profiles of soil pH for Kyalite Boat Ramp sites KBR_7 and KBR_8, showing soil pH (pH_W as green line), peroxide treated pH (pH_{FOX} as red line) and ageing pH ($pH_{incubation}$ after at least 8 weeks as purple line). Critical pH_W and $pH_{incubation}$ value of 4 (green dashed line) and critical pH_{FOX} value of 2.5 (red dashed line).

4.2.2. Chromium Reducible Sulfur (S_{CR})

The chromium reducible sulfur (S_{CR}) data for the six locations examined in the Wakool River are presented in Appendix 2 and summarised in Table 4-4. The S_{CR} values ranged between < 0.01 and 1.29% S. Sulfidic soil materials (i.e. $S_{CR} \geq 0.01\%$ S) were observed in each of the six channel systems examined, with 144 materials of the 318 samples collected equal to or greater than the sulfidic criterion.

A summary of the S_{CR} content and number of sulfidic soil materials observed in each channel system is given in Table 4-5. Sites examined in the Wakool Weir had the highest percentage of sites containing sulfidic soil materials (i.e. 100%). Genoe Creek Junction had the highest percentage of layers examined containing sulfidic soil materials (i.e. 84%). Further information on the distribution of sulfidic sediments within each channel is given in Appendix 2.

Table 4-5. Summary of the S_{CR} content and number of sulfidic soil materials (i.e. $S_{CR} \geq 0.01\% S$) observed in each channel examined in the Wakool River (Component 2).

Site No.	Main Name	S_{CR} Range (%S)	No. of sulfidic sites	No. of sulfidic layers
Site 1	Wakool Weir	< 0.01 – 0.15	9 (100%)	26 (65%)
Site 2	Genoe Creek Junction	< 0.01 – 1.29	12 (92%)	47 (84%)
Site 3	Mallan Bridge	< 0.01 – 0.78	7 (58%)	22 (44%)
Site 4	Gee Gee Bridge	< 0.01 – 0.02	4 (31%)	4 (7%)
Site 5	Yarrakool Creek Junction	< 0.01 – 0.02	8 (67%)	22 (37%)
Site 6	Kyalite Boat Ramp	< 0.01 – 0.17	8 (67%)	23 (38%)

4.2.3. Acid volatile sulfide (S_{AV})

The acid volatile sulfide (S_{AV}) data for the six locations examined in the Wakool River are presented in Appendix 2 and summarised in Table 4-4. The S_{AV} values ranged between < 0.01 and 1.03% S. Monosulfidic soil materials (i.e. $S_{AV} \geq 0.01\% S$) were found in all of the six channel systems examined, with 75 materials of the 318 samples collected equal to or greater than the monosulfidic criterion. Further information on the distribution of monosulfidic sediments within each channel system is given in Appendix 2.

4.2.4. Acid Neutralising Capacity (ANC)

The acid neutralising capacity (ANC) data for the six locations examined in the Wakool River are presented in Appendix 2 and summarised in Table 4-4. The ANC ranged between zero and 5.18% $CaCO_3$ (see Table 4-4). A total of 68 samples (i.e. 21% of samples collected) contained ANC, and only six sampling locations contained ANC throughout the soil profile.

4.2.5. Net Acidity (NA)

The net acidity data for the six locations examined in the Wakool River are presented in Appendix 2 and summarised in Table 4-6. Acid-base accounting calculations showed the net acidity ranged between -690 and 590 mole H^+ /tonne, with a median net acidity of 24 mole H^+ /tonne.

Table 4-6. Summary of the net acidity data for all soil materials in each channel examined in the Wakool River (Component 2).

Site No.	Main Name	Net Acidity (mole H^+ /tonne)		
		Minimum	Median	Maximum
Site 1	Wakool Weir	-70	13	67
Site 2	Genoe Creek Junction	-85	39	590
Site 3	Mallan Bridge	-32	3	503
Site 4	Gee Gee Bridge	-18	3	62
Site 5	Yarrakool Creek Junction	15	53	72
Site 6	Kyalite Boat Ramp	-690	26	112

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). A summary of the net acidity data for each channel system is given in Table 4-6, and shows the presence of soil materials with

moderate to high net acidities in all six channel systems. A total of 33 hypersulfidic soil materials from three of the sites (i.e. Sites 2, 3 and 6) had high net acidities (i.e. 10% of samples). These soil materials were predominantly found at Site 2 with 22 hypersulfidic soil materials with high net acidities (i.e. 39% of samples). The acidification hazard from disturbance of acid sulfate soil materials present in the six channel systems containing hypersulfidic soil materials ranged from moderate to high.

The positive net acidities in the non-sulfidic samples were due to the presence of some TAA and the lack of any ANC, although a few layers also contained some retained acidity (Appendix 2).

4.2.6. Water soluble SO₄

The water soluble SO₄ data for the six locations examined in the Wakool River are presented in Appendix 2 and summarised in Table 4-4. The water soluble SO₄ in the surface soils (i.e. 0-20 cm) in the Edward-Wakool River system ranged between 20 and 8,565 mg/kg. The surface soil layer in 52 of the 71 profiles examined had a water soluble SO₄ content exceeding the trigger value of 100 mg/kg indicating the potential formation of monosulfidic materials. The water soluble SO₄ content exceeded the trigger value at each of the six sites examined.

