

Distribution and ecological risk of reduced inorganic sulfur compounds in river and creek channels of the Murray-Darling Basin. Stage one: desktop assessment

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Cover Photograph

A severely degraded acid sulfate soil site on Merran Creek on the Wakool. Photography by Mitch Tulau (NSW DECCW).

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EXECUTIVE SUMMARY

Recent surveys have shown that sediments containing reduced inorganic sulfur compounds (commonly referred to as sulfidic sediments and/or acid sulfate soils) are widely distributed within wetlands and lakes in the Murray-Darling Basin (MDB). This document provides a desktop assessment of the distribution and environmental hazard associated with reduced inorganic sulfur compounds in river and creek channels within the MDB. This study also aims to provide an overall assessment of the potential environmental risk posed by these compounds in channels across the MDB. The presence of reduced inorganic sulfur compounds in channel sediments is of particular concern because adverse water quality caused by the disturbance of sediments containing these compounds can be transferred downstream and may result in adverse environmental impacts downstream.

This study presents a series of reported case studies on the properties and distribution of reduced inorganic sulfur compounds within the MDB. A range of acid sulfate soil materials have been identified in channel systems, including sulfuric, hypersulfidic, hyposulfidic and monosulfidic materials. However, this study has shown that there is currently limited reported data on the presence of these sulfur compounds in river and creek channel sediments. The presence of reduced inorganic sulfur compounds in channels is highly variable, and has largely been reported in the Murray catchment where most detailed studies have been undertaken. Generally, the greatest concentration of reduced inorganic sulfur compounds was reported within the Lower River Murray floodplains, South Australia.

There are many visual records of suspected compounds, in particular monosulfidic black ooze (MBO), but without proper testing for sulfides it is difficult to say whether this is evidence of reduced inorganic sulfur compounds. Where water quality data was available, many sites with the presence of reduced inorganic sulfur compounds had high SEC (specific electrical conductance) (i.e. $> 2,000 \mu\text{S cm}^{-1}$). However, this was not always the case. Elevated sulfate concentrations have been suggested as potential drivers for contemporary sulfide accumulations in channels. Further data specifically on sulfate concentration and trends in channels will be required to clarify this potential factor.

The main hazards associated with reduced inorganic sulfur compounds include the contemporary accumulation of sulfides, deoxygenation, accumulation and release of contaminants and acidification. Acid-base accounting data has shown that the net acidity within channel systems is highly variable, with many sites containing sufficient net acidity to represent a potential hazard if disturbed. A greater hazard of acidification and subsequent metal mobilisation from acid sulfate soil materials was identified in streambed sediments, stream banks and mid-stream bars than in high banks and terraces.

There is not enough data on reduced inorganic sulfur compounds in the MDB to draw strong conclusions on the level of hazard it poses on a basin wide perspective. There is also insufficient information available to assess the relative risk posed by these sediments when compared to other risks to water resources and water-dependent ecosystems already identified in the MDB. From the available data there are some areas within the MDB that have an acute problem. It is reasonable to suggest that the issue may not be a priority across the entire basin, but will be in a few priority locations.

We know from our understanding of sulfides in other landscapes that the formation and disturbances of these compounds can have significant impact upon water quality and aquatic life. We need more information in order to assess the risk and hazard of reduced inorganic sulfur compounds in channels at a basin level. In particular we do not have sufficient understanding of reduced inorganic sulfur compounds within the MDB landscape to predict where they will form and at what magnitude.

The broad recommendation from this study is:

- We need a greater understanding of reduced inorganic sulfur compounds in river and creek channels within the MDB landscape. We have an understanding of sulfides in other landscapes (i.e. coastal estuaries, wetlands and salt marshes), but will require new primary data to establish a fundamental understanding of the processes and controls on sulfur accumulation in the MDB. There is insufficient data to assess the direct applicability of knowledge on sulfur cycling from other well studied systems such as coastal and marine environments.

CONTENTS

ACKNOWLEDGEMENTS	I
EXECUTIVE SUMMARY	II
CONTENTS	IV
LIST OF FIGURES	VI
LIST OF TABLES	VIII
1. INTRODUCTION	1
1.1 PROJECT OBJECTIVES	3
1.2 PROJECT APPROACH AND METHODOLOGY	3
1.3 BACKGROUND	3
1.3.1 <i>Reduced sulfur compounds</i>	3
1.3.2 <i>Acid sulfate soils</i>	7
1.3.3 <i>Monosulfidic black ooze (MBO)</i>	11
1.3.3.1 What is MBO?	11
1.3.3.2 MBO formation	13
1.3.3.3 Disulfides in MBO	14
1.3.3.4 Environmental issues with MBO	15
1.3.3.5 Divalent trace metal accumulation with MBO	16
1.3.3.6 MBO oxidation	17
1.3.4 <i>Classification of acid sulfate soil materials</i>	19
2. REPORTED DISTRIBUTION OF REDUCED INORGANIC SULFUR COMPOUNDS ..	21
2.1 REDUCED INORGANIC SULFUR COMPOUNDS IN WETLANDS OF THE MURRAY-DARLING BASIN	21
2.2 REDUCED INORGANIC SULFUR COMPOUNDS IN CHANNELS OF THE MURRAY-DARLING BASIN	23
2.2.1 <i>Lower Murray River floodplain, South Australia</i>	24
2.2.1.1 River Murray below Blanchetown (Lock 1)	24
2.2.1.2 Finnis River, Currency Creek, Black Swamp and Goolwa Channel	29
2.2.1.3 Mundic Creek and Pike River systems	35
2.2.2 <i>Lower Loddon River and Burnt Creek, central Victoria</i>	37
2.2.3 <i>Channels associated with River Murray Locks 8 and 9 weir pools, New South Wales and Victoria</i>	41
2.2.4 <i>Salt Creek, south-west New South Wales</i>	44
2.2.5 <i>Edward-Wakool River system, New South Wales</i>	46
2.2.6 <i>Talbragar River, central New South Wales</i>	48
2.2.7 <i>Irrigation channels, Queensland</i>	50
2.2.8 <i>Summary of the reported distribution of reduced inorganic sulfur compounds in channels in the Murray-Darling Basin</i>	54
3. FURTHER INFORMATION INDICATING THE POTENTIAL PRESENCE OF REDUCED INORGANIC SULFUR COMPOUNDS IN CHANNEL SYSTEMS	59
3.1 ATLAS OF AUSTRALIAN ACID SULFATE SOILS	59
3.2 WATER QUALITY DATA	60
3.3 ALGAL BLOOMS	64
3.4 LANDSCAPE INFORMATION	66
4. HAZARD AND ECOLOGICAL RISK OF REDUCED INORGANIC SULFUR COMPOUNDS	69
4.1 DEFINING AND ASSESSING ACID SULFATE SOIL MATERIALS	69
4.2 DEFINING AND ASSESSING HAZARDS	70
4.2.1 <i>Contemporary accumulation of sulfides</i>	72
4.2.2 <i>Deoxygenation hazard</i>	74
4.2.3 <i>Accumulation and release of contaminants</i>	77
4.2.4 <i>Acidification hazard</i>	79
4.2.5 <i>Additional potential hazards</i>	83

4.3 DEFINING AND ASSESSING RISK	84
4.4 POTENTIAL IMPACTS OF CLIMATE CHANGE	87
4.4.1 Drought	87
4.4.2 Floods	88
5. MANAGEMENT OPTIONS AVAILABLE	89
6. FUTURE RESEARCH ON CHANNELISED SYSTEMS IN THE BASIN	91
7. CONCLUSIONS AND RECOMMENDATIONS.....	93
8. REFERENCES	95
APPENDICES	107
APPENDIX 1: LABORATORY ANALYTICAL SOIL DATA	108
APPENDIX 2: ACID-BASE ACCOUNTING METHODOLOGY	123
APPENDIX 3: SUMMARY OF ACID SULFATE SOIL RAPID ASSESSMENT SITES IN RIVER AND CREEK CHANNELS WITHIN THE MURRAY-DARLING BASIN.....	125