4.2.7. Titratable actual acidity (TAA)

The titratable actual acidity (TAA) data for the six locations examined in the Wakool River are presented in Appendix 2 and summarised in Table 4-4. The TAA ranged between zero and 75 mole H⁺/tonne, with a median TAA of 6 mole H⁺/tonne. Both an increase and decrease in the TAA with depth was observed at the sites examined.

4.2.8. Retained acidity (RA)

The retained acidity data for six locations examined in the Wakool River are presented in Appendix 2 and summarised in Table 4-4. The retained acidity ranged between zero and 5 mole H⁺/tonne, with the majority of soil layers having a no retained acidity. Retained acidity was only detected in 63 layers from Sites 5 and 6 (i.e. 20% of samples collected).

4.3. Hydrochemistry (Components 1 and 2)

Some hydrochemical characteristics of the surface water in the Edward-Wakool River system were measured to provide an indication of the baseline water chemistry. Some of the chemical parameters measured may show temporal variations, and therefore the data collected only represents a snapshot of the water quality in the Edward-Wakool River system.

Surface water quality data was collected from a total of 65 sites in the Edward-Wakool River system (Appendix 1 and 2). At the six Component 2 channel sites in the Wakool River surface water quality data was collected from up to three depths due to potential stratification. A summary of the surface water characteristics measured in the field are presented below in Table 4-7. The field pH of the surface waters ranged between 3.30 and 8.50 (Table 4-7), with 24 sites outside the most relevant ANZECC/ARMCANZ (2000) trigger values for aquatic ecosystems of 6.5 and 8.0. The water data indicates that the surface water at many of these sites has been affected by acidification. The surface waters were occasionally highly saline with a maximum SEC of 59,600 $\mu\text{S}/\text{cm}$. Some dissolved oxygen, SEC and turbidity values were found to be outside the most relevant ANZECC/ARMCANZ (2000) guideline value at some sites (see Appendix 1 and 2).

Table 4-7. Summary of surface water hydrochemical characteristics (field).

	pH	SEC $\mu\text{S}/\text{cm}$	DO mg/L	ORP mV	Turbidity NTU
Minimum	3.30	13.9	0.11	-104	9
Median	7.03	185.1	9.34	313	55
Maximum	8.50	59,600	16.54	2,014	575
n ¹	77	81	54	54	51

¹ n: number of samples

4.4. Discussion of laboratory results (Components 1 and 2)

This study identified the presence of acid sulfate soil materials at 76 of the 131 sites examined in the Edward-Wakool River system (i.e. 58% of sites). The soluble sulfate contents of surficial soil materials at 89 sites (i.e. 68%) were equal to or exceeded the trigger value of 100 mg/kg indicating the potential formation of monosulfidic materials.

The type and prevalence of acid sulfate soil materials observed in each channel system is summarised below in Tables 4-8 and 4-9 for Components 1 and 2, respectively. The presence of acid sulfate soils was identified in all channel systems examined, except for Yallakool and Pissen Creeks. Sulfuric materials were only observed at sites within Barbers and Wyam Creeks. All sulfuric soil materials had moderate net acidities. Hypersulfidic soil materials were observed in all channels except Yallakool, Yarrein and Pissen Creeks. A total of 51 hypersulfidic soil materials from Components 1 and 2 had high net acidities (i.e. > 100 mole H⁺/tonne). Hypersulfidic soils with high net acidities were found in six of the channels examined in Component 1 (i.e. Wakool River, Jimaringle – Cockran Creek, Barbers Creek, Mallan Mallan Creek, Merran Creek and Wyam Creek) and at three of the sites examined in the Wakool River as part of Component 2 (i.e. Genoe Creek Junction, Mallan Bridge and Kyalite Boat Ramp). All other hypersulfidic soil materials had low to moderate net acidities. Hyposulfidic soil materials were observed at all sites containing acid sulfate soils except Barbers Creek (Component 1), and Mallan Bridge, Gee Gee Bridge and Yarrakool Creek Junction (Component 2).

Table 4-8. Type and prevalence of acid sulfate soil materials in each channel system (Component 1).

Type of actual or potential acid sulfate soil material	Channel system (No. of sites)									
	Wakool R	Niemur R – Collagen Ck	Yallakool Ck	Jimaringle – Cockran Ck	Barbers Ck	Mallan Mallan Ck	Merran Ck	Yarrein Ck	Wyam Ck	Pissen Ck
Sulfuric	0	0	0	0	1	0	0	0	1	0
Hypersulfidic	6	5	0	3	2	1	6	0	2	0
Hyposulfidic (S _{CR} ≥ 0.10%)	0	0	0	1	0	2	0	0	1	0
Monosulfidic (observed)	3	2	0	1	2	2	4	1	2	0
Monosulfidic (potential)	6	3	1	8	2	2	7	2	2	0
Hyposulfidic (S _{CR} < 0.10%)	1	1	0	1	0	2	1	1	0	0
Other acidic (pH _w &/or pH _{INCUBATION}) 4 – 5.5	10	9	2	5	1	0	2	1	0	1
Other soil materials	0	1	0	0	0	0	0	0	0	0

Table 4-9. Type and prevalence of acid sulfate soil materials at each site (Component 2).

Type of actual or potential acid sulfate soil material	Wakool River site (No. of sites)					
	Wakool Weir	Genoe Creek Junction	Mallan Bridge	Gee Gee Bridge	Yarrakool Creek Junction	Kyalite Boat Ramp
Sulfuric	0	0	0	0	0	0
Hypersulfidic	9	12	7	4	8	8
Hyposulfidic ($S_{CR} \geq 0.10\%$)	0	2	0	0	0	1
Monosulfidic (observed)	7	11	5	2	1	4
Monosulfidic (potential)	9	11	10	2	10	10
Hyposulfidic ($S_{CR} < 0.10\%$)	1	2	0	0	0	1
Other acidic (pH_w &/or $pH_{INCUBATION}$) 4 – 5.5	0	1	5	9	4	4
Other soil materials	0	0	0	0	0	0

Many of the hypersulfidic and hyposulfidic soil materials were classified as hypermonosulfidic and hypomonosulfidic, respectively (Sullivan *et al.* 2010) (see Appendix 1 and 2). A total of 47 sites examined (i.e. 36% of sites) contained monosulfidic soil materials. Monosulfidic soil materials were found in all channel systems with acid sulfate soils (i.e. all channels except Yallakool and Pissen Creeks). Monosulfidic soil materials were observed in the upper 0-10 cm layers in all sulfidic channel systems except Yarrein Creek. The monosulfidic materials in upper 0-10 cm layers represent a high deoxygenation hazard. The potential formation of monosulfidic materials was identified in the upper soil layers at 68% of sites examined. Other acidic soil materials, often with a $pH < 5$, were observed at an additional 54 sites. Soil acidity may be sufficient for mobilisation of aluminium at some sites.

The laboratory results show that sulfidic/monosulfidic soil materials often have elevated water soluble sulfate contents (i.e. >100 mg/kg) (see Figures 4-3 and 4-4). The data also shows that some of the surface soil materials with elevated soluble sulfate contents have no detectable sulfide. The lack of sulfide formation in soil materials with elevated soluble sulfate contents indicates that sulfidisation is limited by a factor other than the sulfate content. Additional factors limiting sulfide formation include a lack of easily reducible iron, low content of easily metabolisable organic matter, adverse effect of acidity on the activity of microbes, and soil nutrient status (Ponnamperuma *et al.* 1973; van Breemen 1976; Berner 1984).

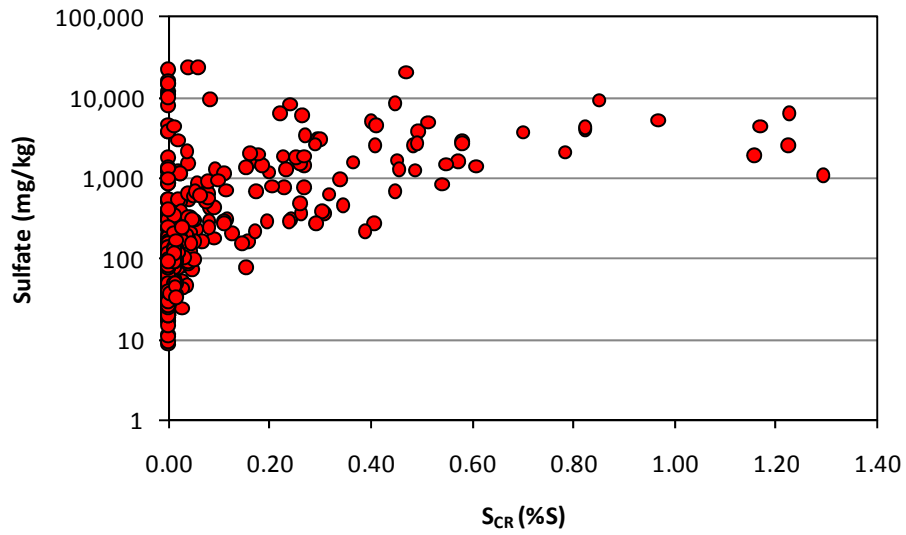


Figure 4-3. The relationship between water soluble sulfate (mg/kg) and S_{CR} (%S).