LIST OF FIGURES

FIGURE 1-1: CONCEPTUAL MODEL OF IN-SITU IRON TRANSFORMATIONS IN ACCRETING COASTAL LOWLAND ACID SULFATE SOIL (CLASS) DRAIN SEDIMENTS. (A) PRECIPITATION OF SCHWERTMANNITE ($\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)$), (B) REDUCTIVE DISSOLUTION OF SCHWERTMANNITE, (C) TRANSFORMATION OF SCHWERTMANNITE TO GOETHITE (aFeOOH), (D) REDUCTIVE DISSOLUTION OF GOETHITE, (E) UPWARD DIFFUSION AND OXIDATION OF Fe^{II} , (F) PRECIPITATION-DISSOLUTION OF DISORDERED MACKINAWITE (FeS), (G) REGULATION OF PORE-WATER Fe^{II} VIA PRECIPITATION-DISSOLUTION OF SIDERITE (FeCO_3), (H) AND FORMATION OF PYRITE (FeS_2 ; KINETICALLY RETARDED DUE TO HIGH PORE-WATER Fe^{II} CONCENTRATIONS) (SOURCE: BURTON <i>ET AL.</i> 2006D).	9
FIGURE 1-2: MINERALOGICAL DATA FOR IRON MONOSULFIDES IN MBO FROM AN ACID SULFATE SYSTEM. (A) CLUSTER OF NANO-CRYSTALLINE IRON SULFIDE MINERALS FROM AN MBO; (B) ELECTRON DIFFRACTION PATTERN FOR MATERIAL IN (A). (C) AND (D) HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPE IMAGE SHOWING LATTICE SPACINGS CONFIRMING MACKINAWITE (SOURCE: BURTON <i>ET AL.</i> 2007).	12
FIGURE 1-3: CONCEPTUAL MODEL OF SULFIDE FORMATION IN THE RIVER MURRAY WETLANDS AND THE POTENTIAL REACTIONS FOLLOWING DISTURBANCE (SOURCE: LAMONTAGNE <i>ET AL.</i> 2004).	18
FIGURE 2-1: MAP SHOWING THE RAMSAR-LISTED WETLANDS SURVEYED IN THE MURRAY-DARLING BASIN (SOURCE: THOMAS <i>ET AL.</i> 2009A).	22
FIGURE 2-2: LOCATIONS OF SELECTED REPRESENTATIVE ACID SULFATE SOIL SURVEY SITES FROM THE MURRAY RIVER CHANNEL BELOW LOCK 1 AND THE LOWER LAKES (SOURCE: FITZPATRICK <i>ET AL.</i> 2008E).	25
FIGURE 2-3: PREDICTIVE ACID SULFATE SOIL SUBTYPE MAPS OF THE RIVER CHANNEL BELOW LOCK 1 AT PRE-DROUGHT WATER LEVELS (I.E. +0.5 M AHD) (SOURCE: FITZPATRICK <i>ET AL.</i> 2008E)..	27
FIGURE 2-4: PREDICTIVE ACID SULFATE SOIL SUBTYPE MAPS OF THE RIVER CHANNEL BELOW LOCK 1 AT DROUGHT WATER LEVELS (I.E. -0.5 M AHD) (SOURCE: FITZPATRICK <i>ET AL.</i> 2008E).	28
FIGURE 2-5: LOCATIONS OF RAPID AND DETAILED ASSESSMENT SURVEY SITES FOR FINNISS RIVER, CURRENCY CREEK, BLACK SWAMP AND GOOLWA CHANNEL (SOURCE: FITZPATRICK <i>ET AL.</i> 2009B).	29
FIGURE 2-6: CONCEPTUAL TOPOSEQUENCE MODEL FOR SITES CUR11 TO 14, LOCATED ON THE WESTERN SIDE OF GOOLWA CHANNEL/CURRENCY CREEK (SOURCE: FITZPATRICK <i>ET AL.</i> 2009B).	33
FIGURE 2-7: MAP SHOWING PREDICTED OCCURRENCES OF ASS SUBTYPES FOR LAKE LEVELS AT -1.0 M AHD (BASED ON FITZPATRICK <i>ET AL.</i> 2008E), WHICH CLOSELY APPROXIMATE THE CURRENT DISTRIBUTION OF SULFURIC AND SULFIDIC MATERIALS, VERIFIED FROM FIELD WORK ALONG 12 TRANSECTS IN LATE NOVEMBER 2008 (SOURCE: FITZPATRICK <i>ET AL.</i> 2009A).	33
FIGURE 2-8: MAP OF UPPER PIKE SYSTEM SHOWING THE MAIN CONTROLLING STRUCTURES (SOURCE: SHAND <i>ET AL.</i> 2009).	35
FIGURE 2-9: MAP OF CENTRAL VICTORIA SHOWING AREAS ASSESSED ON THE LOWER LODDON RIVER AND BURNT CREEK (SOURCE: THOMAS <i>ET AL.</i> 2009C).	37
FIGURE 2-10: LOCATION OF THE CHANNEL SAMPLING SITES INCLUDING CARR'S CREEK (SITE 954), CAPPITS CREEK (SITE 1014), WALPOLLA CREEK (SITE 1026) AND LOWER DARLING ANABRANCH (SITES 220 AND 3740) (SOURCE: SHAND <i>ET AL.</i> 2008).	41
FIGURE 2-11: LOCATION OF SAMPLING SITES SC1-4 AND SC7-8 AT SALT CREEK. TAREENA BILLABONG IS LOCATED ON THE RIGHT SIDE OF THE IMAGE (SOURCE: FITZPATRICK <i>ET AL.</i> 2008B).	44
FIGURE 2-12: MAP SHOWING THE ASSRAP PRIORITY ACID SULFATE SOIL ASSESSMENT SITES IN THE EDWARD-WAKOOL RIVER SYSTEM (SOURCE: MDBA UNPUBLISHED).	46
FIGURE 2-13: A SEVERELY DEGRADED ACID SULFATE SOIL SITE ON MERRAN CREEK ON THE WAKOOL RIVER (SOURCE: TULAU 2009).	47
FIGURE 2-14: ACID-VOLATILE SULFIDE CONTENT IN SEDIMENTS (26/02/02) AND SULFATE CONTENT OF WATER IN THE TALBRAGAR RIVER (15/02/02) (SOURCE: SULLIVAN <i>ET AL.</i> 2002B).	48
FIGURE 2-15: ACID-VOLATILE SULFIDE CONTENT IN SEDIMENTS (26/02/02) AND DISSOLVED OXYGEN CONTENT OF WATER IN THE TALBRAGAR RIVER (15/02/02) DURING THE TAIL END OF A FLOW EVENT (SOURCE: SULLIVAN <i>ET AL.</i> 2002B).	49

FIGURE 2-16: MAP SHOWING THE RAPID ASSESSMENT SAMPLING LOCATIONS IN THE IRRIGATION CHANNELS IN THE TALWOOD-MUNGINDI REGION, QUEENSLAND.	52
FIGURE 2-17: MAP SHOWING THE RAPID ASSESSMENT SAMPLING LOCATIONS IN THE WHYENBAH CHANNELS, QUEENSLAND.	52
FIGURE 2-18: MAP SHOWING THE GEOGRAPHICAL DISTRIBUTION OF REDUCED INORGANIC SULFUR COMPOUNDS REPORTED IN CHANNEL SEDIMENTS IN THE MDB.	57
FIGURE 3-1: ATLAS OF AUSTRALIAN ACID SULFATE SOILS SHOWING THE LIKELIHOOD OF ACID SULFATE SOILS IN THE LOWER RIVER MURRAY (SOURCE: ASRIS; HTTP://WWW.ASRIS.CSIRO.AU).....	59
FIGURE 3-2: LOCATIONS OF SELECTED WATER QUALITY MONITORING STATIONS IN THE MDB. THE SPATIAL REPRESENTATIONS OF MONITORING LOCATIONS ARE INDICATIVE ONLY AND MAY NOT REPRESENT THE ACTUAL LOCATION (SOURCE: MDBA).	63
FIGURE 3-3: SITES OF MAJOR ALGAL BLOOMS IN THE MDB FROM 1991 TO PRESENT. THE SPATIAL REPRESENTATIONS OF ALGAL BLOOM LOCATIONS ARE INDICATIVE ONLY AND MAY NOT REPRESENT THE ACTUAL LOCATION (SOURCE: MDBA).	65
FIGURE 3-4: MAP SHOWING THE HIGH RESOLUTION DIGITAL PHOTOGRAPHY (ADS40) COVERAGE FOR NEW SOUTH WALES (SOURCE: PERS. COMM. MITCH TULAU).	66
FIGURE 4-1: SCHEMATIC DIAGRAM SHOWING THE BIOGEOCHEMICAL FORMATION OF IRON SULFIDE MINERALS (AFTER VAIRAVAMURTHY <i>ET AL.</i> 1995).....	72
FIGURE 4-2: CHANGES TO THE SULFUR SPECIATION (PYRITE, S_{AV} , ELEMENTAL SULFUR, SULFATE) AND PH DURING OXIDATION OF MBO (SOURCE: BURTON <i>ET AL.</i> 2006A).	75
FIGURE 4-3: SUMMARY OF THE TWO-STEP REACTION PROCESS FOR THE OXIDATION OF MBO (SOURCE: BURTON <i>ET AL.</i> 2006A).	75
FIGURE 9-1: MAP SHOWING THE ACID SULFATE SOIL RAPID ASSESSMENT SITES IN RIVER AND CREEK CHANNELS IN SOUTH AUSTRALIA (SOURCE: MDBA).	126
FIGURE 9-2: MAP SHOWING THE ACID SULFATE SOIL RAPID ASSESSMENT SITES IN RIVER AND CREEK CHANNELS IN VICTORIA (SOURCE: MDBA).	126
FIGURE 9-3: MAP SHOWING THE ACID SULFATE SOIL RAPID ASSESSMENT SITES IN RIVER AND CREEK CHANNELS IN NEW SOUTH WALES (SOURCE: MDBA).	127
FIGURE 9-4: MAP SHOWING THE ACID SULFATE SOIL RAPID ASSESSMENT SITES IN RIVER AND CREEK CHANNELS IN QUEENSLAND (SOURCE: MDBA).....	127