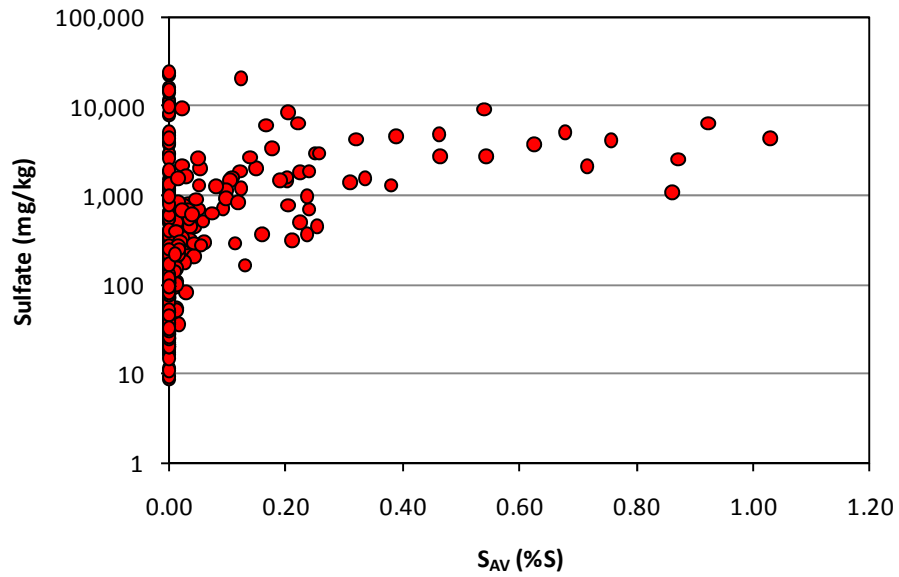


Figure 4-4. The relationship between water soluble sulfate (mg/kg) and S_{AV} (%S).

4.5. Spatial analysis of sulfidic materials, geomorphic links and landscape features

Considerable variability in the nature and spatial distribution of sulfides was found in the recovered materials. Recovered sediments included soft gel-like ooze, grey clays and silts, and very coarse channel sands. Many sites appeared to have undergone recent deposition of channel sands, which had, in some locations, buried accumulations of sulfidic materials. A majority of sulfidic material had accumulated in deeper parts of the channel. However, at some locations sulfidic material was found evenly across the channel. This was also found at some meander bends, where sulfidic material was expected to preferentially accumulate in lower energy parts of the channel such as the inside of bends (e.g. Figure 8-177, Appendix 3). Accumulations with higher AVS content were identified in protected parts of the channel behind submerged logs and channel constrictions (Figure 8-177, Appendix 3). Sulfidic material was also found to accumulate more intensely in the upstream pool of the pool-riffle-run sequence at Site 1 (Figure 8-166, Appendix 3).

In a larger spatial context, no trend was found for research Component 2 in regards to the occurrence of sulfidic material with respect to stream position. Sulfidic material was found at hazardous levels both upstream (East) and downstream (West) (Figure 1-2). It was also identified across a range of channel reach types such as meander bends, straights and pool-riffle-run sequences. Tulau and Morand (2010) did however identify that severely sulfidic sites within the Edward-Wakool River system were mostly associated with modern channels incised into residual Shepparton Formation surfaces.

Bathymetry and channel morphology, bank morphology, channel obstructions, and channel and riparian vegetation are all potential contributing landscape factors to the accumulation and formation of sulfidic sediments. Apart from a general preference for MBO accumulation in deeper or protected parts of the channel, no specific trend emerged for the occurrence of sulfidic sediments. Further research including a temporal component and control sites is necessary to unravel the relative contribution of particular landscape factors to the occurrence of sulfidic sediments.

4.6. Efficiency and utility of sampling devices

Different sampling devices (i.e. gouge auger, D-section and ball-valve corer) were assessed to determine their efficiency and utility for routine survey application. Ball-valve coring was the only viable way to retrieve intact and representative cores in the range of sediments and from a range of depths.

The D-section corer widely used for sampling unoxidised fine textured acid sulfate soils could not penetrate the coarse river bed sediments in this study. Also, the standard gouge augers could not reliably be used to retrieve soft gel-like material underwater due to loss of sample when bringing the corer up from depth.

A ball-valve coring device achieved less penetration in sandy sediments than in silty/clayey sediments. However, it provided better penetration than the D-section corer and was sufficient to assess the presence of sulfidic sediments in all study areas. When the ball-valve corer was used with a vertical extractor, soft unconsolidated sediment could be accurately subsampled. The ball-valve corer is shown in Figure 4-5 and the vertical extractor is shown in Figure 4-6. The device works by allowing overlying water to exhaust as the core is inserted, forming a vacuum seal on extrusion and effectively holding the sediment within the core.



Figure 4-5. Ball-valve corer and corer head (inset).



Figure 4-6. Vertical core extractor.

4.7. Statistical spatial analysis

Geostatistical analysis was performed using ArcGIS v10, to examine the percent AVS and CRS vs depth relationships across sites 1 to 3 (Appendix 3); these three sites had a higher frequency of sulfidic sediments (Figure 4-7). Interpolation between profiles to model the occurrence of sulfidic material across the sites was achieved by the application of kriging.

Figure 4-7 shows percent frequency plot of profiles containing CRS and AVS for each site based on occurrence alone. Within the sampling constraints of this project ($n = 71$) the statistical analysis of sulfidic profile distribution suggests an 85% confidence level for positive identification when using 15 profiles in a 200 m channel reach (average channel width = 30 m). A post-hoc power analysis, however, indicates that more profiles would be necessary to fully encapsulate the variability of these parameters. The observed power for a two-tailed hypothesis utilising the results from this study of 15 profiles is 0.718. Using 24 profiles the results from this study gives an observed power of 0.903. One profile per 250 square meters based on these results will give an observed power of > 0.9 , and is a reasonable guide for sampling intensity.