LIST OF TABLES

TABLE 2-1: ACID SULFATE SOIL MATERIAL TYPES COUNTED BY SITE OCCURRENCE (SOURCE: FITZPATRICK <i>ET AL.</i> 2009B).	31
TABLE 2-2: SUMMARY OF NUMBER OF SITES IN EACH ACID HAZARD CLASS BASED ON THE LIME TREATMENT CATEGORY (SOURCE: FITZPATRICK <i>ET AL.</i> 2009B).	31
TABLE 2-3: GENERAL RELATIONSHIP BETWEEN ACID SULFATE SOIL MATERIAL TYPE AND HAZARD CONDITION (SOURCE: FITZPATRICK <i>ET AL.</i> 2009B).	32
TABLE 2-4: TYPE AND PREVALENCE OF ACID SULFATE SOIL MATERIALS FOR LODDON RIVER AND BURNT CREEK (SOURCE: THOMAS <i>ET AL.</i> 2009C).	39
TABLE 2-5: RISK CATEGORISATION FOR THE VARIOUS HAZARDS ASSOCIATED WITH ACID SULFATE SOIL FOR SOIL LANDSCAPES AND SUBTYPES OF ACID SULFATE SOIL IDENTIFIED (SOURCE: THOMAS <i>ET AL.</i> 2009C).	40
TABLE 2-6: SUMMARY OF SOIL TYPES IDENTIFIED IN CHANNEL SEDIMENTS (SOURCE: SHAND <i>ET AL.</i> 2008).	42
TABLE 2-7: SUMMARY OF THE CONCENTRATION OF REDUCED INORGANIC SULFUR COMPOUNDS IN CHANNEL SEDIMENTS IN THE MDB.	56
TABLE 3-1: 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).	61
TABLE 3-2: LIST OF SOIL, WATER AND VEGETATION INDICATORS THAT ARE SUGGESTIVE OF THE PRESENCE OF COASTAL ACID SULFATE SOILS (SOURCE: DEC 2009).	68
TABLE 4-1: GENERAL RELATIONSHIP BETWEEN ACID SULFATE SOIL MATERIAL TYPE AND HAZARD CONDITION (SOURCE: FITZPATRICK <i>ET AL.</i> 2009B).	71
TABLE 4-2: ACID SULFATE SOIL ACTION CRITERIA INDICATING THE NEED FOR AN ACID SULFATE SOIL MANAGEMENT PLAN BASED ON SOIL TEXTURE RANGE, CHROMIUM REDUCIBLE SULFUR (S_{CR}) CONCENTRATION AND MASS OF SOIL THAT WILL BE DISTURBED (SOURCE: DEAR <i>ET AL.</i> 2002). ..	81
TABLE 4-3: SUMMARY OF REDUCED INORGANIC SULFUR CONCENTRATIONS AND CALCULATED NET ACIDITIES IN CHANNEL SEDIMENTS IN THE MDB.	82
TABLE 4-4: STANDARDISED TABLE USED TO DETERMINE THE CONSEQUENCES OF A HAZARD OCCURRING (SOURCE: MDBA 2010).	84
TABLE 4-5: LIKELIHOOD RATINGS FOR THE DISTURBANCE SCENARIO (SOURCE: MDBA 2010).	85
TABLE 4-6: RISK ASSESSMENT MATRIX (SOURCE: STANDARDS AUSTRALIA / STANDARDS NEW ZEALAND 2004).	85
TABLE 5-1: SUMMARY OF MANAGEMENT OBJECTIVES AND POSSIBLE ACTIVITIES (SOURCE: DEWHA IN PRESS).	90
TABLE 9-1: TABLE SHOWING PH DATA, ACID SULFATE SOIL MATERIALS, CLASSIFICATION, S_{CR} , LIME CALCULATION AND RISK FOR MURRAY RIVER BELOW BLANCHETOWN (LOCK 1) (SOURCE: FITZPATRICK <i>ET AL.</i> 2008E).	109
TABLE 9-2: SELECTED SULFUR-BASED ACIDITY AND ACID NEUTRALISING CAPACITY ANALYSES AND CALCULATIONS FOR MURRAY RIVER BELOW BLANCHETOWN (LOCK 1) (SOURCE: FITZPATRICK <i>ET AL.</i> 2008E).	110
TABLE 9-3: LABORATORY SOIL DATA SUMMARY INCLUDING PH TESTING AND ACID-BASE ACCOUNTING FOR FINNISS RIVER, CURRENCY CREEK, BLACK SWAMP AND GOOLWA CHANNEL SAMPLES (SOURCE: FITZPATRICK <i>ET AL.</i> 2009B).	111
TABLE 9-4: PH OF FIELD SOILS IN WATER (PH_W), AFTER TREATMENT WITH HYDROGEN PEROXIDE (PH_{FOX}) AND AFTER INCUBATING FOR 16 WEEKS (PH_{AGING}) FOR MUNDIC CREEK (PIKE 1-15), SALT LAKE (PIKE 16), PIKE RIVER (PIKE 17-23), SNAKE CREEK (PIKE 24) AND COL COL AREA (PIKE 25-27) (SOURCE: SHAND <i>ET AL.</i> 2009).	112
TABLE 9-5: ACID-BASE ACCOUNTING DATA FOR MUNDIC CREEK (PIKE 1-15), SALT LAKE (PIKE 16), PIKE RIVER (PIKE 17-23), SNAKE CREEK (PIKE 24) AND COL COL AREA (PIKE 25-27) (SOURCE: SHAND <i>ET AL.</i> 2009).	113
TABLE 9-6: SUMMARY OF LABORATORY ANALYSIS OF SOIL SAMPLES INCLUDING PH AND ACID-BASE ACCOUNTING FOR THE LODDON RIVER (SOURCE: THOMAS <i>ET AL.</i> 2009C).	114
TABLE 9-7: SUMMARY OF LABORATORY ANALYSIS OF SOIL SAMPLES INCLUDING PH AND ACID-BASE ACCOUNTING FOR BURNT CREEK (SOURCE: THOMAS <i>ET AL.</i> 2009C).	114
TABLE 9-8: PH OF FIELD SOILS IN WATER (PH_W) AND AFTER TREATMENT WITH HYDROGEN PEROXIDE (PH_{FOX}) FOR CARR'S CREEK (SITE 954), CAPPITS CREEK (SITE 1014), WALPOLLA CREEK	

(SITE 1026) AND DARLING ANABRANCH (SITES 220 AND 3470) (SOURCE: SHAND <i>ET AL.</i> 2008).	115
TABLE 9-9: ACID-BASE ACCOUNTING DATA FOR CARR'S CREEK (SITE 954), CAPPITS CREEK (SITE 1014), WALPOLLA CREEK (SITE 1026) AND DARLING ANABRANCH (SITE 3470) (SOURCE: SHAND <i>ET AL.</i> 2008).....	116
TABLE 9-10: ACID-BASE ACCOUNTING DATA FOR DARLING ANABRANCH (SITE 220) (SOURCE: SHAND <i>ET AL.</i> 2008).	116
TABLE 9-11: PH OF SOILS IN WATER (PH _w) AND AFTER TREATMENT WITH HYDROGEN PEROXIDE (PH _{Fox}) (AHERN <i>ET AL.</i> 2004) FOR SITES SAMPLED AT SALT CREEK (SOURCE: FITZPATRICK <i>ET AL.</i> 2008D).....	117
TABLE 9-12: SELECTED SULFUR-BASED ACIDITY AND ACID NEUTRALISING CAPACITY ANALYSES AND CALCULATIONS FOR SITES SAMPLED AT SALT CREEK (SOURCE: FITZPATRICK <i>ET AL.</i> 2008D).118	
TABLE 9-13: SUMMARY OF LABORATORY SULFIDE DATA FOR WAKOOL RIVER COLLECTED IN 2009 (SOURCE: BUSH UNPUBLISHED DATA).	119
TABLE 9-14: SUMMARY OF LABORATORY SULFIDE DATA FOR THE NIEMUR RIVER COLLECTED IN 2009 (SOURCE: BUSH UNPUBLISHED DATA).	119
TABLE 9-15: SUMMARY OF LABORATORY DATA INCLUDING SOIL PH, SOIL ELECTRICAL CONDUCTIVITY (EC) AND SULFIDE LEVELS IN CHANNELS SAMPLED IN FEBRUARY/MARCH 2004 IN THE MURRAY-DARLING BASIN (SOURCE: SULLIVAN UNPUBLISHED DATA).	120
TABLE 9-16: SUMMARY OF LABORATORY DATA FOR TALWOOD-MUNGINDI REGION AND WHYENBAH CHANNELS IN QUEENSLAND (SOURCE: QLD DERM UNPUBLISHED DATA).	121
TABLE 9-17: SUMMARY OF ACID SULFATE SOILS RAPID ASSESSMENT DATA FOR TALWOOD-MUNGINDI REGION AND WHYENBAH CHANNELS IN QUEENSLAND (SOURCE: MDBA UNPUBLISHED DATA).	122
TABLE 9-18: SUMMARY OF LABORATORY DATA INCLUDING PH AND ACID-BASE ACCOUNTING FOR BUTLERS CREEK (SOURCE: BALDWIN 2008B).	122
TABLE 9-19: SUMMARY OF LABORATORY DATA INCLUDING PH AND ACID-BASE ACCOUNTING FOR WASHPEN CREEK, NSW (SOURCE: BALDWIN <i>ET AL.</i> 2008).....	122

1. INTRODUCTION

This document provides a desktop assessment of the distribution and environmental hazard of reduced inorganic sulfur compounds in river and creek channels of the Murray-Darling Basin (MDB). This study aims to provide an overall assessment of the potential environmental risk posed by reduced inorganic sulfur compounds in channels across the Basin. To develop detailed appropriate sampling and risk assessment strategies for channel systems that may be at risk from reduced inorganic sulfur compounds in channels in the Basin will require environmental studies to gather primary data.

Recent surveys have shown that sediments containing reduced inorganic sulfur compounds (commonly referred to as sulfidic sediments and/or acid sulfate soils) are widely distributed within wetlands and lakes in the MDB (e.g. Hall *et al.* 2006a,b; Fitzpatrick and Shand 2008a; Fitzpatrick *et al.* 2008e), particularly in the Lower River Murray floodplains (e.g. Lamontagne *et al.* 2004, 2006; Fitzpatrick *et al.* 2008a, 2009c). Detailed acid sulfate soil assessments of ecologically significant Ramsar-listed wetland complexes throughout the Basin have also found the presence of reduced inorganic sulfur compounds in many Ramsar wetlands (e.g. Bush *et al.* 2009a,b; Sullivan *et al.* 2009c,d,e; Thomas *et al.* 2009a,b,d,e).

Reduced inorganic sulfur compounds are also known to be present in the sediments of rivers and creeks in the MDB (e.g. Sullivan *et al.* 2002b; Fitzpatrick *et al.* 2008e, 2009b; Baldwin 2009). The presence of reduced inorganic sulfur compounds in channel sediments is of particular concern because adverse water quality caused by the disturbance of sulfidic sediments in channels can be transferred downstream and may result in adverse environmental impacts downstream.

This project is the first desktop assessment to compile existing information and examine the issue of reduced inorganic sulfur compounds in sediments within river and creek channels from a Basin-wide perspective. This compilation of the current knowledge on within-channel sulfidic sediments in the MDB will help identify the nature, extent and magnitude of the currently known hazard. The findings of this study will also provide an indication of the range of environmental conditions where in-channel sulfidic sediments are likely to occur within the MDB.

There is a broad base of knowledge on sulfidic materials and their environmental hazards in marine, estuarine and coastal landscapes (e.g. Berner 1970; van Breemen 1973; Dent 1986; Morse *et al.* 1987; Sullivan *et al.* 2002a; Burton *et al.* 2006a). The hazard from sulfidic materials covers the following fundamental areas: oxidation of sulfides, release of contaminants and the deoxygenation of surface waters. These fundamental areas will be examined in this desktop assessment.

This report consists of eight chapters and a summary of the contents of each chapter, shown below.

- **Chapter 1:** The project objectives, approach and methodology are presented. Background information on acid sulfate soils including monosulfidic black ooze (MBO) is also presented.
- **Chapter 2:** Summaries of the reported distribution of reduced inorganic sulfur compounds in the wetlands and channels in the MDB. A series of case studies on the reported distribution of reduced inorganic sulfur species in channels are presented.
- **Chapter 3:** Summaries of additional information that may be used to indicate the presence of reduced inorganic sulfur compounds in channelised systems in the MDB.
- **Chapter 4:** Outlines a framework for defining and assessing the hazard and risk of reduced inorganic sulfur compounds in channels in the MDB.
- **Chapter 5:** Provides a brief summary of the management options available. A national guidance document covering detailed management options will soon be released (DEWHA In press).
- **Chapter 6:** Identifies the areas for potential future research on channel systems in the MDB.
- **Chapter 7:** Conclusions and recommendations.
- **Chapter 8:** A list of references referred to in the document.

The appendices summarise the analytical data for the sites reported to contain reduced inorganic sulfur compounds in the MDB (Appendix 1), details on the acid-base accounting methodology (Appendix 2), and include maps showing the location of acid sulfate soil rapid assessment sites for channels in the MDB (Appendix 3).

1.1 Project objectives

The objectives of this desktop assessment are (i) to undertake a catchment to Basin scale risk assessment of the likely occurrence of reduced inorganic sulfur compounds in sediments within channels, and (ii) identify their potential impacts on ecosystem condition and function. This assessment is based on existing knowledge including published, unpublished and grey literature, past work and records.

1.2 Project approach and methodology

This desktop assessment will provide an overall assessment of the potential hazards posed by reduced inorganic sulfur compounds in sediments in channels across the Basin using existing information. While it is recognised that this information is incomplete, the findings of this project will provide an indication of the types of risk posed by these sediments (based on their likelihood of occurrence and potential impacts) when compared to other risks to water resources and water-dependent ecosystems already identified.

1.3 Background

1.3.1 Reduced sulfur compounds

A number of reduced inorganic sulfur compounds have been observed in sedimentary environments, particularly in acid sulfate soils (Section 1.3.2) (including monosulfidic black ooze (MBOs) (Section 1.3.3)). Their presence often plays an essential role in the acidification of these materials. While the presence of reduced organic sulfur compounds may also provide a potential source of acidity, these compounds generally transform slowly under natural conditions and usually do not represent a significant hazard.

The term reduced inorganic sulfur is commonly used to refer to inorganic sulfur compounds containing sulfur in a reduced state (i.e. sulfur in the oxidation state of less than +6), compared to oxidised sulfur (S +6) in sulfate. The total reduced

inorganic sulfur fraction is commonly measured using the modified chromium reducible sulfur (CRS) method of Sullivan *et al.* (2000).

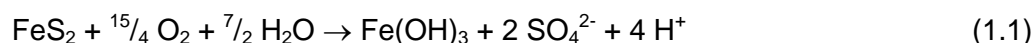
The reduced inorganic sulfur compounds found in sedimentary environments may include:

- iron disulfides (i.e. pyrite (FeS₂) and marcasite (FeS₂)),
- iron monosulfides (e.g. mackinawite (FeS), greigite (Fe₃S₄)),
- elemental sulfur (S⁰),
- dissolved sulfide species (e.g. H₂S, HS⁻, FeHS⁺), and
- a variety of sulfoxyanion intermediates (e.g. thiosulfate (S₂O₃²⁻), tetrathionate (S₄O₆²⁻), sulfite (SO₃²⁻)) (Goldhaber and Kaplan 1974; Rickard and Morse 2005).

The emission of sulfur dioxide (SO₂) has also been reported to occur in acid sulfate soil landscapes (Denmead *et al.* 2002; Macdonald *et al.* 2004; Hicks and Lamontagne 2006). Sulfate (SO₄²⁻) is not a reduced inorganic sulfur compound as the sulfur here has an oxidation state of +6.

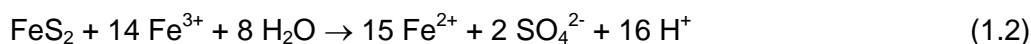
Reduced inorganic sulfur compounds often form directly through reduction processes under anoxic conditions, however, some of these compounds may also form as intermediate products during oxidation processes. For example, elemental sulfur can form as a product of sulfate reduction or as a result from the oxidation of pyrite and iron monosulfides (Bloomfield 1972; Burton *et al.* 2006b).

Pyrite is usually the dominant reduced inorganic sulfur fraction in acid sulfate soil materials. This sulfide mineral is generally stable under reducing conditions below the watertable, but acidity is produced as a result of oxidation when exposed to oxygenated water and particularly to the atmosphere according to Equation 1.1 (van Breemen 1973):



The main pyrite oxidising agents present in natural systems are oxygen (O₂) and ferric iron (Fe³⁺). Oxygen is primarily important as the initial oxidant and, once formed, ferric iron becomes the most effective pyrite oxidant (Moses *et al.* 1987;

Brown and Jurinak 1989; Moses and Herman 1991). The chemical oxidation of pyrite at around neutral pH is slow (Bloomfield 1973). When pH decreases to < 4, rapid oxidation by the microbially-mediated process involving ferric iron begins according to Equation 1.2 (Dent 1986):



The rate-limiting step in the rapid oxidation of pyrite by ferric iron is the oxidation of ferrous iron (Fe^{2+}) (Singer and Stumm 1970). Iron-oxidising bacteria (i.e. mostly *Thiobacillus ferrooxidans*) can accelerate the rate of ferrous iron oxidation by a factor of 10^6 (Singer and Stumm 1970), but are only active at $\text{pH} < 4$ (Bloomfield 1972; Arkesteyn 1980).

Other iron sulfides observed in acid sulfate soils include the more reactive iron disulfide mineral, marcasite (Sullivan and Bush 1997; Bush 2000), and iron monosulfides (Bush and Sullivan 1997; Bush *et al.* 2000). Iron monosulfides are highly reactive and undergo rapid chemical oxidation over a wide pH range (van Breemen 1973; Bush *et al.* 2000). Iron monosulfides and their presence in monosulfidic black ooze (MBO) are discussed in further detail in Section 1.3.3.

Elevated elemental sulfur concentrations have recently been identified in channel sediments associated with acid sulfate soils (Burton *et al.* 2006b; Ward *et al.* 2009, in press). Elemental sulfur plays an important dual role as the major direct immediate source of acidity under oxic conditions, and a necessary intermediate in the formation of pyrite in sediments under reducing conditions.

Dissolved sulfide species (e.g. H_2S , HS^- , FeHS^+) are commonly observed in the pore-waters of sulfidic sediments (e.g. Morse *et al.* 1987; Rickard and Morse 2005). However, substantial concentrations of dissolved sulfide only seem to accumulate in MBO where there is limited iron availability (Ward *et al.* 2009, in press). Dissolved sulfide may also accumulate in the water column under sufficiently reducing conditions (e.g. Morse *et al.* 1987).

Various soluble sulfoxyanion intermediates (i.e. $\text{S}_2\text{O}_3^{2-}$, $\text{S}_4\text{O}_6^{2-}$, SO_3^{2-}) have been detected during the chemical oxidation of pyrite (Goldhaber 1983; Moses *et al.* 1987). However, these sulfur species only seem to be present at low concentrations in the early stages of oxidation in acid sulfate soil materials (Ward 2004; Ward *et al.* 2004).

Finally, the emission of sulfur dioxide has been reported from bare acid sulfate soil materials (Denmead *et al.* 2002; Macdonald *et al.* 2004). Denmead *et al.* (2002) reported that sulfur dioxide appeared to be liberated during periods of evaporation, and therefore, was more likely to evolve from drying soils than from soils that are very wet or very dry.

1.3.2 Acid sulfate soils

Acid sulfate soil is the term commonly given to soil and sediment that contain iron sulfides or the products of sulfide oxidation. Sulfidic sediments accumulate naturally under waterlogged conditions where there is a supply of sulfate, metabolisable organic matter and iron (Berner 1984; Dent 1986). Under reducing conditions, sulfate is bacterially reduced to sulfide, which reacts with ferrous iron (Fe^{2+}) to form iron sulfide minerals. These sulfide minerals are generally stable under reducing conditions. However, on exposure to the atmosphere, acidity produced from sulfide oxidation can impact on water quality, crop production, and corrode concrete and steel structures (Dent 1986). In addition to 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), high concentrations of Al and Fe (Ferguson and Eyre 1999; Ward *et al.* 2002), and the mobilisation of other trace metals (Preda and Cox 2001; Sundström *et al.* 2002; Burton *et al.* 2008; Simpson *et al.* 2008; Sullivan *et al.* 2008a). The mobilisation of sulfidic sediments may also result in the release of nutrients into the water column (Sullivan *et al.* 2008a) which could contribute to algal blooms. In severe cases, these hazards can potentially lead to environmental degradation, and impact water supplies, and human and livestock health.

Until recently, acid sulfate soils in Australia were thought to be largely confined to coastal regions. The presence of acid sulfate soils in inland regions was first identified in areas impacted by salinisation (Fitzpatrick *et al.* 1992, 1993, 1996; Sullivan *et al.* 2002b). Fitzpatrick and co-workers identified sulfidic sediments in inland, non-tidal seepage and marsh areas of the Mt. Lofty Ranges, SA, which were thought to form as a result of a rising saline groundwater aquifer containing high levels of sulfate. Sullivan *et al.* (2002b) found that sulfate reduction processes were sufficient to result in the accumulation of iron sulfides within both freshwater river environments and irrigated landscapes as a consequence of elevated sulfate concentrations due to salinisation.