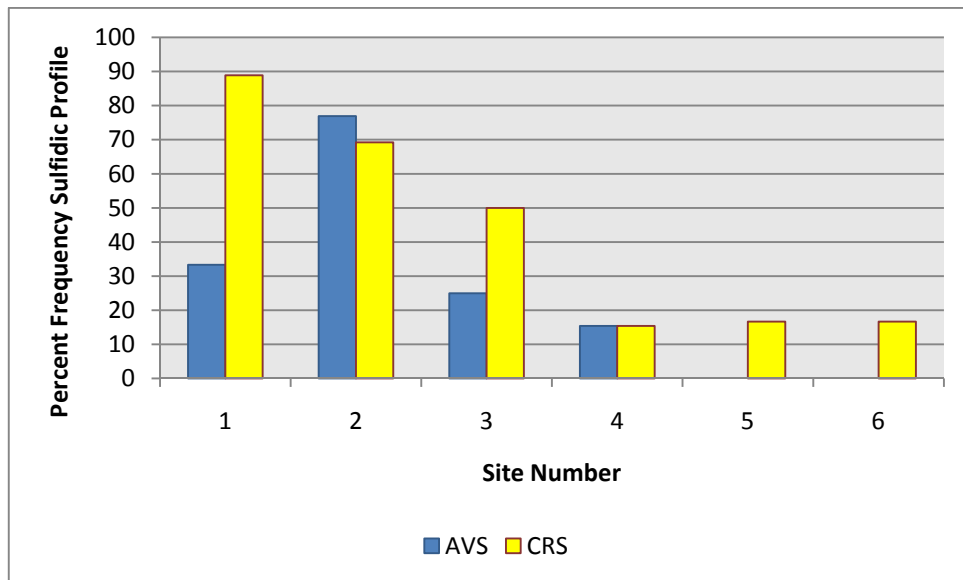


Figure 4-7. Percent frequency plot of sulfidic sediments for each site.

5. DISCUSSION

5.1. Distribution and hazard assessment of acid sulfate soil materials

This study identified the presence of acid sulfate soil materials at 76 of the 131 sites examined in the Edward-Wakool River system (i.e. 58% of sites). The presence of acid sulfate soils was identified in all channel systems examined, except for Yallakool and Pissen Creeks (Figure 5-1).

Sulfuric soil materials were only observed at two of the sampling sites (Table 5-1), including Barbers and Wyam Creeks. Hypersulfidic materials occurred in the soil profile at 73 of the 131 sampling locations (Table 5-1). Hypersulfidic soil materials were observed in all channels examined except Yallakool, Yarrein and Pissen Creeks (see Tables 4-8 and 4-9).

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

Type of actual or potential acid sulfate soil material	Number of sampling sites containing sulfuric or sulfidic materials (Total sites = 131)	Proportion of total sampling sites (%)
Sulfuric	2	2
Hypersulfidic	73	56
Hyposulfidic ($S_{CR} \geq 0.10\%$)	7	5
Monosulfidic	47	36
Monosulfidic (potential)	89	68
Hyposulfidic ($S_{CR} < 0.10\%$)	11	8
Other acidic (pH_w &/or $pH_{incubation}$) 4 – 5.5	54	41
Other soil materials	1	1

The data indicate that in the channels examined the degree of acidification hazard ranged from low to high (see Table 5-2). The three creeks with an absence of hypersulfidic soil materials (i.e. Yallakool, Yarrein and Pissen Creeks) all had a low acidification hazard. Hypersulfidic soils with high net acidities were found in six of the channels examined in Component 1 (i.e. Wakool River, Jimaringle – Cockran Creek, Barbers Creek, Mallan Mallan Creek, Merran Creek and Wyam Creek) and at three of the sites examined in the Wakool River as part of Component 2 (i.e. Genoe Creek Junction, Mallan Bridge and Kyalite Boat Ramp). All sites with the presence of hypersulfidic soil materials with high net acidities (except for Kyalite Boat Ramp) represent a high acidification hazard (Table 5-2). The overall degree of acidification hazard for Kyalite Boat Ramp is moderate as this site only contains a single hypersulfidic soil material with a high net acidity at depth (i.e. 20-40 cm). The sulfuric materials identified at Barbers and Wyam Creeks all had moderate net acidities therefore represent a moderate acidification hazard.

Hyposulfidic soil materials with $S_{CR} \geq 0.10\%$ and $S_{CR} < 0.10\%$ were present at seven and 11 sampling sites, respectively (Table 5-1). In addition, other acidic soil materials, often with a $pH < 5$, were observed at an additional 54 sites. Soil acidity may be sufficient for mobilisation of aluminium at some sites.