Since these initial studies, reduced inorganic sulfur compounds have been observed to be widespread in inland wetlands in the MDB (e.g. Lamontagne *et al.* 2004, 2006; Hall *et al.* 2006a,b; Fitzpatrick and Shand 2008a; Fitzpatrick *et al.* 2008e,f). Acidification of Bottle Bend Lagoon, south-west NSW in 2002 resulted in substantial

fish kills following partial drying (McCarthy *et al.* 2006). Evidence of oxidised acid sulfate soils was present which may have contributed to the fish kills (Lamontagne *et al.* 2006). Further information on the presence of reduced inorganic sulfur compounds in wetland and channel systems in the MDB is provided in Sections 2.1 and 2.2, respectively.

Significant changes to the hydrology of regulated sections of the MDB system (due to higher weir pool levels), and the chemistry of both rivers and wetlands (particularly as a result of salinisation) have led to the accumulation of sulfidic sediments in parts of the MDB. An accumulation of sulfides in surface sediments is usually minimised under natural wetting and drying cycles. If left undisturbed and inundated with water, sulfidic sediments pose little or no hazard. However, in recent years the record low inflows and river levels in the MDB has resulted in the exposure and oxidation of sulfidic sediments, which, in turn, has led to oxidation of sediments and soils, and in some cases to acidification and the formation of sulfuric sediments (i.e. pH < 4). The rewetting and/or mobilisation of these sediments may result in acidification and the release of contaminants (Simpson *et al.* 2008; Sullivan *et al.* 2008a).

In freshwater systems, the availability of sulfate is usually the main limiting factor to sulfate reduction and the formation of sulfides in benthic sediments (Berner 1984). Sulfate is often a major anion component of salinisation of freshwater bodies (Sullivan *et al.* 2002b). In the Australian landscape most of the salt is derived from marine sources (Fraser *et al.* 2008), however, sulfate may also be derived from anthropogenic sources such as fertilizers (Baldwin and Fraser 2009). The presence of high levels of sodium from salinisation also inhibits methanogenesis, giving a competitive advantage to sulfate-reducing bacteria (Fraser *et al.* 2008). The threshold sulfate concentration required to induce sulfate reduction ranges between 8 to 40 μM (i.e. 0.08 - 0.42 $\text{mg L}^{-1} \text{SO}_4^{2-}$) (Holmer and Storkholm 2001), and the rate of sulfate reduction is generally only limited at sulfate concentrations of less than approximately 5 mM (i.e. $\sim 500 \text{ mg L}^{-1} \text{SO}_4^{2-}$) (Berner 1984).

Lamontagne *et al.* (2004) found that conditions suitable for sulfide formation were widespread in the Lower River Murray floodplains (i.e. sufficient sulfate, iron and carbon), with their formation limited by labile carbon. Laboratory experiments have shown that levels of reduced inorganic sulfur in sediment that can lead to ecological damage when oxidised can form in very short time frames (i.e. months) under elevated salinity conditions (Fraser *et al.* 2008). However, there is currently limited

information on the distribution of reduced inorganic sulfur compounds within the MDB.

The geochemical processes and mineral transformations associated with sulfidic sediments have been extensively examined in coastal floodplain drainage systems (e.g. Sullivan *et al.* 2002a; Burton *et al.* 2006a,b,c,d). A geochemical model summarising the sedimentary iron transformations observed in coastal lowland acid sulfate soil (CLASS) associated waterways was recently developed by Burton *et al.* (2006d) (Figure 1-1). This model shows the pathways to the formation of a variety of minerals which are also commonly found in inland acid sulfate soil landscapes, including schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)$), goethite (αFeOOH), mackinawite (FeS), siderite (FeCO_3) and pyrite (FeS_2) (e.g. Fitzpatrick and Shand 2008a). Mackinawite (FeS) is commonly found associated with monosulfidic black oozes (MBO), which are discussed in detail in the following section (Section 1.3.1).

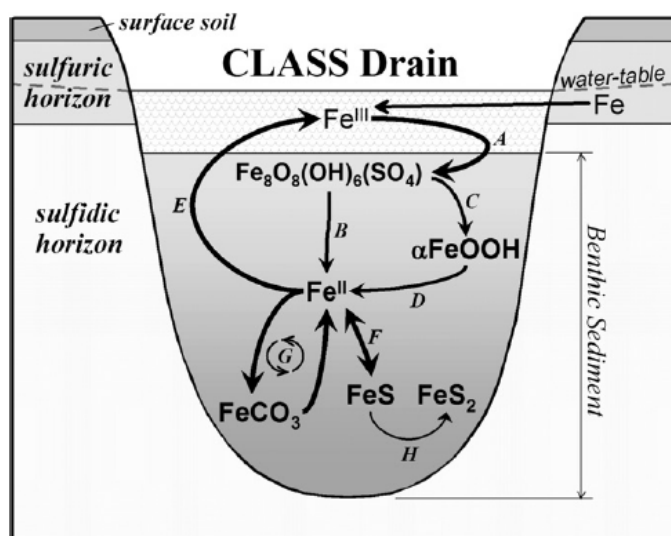


Figure 1-1: Conceptual model of in-situ iron transformations in accreting coastal lowland acid sulfate soil (CLASS) drain sediments. (A) precipitation of schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)$), (B) reductive dissolution of schwertmannite, (C) transformation of schwertmannite to goethite (αFeOOH), (D) reductive dissolution of goethite, (E) upward diffusion and oxidation of Fe^{II} , (F) precipitation-dissolution of disordered mackinawite (FeS), (G) regulation of pore-water Fe^{II} via precipitation-dissolution of siderite (FeCO_3), (H) and formation of pyrite (FeS_2 ; kinetically retarded due to high pore-water Fe^{II} concentrations) (source: Burton *et al.* 2006d).

Where waterways are impacted by sulfidic sediments there are a range of management options available. Baldwin and Fraser (2009) recently summarised the management options for inland waterways impacted by sulfidic sediments. The main strategies included minimising the formation of sulfidic sediments (such as reducing the salt load or re-instating more natural flow regimes), rehabilitation of impacted waterways (including inundation and/or neutralisation), or isolation of the acidified water body from the surrounding environment for wetland systems.

1.3.3 Monosulfidic black ooze (MBO)

1.3.3.1 What is MBO?

Monosulfidic black ooze (MBO) is typically a distinct black organic-rich sediment with an ooze-like consistency that is enriched in chemically reactive iron monosulfides (Bush *et al.* 2004). Iron monosulfides are the initial products formed in the reaction between ferrous iron (Fe^{2+}) and hydrogen sulfide (H_2S) under reducing conditions in sediments (Goldhaber and Kaplan 1974). Their presence is a prerequisite for sedimentary pyrite formation (Rickard and Luther III 1997). Although iron monosulfides 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 *et al.* 2002a,b, 2008a; Bush *et al.* 2004; Smith 2004; Burton *et al.* 2006a,c).

The presence of iron monosulfide minerals distinguishes MBO from other oozes of similar appearance. Although the presence of iron monosulfides is the defining geochemical property of MBO, pyrite and elemental sulfur can be important components of the total reduced inorganic sulfur. Under prolonged reducing conditions, iron monosulfides transform to pyrite. Conversely, under oxic conditions, elemental sulfur is an oxidation product of iron monosulfides. Therefore, the co-occurrence of all three major reduced inorganic sulfur fractions is common for MBO where fluctuating oxic and anoxic-reductive redox conditions occur. For example, this is common for MBO that accumulates in drains that experience periodic high flows causing sediment turnover (Burton *et al.* 2006c).

The properties of MBO are highly variable. The black colour is usually a poor indicator of their sulfide content and other geochemical properties. Iron monosulfides are a major contributor to the black appearance of MBO. Because iron monosulfides are nano-crystalline, only a small amount present can create the black colour. A range of MBOs of similar appearance were recently found to have vastly differing sulfur geochemical properties, with iron monosulfide contents (quantified as acid-volatile sulfide - S_{AV}), ranging from approximately 100 - 1000 $\mu\text{mol g}^{-1}$ (Burton *et al.* 2006c).

Mackinawite (FeS) is a tetragonal Fe(II) monosulfide that is the dominant iron monosulfide mineral known to occur in MBO (Burton *et al.* 2007). The presence of a single broad X-ray diffraction peak at ~ 0.5 nm is characteristic of nano-particulate mackinawite, and typically lacks the other X-ray diffraction peaks of bulk mackinawite (Rickard and Morse 2005). Electron microscopy of mackinawite (i.e. stoichiometric $\text{FeS}_{(s)}$) from an MBO is shown in Figure 1-2. In MBO, mackinawite occurs as aggregates of sub-micron size crystals, with each individual crystal measuring 5 - 8 nm in size.

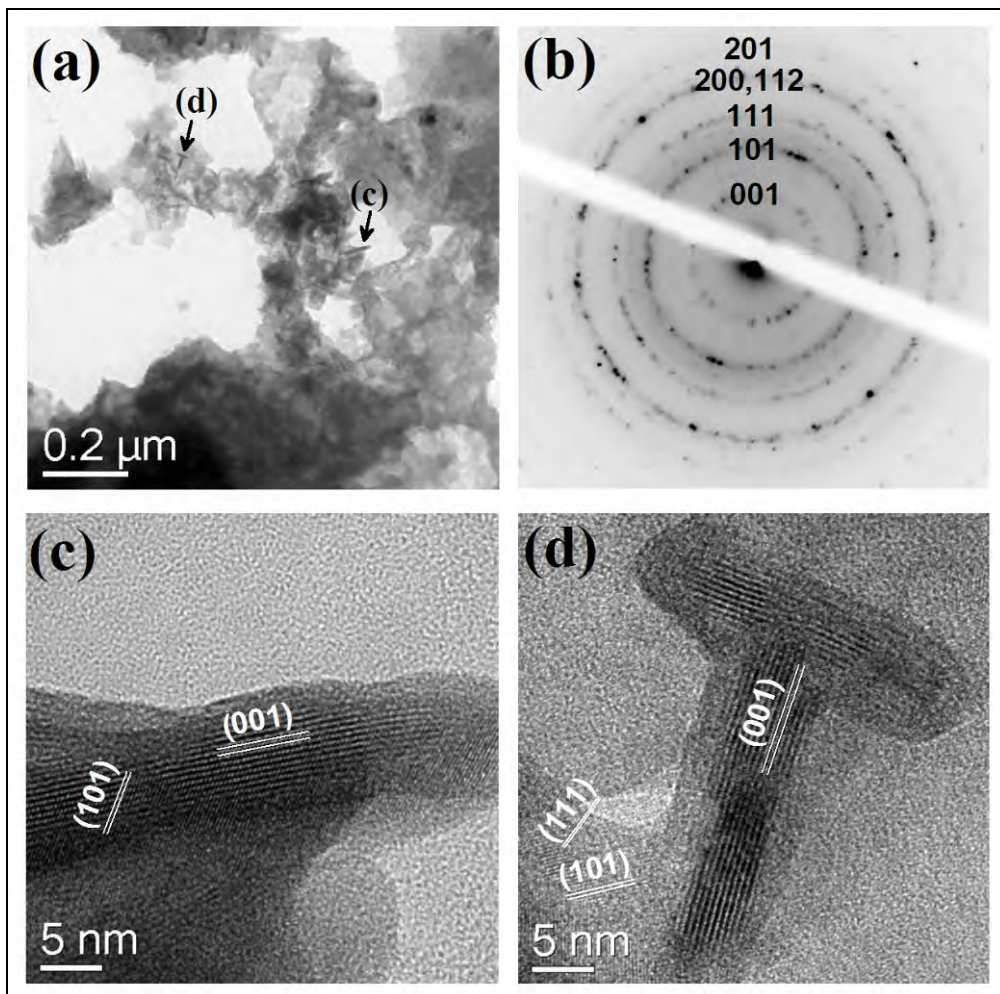


Figure 1-2: Mineralogical data for iron monosulfides in MBO from an acid sulfate system. (A) Cluster of nano-crystalline iron sulfide minerals from an MBO; (B) electron diffraction pattern for material in (A). (C) and (D) High-resolution transmission electron microscope image showing lattice spacings confirming mackinawite (source: Burton *et al.* 2007).

1.3.3.2 MBO formation

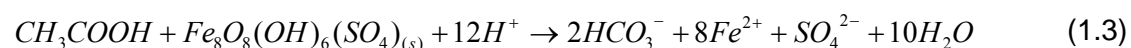
Monosulfides can occur in soils and sediments where there is sufficient sulfate, iron and organic matter for their formation (Bush *et al.* 2004). Monosulfides are the initial sulfides formed under reducing conditions in estuaries, mangrove swamps, coastal lake bottoms, salt marshes, tidal swamps and brackish lake sediments (Sammut *et al.* 1996). The accumulation of monosulfide has also been observed in freshwater river environments and irrigated landscapes in the MDB (Sullivan *et al.* 2002b). These environments experience rapid removal of dissolved oxygen, allowing the initiation of sulfate reduction. Monosulfide minerals include mackinawite ($\text{FeS}_{0.94}$), amorphous sulfide (FeS), and the amorphous monosulfides of other metals (e.g. Ni, Zn, Cd, and Pb) (Rickard and Morse 2005).

The conditions necessary for monosulfides to form are also readily met in degraded acid sulfate soil landscapes. Inundation and waterlogging of acid sulfate soil induces microbially-driven reductive processes. The onset of reductive processes is often rapid (i.e. within a few days) and is evident by a decrease in redox potential (Eh) and an increase in pH. Where there is a strong shift to reductive processes, the soils can move from a predominantly oxic to a reductive condition. This major geochemical process results in the contemporary formation and accumulation of sulfide minerals. The responsiveness of an acid sulfate soil to waterlogging varies according to the availability of labile organic carbon, soil temperature, and importantly, the availability of 'reactive iron' and sulfate (Burton *et al.* 2006a).

The two major processes leading to iron monosulfide formation are microbial reduction of Fe (III) minerals and dissimilatory sulfate reduction by bacteria, described in more detail below.

Step 1: Microbial reduction of Fe (III) minerals

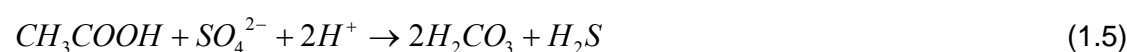
Equation 1.3 describes the reduction of schwertmannite, a common Fe (III) mineral in acid sulfate soil landscapes (from Burton *et al.* 2007):



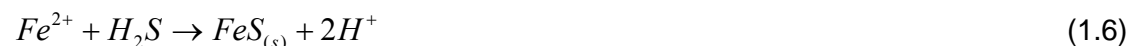
Relatively high aqueous iron (II) and bicarbonate (HCO_3^-) concentrations result from schwertmannite reduction, leading to the precipitation of siderite ($\text{FeCO}_{3(s)}$), a common component of MBO (Equation 1.4):



Step 2: Bacterial dissimilatory sulfate (SO_4^{2-}) reduction (where acetic acid represents a variety of utilizable organic electron donating substances) occurs according to Equation 1.5:



Pore-water sulfide (S^{2-}) is a major product of sulfate reduction, but is usually not detectable ($< 1 \mu\text{M S}^{2-}$) in MBO. The relative rate of sulfide formation rarely exceeds its loss from pore-waters by rapid precipitation of nano-particulate mackinawite (FeS) (Rickard 1995). Mackinawite forms within seconds at near-neutral pH when solutions of ferrous iron (Fe^{2+}) and sulfide are mixed according to Equation 1.6:



However, the accumulation of substantial concentrations of dissolved sulfide (up to 613 mg L^{-1}) has recently been observed in MBOs where iron availability is limited (Ward *et al.* 2009, in press).

1.3.3.3 Disulfides in MBO

Disulfide minerals include pyrite (FeS_2) and marcasite (FeS_2) (Deer *et al.* 1985). Pyrite is the most common disulfide mineral (Morse *et al.* 1987) and is considered to be the most important source of acidity in acid sulfate soil landscapes. Approximately 50% of organic matter in coastal sediments is potentially metabolised by sulfate-reducing bacteria, with the majority of the sulfide produced ending up in pyrite (Rickard 1995).

Monosulfides are a precursor to disulfides (Berner 1984), with their transformation controlled by the availability of oxidants supplied through diffusion, burial or bioturbation (Gagnon *et al.* 1995). Therefore, monosulfides may remain in sediments for long periods of time (Goldhaber and Kaplan 1974), particularly under anaerobic conditions where there is insufficient H₂S for conversion to pyrite.

The presence of intermediate aqueous reduced inorganic sulfur species (i.e. elemental sulfur, polysulfides, polythionates or thiosulfates) promotes the conversion of monosulfides to pyrite (Gagnon *et al.* 1995). Enhancing the conversion of monosulfides to pyrite is potentially an important acid sulfate soil management tool as pyrite is a more stable form of reduced inorganic sulfur (Gagnon *et al.* 1995).

Morse *et al.* (1987) described the major steps in sedimentary disulfide formation as:

- reduction of sulfate to H₂S by bacteria,
- reaction of H₂S with iron minerals to form iron monosulfides, and
- reaction of iron monosulfides with elemental sulfur to form pyrite.

Berner (1970) stated that the extent of disulfide formation is controlled by:

- availability of organic matter for bacterial reduction of sulfate,
- diffusion of sulfate into the sediment,
- concentration and reactivity of iron minerals, and
- production of elemental sulfur.

1.3.3.4 Environmental issues with MBO

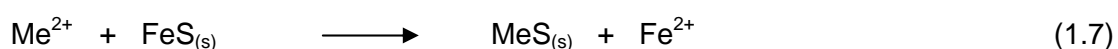
Monosulfides have been studied in both marine and estuarine sediments (Morse *et al.* 1987; Bush *et al.* 2004). Morse *et al.* (1987) noted that small, highly dispersed concentrations of monosulfides can be found in both soils and sediments. Similarly, Bush and Sullivan (1999) identified thin coatings of monosulfides around pyrite framboidal clusters in acid sulfate soil. However, substantial quantities of monosulfides have been found in some Australian estuarine sediments (Bush *et al.* 2004). Recent studies have revealed high concentrations of monosulfides in the soils and channel sediments of acid sulfate soil landscapes (e.g. Bush *et al.* 2004; Burton *et al.* 2006c; Sullivan *et al.* 2006a; Ward *et al.* 2009). Unlike the oxidation of

pyrite which is rapid at pH < 4, the chemical oxidation of monosulfides is rapid over a wide range of pH values. When these sediments are mobilised and subsequently oxidised during flooding or clearing practices the high reactivity of monosulfides poses a potential environmental threat. Monosulfides can rapidly deoxygenate surface waters, cause severe acidification and may release contaminants (Sullivan and Bush 2000; Sullivan *et al.* 2002a; Burton *et al.* 2006a).

The acidic conditions in acid sulfate soils following oxidation can significantly affect the chemical behaviour of heavy metals bound in sediments (Lin *et al.* 2001). Under 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 potentially become bioavailable if the pyrite is oxidised (Morse and Arakaki 1993). Pyrite does not exchange trace metals as readily as monosulfides (Allen *et al.* 1993) due to its chemical stability where pH > 4. Morse and Arakaki (1993) stated that a major portion (from 20% to over 90%) of pyrite-bound metals could be released in one day if anoxic sediments were exposed to oxic seawater. The mobilisation of MBO materials in laboratory experiments collected from the Lower Lakes region of SA resulted in high concentrations of a wide range of contaminants including Al, Mn, NH₄⁺ and NO₃⁻ (Sullivan *et al.* 2008a).

1.3.3.5 Divalent trace metal accumulation with MBO

Cationic metals in sediments are derived from both natural and anthropogenic sources. The metals found in sediments are strongly influenced by the parent material, however, metals may also be derived from organic matter which can be a major source of As, Cu and Hg found in sediments (Simpson *et al.* 2005). Sulfide, usually in the form of iron sulfides, is the primary reactant of many trace metals in anoxic sediments. Casas and Crecelius (1994) found that iron sulfides remove certain metals from pore-waters by exchange to form insoluble metal sulfides (MeS_(s)) according to Equation 1.7:



Monosulfides are an important sink for trace metals, accumulating by co-precipitation with sulfides and/or sorption processes. The precipitation of iron sulfides, particularly

iron monosulfides, actively scavenges trace metals. Therefore, trace contaminant metal precipitation is closely linked to the abundance of monosulfides.