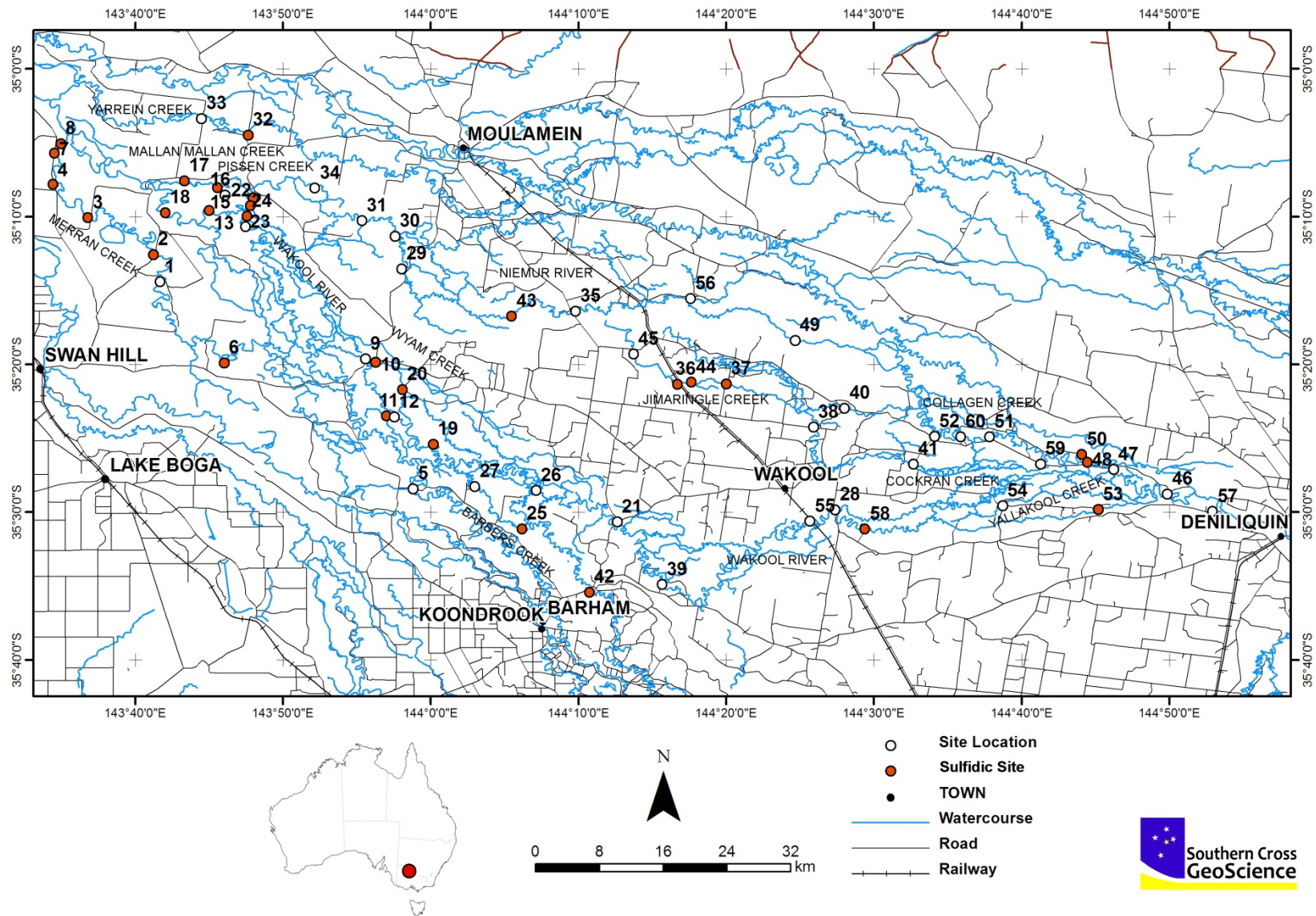


Figure 5-1. Map showing the distribution of sulfidic sediments in the Edward-Wakool River system.

Monosulfidic soil materials ($S_{AV} \geq 0.01\%$) occurred in the soil profile at 47 sampling locations. The distribution of monosulfidic sediments within the Edward-Wakool River system is shown in Figure 5-2. Monosulfidic soil materials ($S_{AV} \leq 1.03\%$ S) were observed in the upper 0-10 cm layers in all sulfidic channel systems except Yarrein Creek. The soluble sulfate contents of surficial soil materials at 89 sites sampled were equal to or exceeded the trigger value of 100 mg/kg indicating the potential formation of monosulfidic materials (Table 5-1). The potential formation of MBO was identified in all of the channels examined (except Pissen Creek), and represent a high deoxygenation hazard (Table 5-2).

The degree of metal mobilisation hazard is directly related to both the acidification and deoxygenation hazards (see Table 5-2). A moderate-high acidification hazard at sites containing acid sulfate soils indicates that soil acidification may increase the solubility of metals. In addition, the presence of monosulfidic materials in upper soil layers and the potential for MBO formation may also result in an appreciable metal release hazard. However, this would depend on factors such as the potential for MBO formation and the metal loading in the channel system.

The water data indicates that the surface water at many of these sites has been affected by acidification (see Section 4.3).

Table 5-2. Summary of the potential hazards posed by acid sulfate soil materials in the Edward-Wakool River system (Component 1 and 2).

Name	Hazard Type and Class		
	Acidification	Deoxygenation	Metal mobilisation
Component 1:			
Wakool River	High	High	High
Niemur River – Collagen Creek	Moderate	High	High
Yallakool Creek	Low	High	Low-moderate
Jimaringle – Cockran Creek	High	High	High
Barbers Creek	Moderate	High	High
Mallan Mallan Creek	High	High	High
Merran Creek	High	High	High
Yarrein Creek	Low	High	Low-moderate
Wyam Creek	High	High	High
Pissen Creek	Low	Low	Low
Component 2:			
Wakool Weir (Site 1)	Moderate	High	High
Genoe Creek Junction (Site 2)	High	High	High
Mallan Bridge (Site 3)	High	High	High
Gee Gee Bridge (Site 4)	Low	High	Low-moderate
Yarrakool Creek Junction (Site 5)	Moderate	High	High
Kyalite Boat Ramp (Site 6)	Moderate	High	High

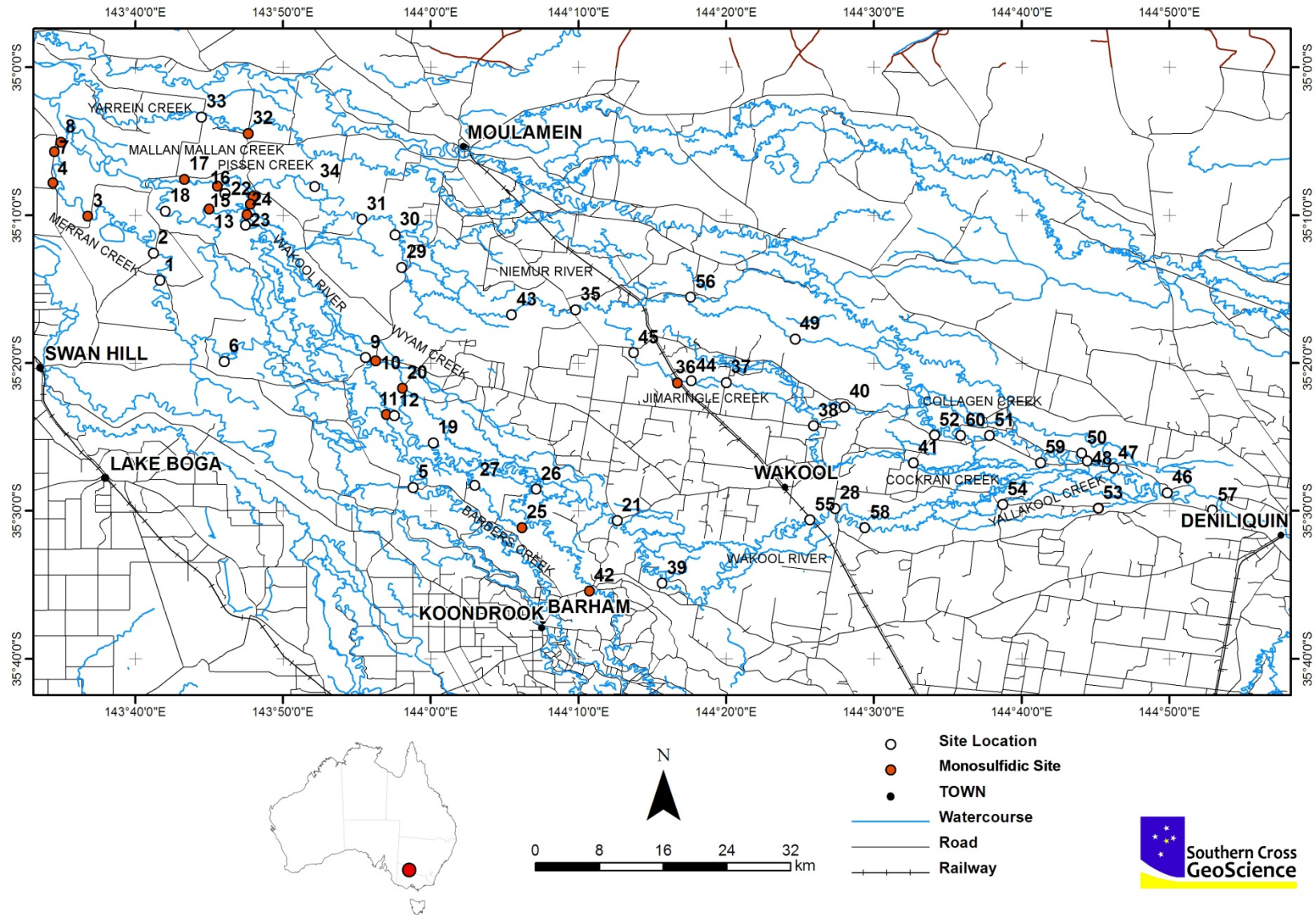


Figure 5-2. Map showing the distribution of monosulfidic sediments in the Edward-Wakool River system.

5.2. Potential contributing landscape factors

The potential landscape factors influencing the distribution of sulfidic sediments in the Edward-Wakool channel system are described in detail in Tulau and Morand (2010). The main conclusions are presented below.