The formation of insoluble metal species dramatically reduces their bioavailability (Casas and Crecelius 1994) and may be an important buffer mechanism in controlling metal flux in ground and surface waters. However, these metals can also be rapidly released when MBO is oxidised, often resulting in acute high concentrations that greatly exceed water quality guidelines (Burton *et al.* 2006a).

Heavy metals have been reported in acid sulfate soils (e.g. Lin *et al.* 2001), and general guidelines for sediments are available (ANZECC/ARMCANZ 2000; Simpson *et al.* 2005). The guidelines are based on categories which relate to their potential impacts on biota. These effects are described as effects range low (ERL) and effects range median (ERM), where ERL is a very low and ERM is a high (>50%) probability of effects on biota above these levels.

1.3.3.6 MBO oxidation

Monosulfidic sediments can contain very high concentrations of S_{AV} (Sullivan and Bush 2000). The mobilisation and subsequent oxidation of these sediments has the potential to adversely affect water quality. MBOs can rapidly decrease the dissolved oxygen content of water in minutes, with acidification continuing over several days (Sullivan and Bush 2000). Recently, concerns have been raised about the role of MBO and its known impacts on water quality during a major flood (February 2001), which resulted in a large fish kill event in eastern Australia (Eyre *et al.* 2006). The oxidation dynamics of MBO are discussed in detail in Section 4.2.2.

The key impacts from MBO oxidation include extreme deoxygenation, acidification and the potential release of contaminants. Extreme deoxygenation and acidification are known to occur, and have large impacts when MBO is suspended in floodwaters (Bush *et al.* 2004). As mentioned previously, the mobilisation of MBO collected from the Lower Lakes region resulted in high concentrations of a wide range of contaminants (Sullivan *et al.* 2008a). A conceptual model summarising sulfide formation in the River Murray wetlands and some of the potential reactions following disturbance are shown in Figure 1-3.

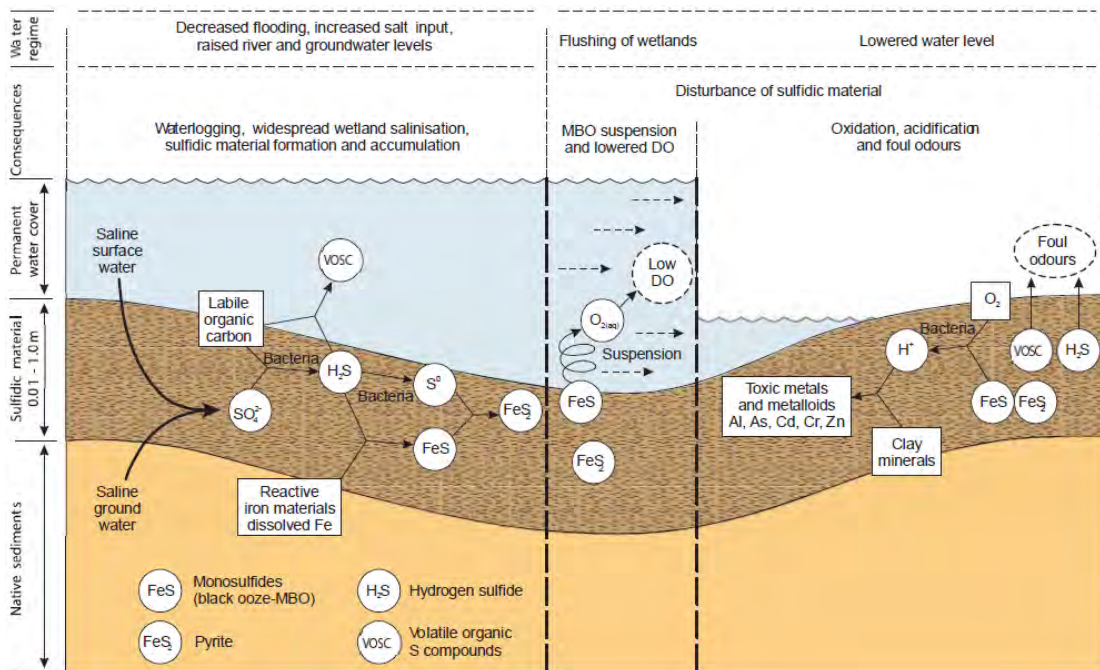


Figure 1-3: Conceptual model of sulfide formation in the River Murray wetlands and the potential reactions following disturbance (source: Lamontagne *et al.* 2004).

1.3.4 Classification of acid sulfate soil materials

A new classification system for acid sulfate soil materials was adopted in October 2008 by the Scientific Reference Panel of the MDB Acid Sulfate Soil Risk Assessment Project (ASSRAP) for use in the detailed assessment of acid sulfate soils in the MDB. Acid sulfate soil materials have been defined by Sullivan *et al.* (2009b) to include sulfidic, hypersulfidic, hyposulfidic, sulfuric and monosulfidic materials. A description of each of the terms used to classify acid sulfate soils is given below.

- **Sulfuric materials** – soil materials currently defined as sulfuric by the Australian Soil Classification (Isbell 1996). Essentially, these are soil materials with a $\text{pH}_w < 4$ as a result of sulfide oxidation.
- **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).*

- **Hypersulfidic material** – Hypersulfidic material is a sulfidic material that has a field pH of 4 or more and 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.*

- **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.*

- **Monosulfidic materials** – soil materials with an acid volatile sulfur content of 0.01%S or more.

2. REPORTED DISTRIBUTION OF REDUCED INORGANIC SULFUR COMPOUNDS

2.1 Reduced inorganic sulfur compounds in wetlands of the Murray-Darling Basin

Recent studies have found widespread distribution of reduced inorganic sulfur compounds in inland wetlands in the MDB (e.g. Lamontagne *et al.* 2004, 2006; Hall *et al.* 2006a,b; McCarthy *et al.* 2006; Fitzpatrick and Shand 2008a; Fitzpatrick *et al.* 2008e,f). Lamontagne *et al.* (2006) surveyed 9 wetlands in the Lower Murray River floodplains in South Australia and found sulfidic sediments to be widespread, with surface sediment sulfide contents of up to ~1% S_{CR} . Saline and permanently flooded wetlands were more likely to have greater sulfide concentrations than freshwater wetlands or those with regular wetting-drying regimes. However, despite elevated sulfide concentrations in many of the wetlands, the acidification hazard was usually low due to the high acid neutralising capacities (ANC) of these sediments (i.e. up to 30% as $CaCO_3$). Hall *et al.* (2006a,b) examined 81 freshwater wetlands throughout the MDB and found that 21% of wetlands contained sulfide concentrations above a trigger value of $S_{CR} > 0.02\%$. The reduced inorganic sulfur concentration in the sediments was also positively correlated with the sulfate concentration in the overlying water column.

More recently, detailed acid sulfate soil assessments were undertaken at 14 Ramsar-listed wetland complexes as part of the Murray-Darling Basin Acid Sulfate Soil Risk Assessment Project (MDB ASSRAP) (Figure 2-1) (e.g. Bush *et al.* 2009a,b,c; Sullivan *et al.* 2009c,d,e; Thomas *et al.* 2009a,b,d,e). Although the presence of acid sulfate soils (i.e. $S_{CR} \geq 0.01\%$) was identified in most of the Ramsar wetlands assessed, only four wetlands were determined to be a priority concern at a wetland-scale to warrant further investigation. The presence of MBO materials was observed within the Currawinya Lakes Ramsar wetland. The Ramsar wetlands that are presently undergoing a further assessment include Fivebough and Tuckerbil Swamps, Chowilla (Riverlands), Banrock Station and Kerang Wetlands.

Following the completion of the detailed assessments of Ramsar-listed 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 having a high priority or a risk profile. All (except one) of the more than 70 wetlands between Wellington and Lock 1 on the Lower Murray River have received Phase 1 detailed ASS assessment through the MDB ASS Risk Assessment Project (Pers. Comm. Rob Kingham). Currently, 96 priority wetlands within the Basin are also undergoing a detailed acid sulfate soil assessment as part of ASSRAP to determine the presence of acid sulfate soil materials.