- The vast majority of sulfidic channel sites in the study area occur in the lower, western part of the study area. An outlier group of acid sulfate soil sites is also located in the Wakool district.
- Severely sulfidic sites identified within the study area are mostly associated with halite salinity, and to a lesser degree, gypsum.
- The source of salinity appears to be lateral groundwater movement from stream banks.
- Severely sulfidic sites identified within the study area are mostly associated with modern channels incised into residual Shepparton Formation surfaces. Channels formed in younger, reworked Coonambidgal materials do not appear to be affected at this stage.
- Hydraulic gradients have been steepened by natural fluvial geomorphic channel change, the proximity to aeolian deposits, drought, stream regulation and irrigation.
- Subsurface ferruginous hardpans operate as aquicludes, leading to perched watertables and groundwater discharge that may enhance the supply of iron for contemporary iron sulfide formation.

5.3. River channel sulfidic sediment sampling protocol

Based on the outcomes of this study the following recommendations can be made.

5.3.1. Site selection

The site selection should be done randomly within the channel system, however an even spatial distribution along the study reach would be preferred. The outcomes of this study suggest deeper channel reaches and those with protected areas are more prone to sulfidic material accumulation.

5.3.2. Sampling method

A gravity driven, ball-valve corer is an extremely effective and portable instrument to retrieve intact sediment cores in a variety of sediment textures and range of depths from waterways. Used with a vertical extractor, soft unconsolidated sediment can be retrieved in an intact condition. Ideally cores should be taken in duplicate and water depth measured at each location.

5.3.3. Sampling frequency

For a detailed assessment of sulfidic sediment distribution in individual reaches, the outcomes of this study suggest the use of at least one core per 250 square meters of channel reach. These cores should be placed in transects spaced evenly along the reach, with a core taken at the middle of the channel and each bank of the channel.

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 channels in the Edward-Wakool River system. The Phase 1 component of this report is aimed solely at determining whether or not acid sulfate soil materials are present in the Edward-Wakool River system.

This study identified the presence of acid sulfate soil materials at 76 of the 131 sites examined in the Edward-Wakool River system. Sulfuric materials were observed at two sampling sites. The reduced inorganic sulfur content of the samples was high in some channels (i.e. S_{CR} was up to 1.29% S). Hypersulfidic soil materials were present in 73 soil profiles (12 of these profiles also contained hyposulfidic materials), and another three soil profiles contained hyposulfidic materials with $S_{CR} < 0.10\%$ (one of these profiles also contained hyposulfidic materials with $S_{CR} \geq 0.10\%$). Monosulfidic soil materials were observed at 36% (i.e. 47) of the sampling sites. These results indicate that acidity would be produced upon oxidation of sulfides in many of these materials.

The surficial soil materials at 89 sites contained soluble sulfate equal to or in excess of the 100 mg/kg trigger value for monosulfidic black ooze (MBO) formation potential. The potential formation of MBO was identified in all channel systems examined except Pissen Creek. Other acidic soils, often with a $pH < 5$, were also observed at an additional 54 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 sulfuric material, 73 high priority sites based on hypersulfidic material, seven high priority sites based on hyposulfidic ($S_{CR} \geq 0.10\%$) material and 47 high priority sites based on monosulfidic material. There were 11 moderate priority sites based on the presence of a hyposulfidic material with $S_{CR} < 0.10\%$. In addition, 89 of the 131 sampling sites had a high priority ranking for Phase 2 detailed assessment based on MBO formation hazard. All channel systems examined in this study receive a high priority ranking on at least one of the criteria except for Pissen Creek.

The potential hazards posed by acid sulfate soil materials in the Edward-Wakool River system are as below:

- **Acidification:** While low-moderate net acidities were dominant in many of the channel systems examined, several channel reaches contained hypersulfidic materials with high net acidities, indicating the acidification hazard is often high.
- **Deoxygenation:** Monosulfidic soil materials ($S_{AV} \leq 1.03\%$ S) were observed in the upper 0-10 cm layers in all channel systems containing acid sulfate soils except Yarrein Creek. These monosulfidic soil materials represent a high deoxygenation hazard. In addition, the soluble sulfate contents of 89 surface soil materials were equal to or greater than the trigger value for MBO formation indicating the possible development of a high deoxygenation hazard at those locations after prolonged wet conditions.
- **Metal mobilisation:** The moderate-high acidification hazard in all channel systems containing acid sulfate soils (except Yarrein Creek) indicates that soil acidification may increase the solubility of metals. The presence of monosulfidic materials in upper soil layers and the potential for MBO formation identified at the many sites may also result in a high metal release hazard. This would depend on factors such as the potential for MBO formation and the metal loading in the channel.

The findings of this study also show that for a detailed assessment of sulfidic sediment distribution in individual reaches, at least one core per 250 square meters of channel reach should be used. Site selection should be done randomly within the channel system, with even spatial distribution along the study reach. In addition, ball-valve coring was the only viable way to retrieve intact and representative cores in the range of sediments and water depths. D-Section and gouge augers were found to be either ineffective or non-representative.

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