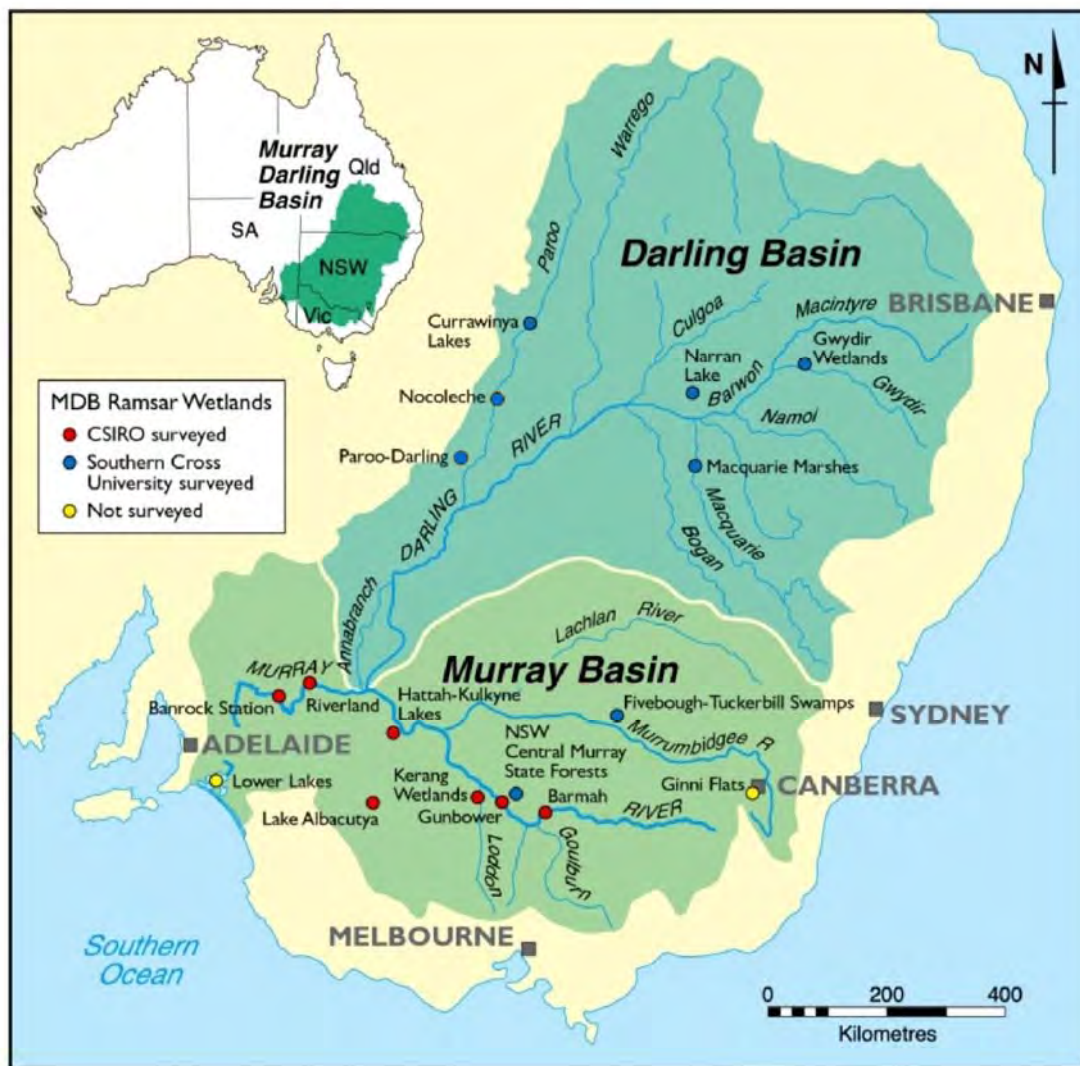


Figure 2-1: Map showing the Ramsar-listed wetlands surveyed in the Murray-Darling Basin (source: Thomas *et al.* 2009a).

2.2 Reduced inorganic sulfur compounds in channels of the Murray-Darling Basin

Sullivan *et al.* (2002b) first reported the presence of sulfidic sediments in channel systems in the MDB. This study found that sulfate reduction processes were sufficient to result in the accumulation of appreciable iron sulfides within both freshwater river environments and irrigated landscapes as a consequence of elevated sulfate concentrations due to salinisation. Sulfides occurred as interstitial accumulations of both pyrite and monosulfides in the sediments, and occurring as MBOs especially in irrigated landscapes (Sullivan *et al.* 2002b).

There has been limited research on sulfides in channel systems in the MDB since the initial identification of sulfides in 2002. This section presents a series of case studies on the properties and reported distribution of sediments containing reduced inorganic sulfur compounds in rivers and creeks in the MDB.

The areas examined in detail in this desktop assessment include:

- Riverland floodplain, South Australia (Section 2.2.1),
- Lower Loddon River and Burnt Creek, Central Victoria (Section 2.2.2),
- Channels associated with River Murray Locks 8 and 9 weir pools, New South Wales and Victoria (Section 2.2.3),
- Salt Creek, south-west New South Wales (Section 2.2.4),
- Edward-Wakool River system, New South Wales (Section 2.2.5),
- Talbragar River, central New South Wales (Section 2.2.6), and
- Irrigation channels, Queensland (Section 2.2.7).

A summary of the reported distribution of reduced inorganic sulfur compounds in channels in the MDB is presented in Section 2.2.8. In addition, maps showing the location of acid sulfate soil rapid assessment sites for rivers and creeks in the MDB are presented in Appendix 3 (Figures 9-1 – 9-4).

2.2.1 Lower Murray River floodplain, South Australia

2.2.1.1 River Murray below Blanchetown (Lock 1)

Fitzpatrick *et al.* (2008e) examined 458 soil samples from 103 representative soil profiles from the River Murray channel below Lock 1, and the Lower Lakes between mid-2007 and April 2008 to assess the current and potential impacts of acid sulfate soils. Four standard methodologies were applied to classify the various subtypes of acid sulfate soils and non-acid sulfate soils to assess risk caused by the prevailing drought conditions including soil morphology, pH testing in water (pH_W), peroxide pH testing (pH_{FOX}), and acid-base accounting (see Appendix 2).

Representative river channel profiles were selected for detailed analyses from the river bank adjacent to the Swanport wetland, downstream of Murray Bridge (Wellington to Lock 1: WL 1, WL 2 and WL 5) (Figure 2-2). Additional samples were also selected approximately 14 km downstream of Lock 1, associated with Morgans wetland (MOR 3, MOR 4 and MOR 7) (Figure 2-2). The profile collected from MOR 7 was from the river bank adjacent to the wetland and MOR 3 and 4 were both located in the wetland. A summary of the data collected including pH, acid sulfate soil classification, acid-base accounting and acid sulfate soil risk are presented in Appendix 1 (Table 9-1 and 9-2).

The pH_W values of the soil materials collected from the river channels ranged between 2.5 and 7.5 (Table 9-1, Appendix 1). One soil profile (WL 5) was classified a sulfuric material (i.e. $\text{pH}_W < 4$ as a result of sulfide oxidation). The pH_{FOX} values ranged between 1.0 and 6.5. All soils showed a decrease in pH after treatment with peroxide. The pH_{FOX} results indicated that all soil materials, except WL 2.3, may have the potential to acidify to $\text{pH} < 4$ as a result of sulfide oxidation. Sulfidic soil materials (i.e. $S_{\text{CR}} \geq 0.01\% \text{ S}$) were observed in all layers analysed, ranging between 0.02 and 0.18% S. The pH_{KCl} (pH in 1M potassium chloride) data showed that the majority of samples had a $\text{pH}_{\text{KCl}} < 6.5$, and therefore, by definition, contained zero ANC (Table 9-2, Appendix 1). Acid-base accounting calculations showed positive net acidity values for all except one sample (WL 2.3), indicating that the majority of samples either contained existing acidity and/or had the potential to produce further acid upon oxidation. The net acidity values of samples collected from the channels ranged from -24 to 352 mole H^+ tonne^{-1} .



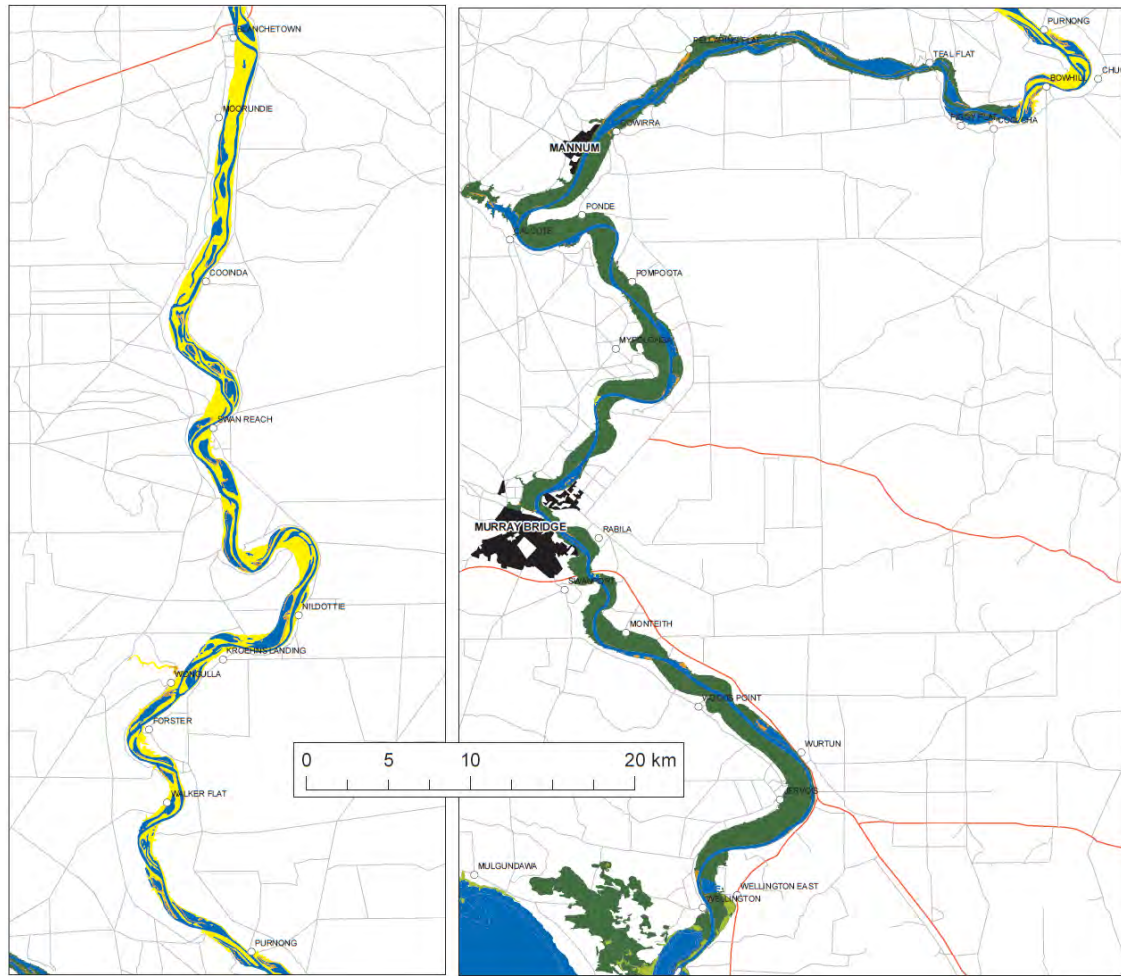
Figure 2-2: Locations of selected representative acid sulfate soil survey sites from the Murray River channel below Lock 1 and the Lower Lakes (source: Fitzpatrick *et al.* 2008e).

A range of acid sulfate soil subtypes were identified, including sulfidic cracking clay soil, sulfuric cracking clay soil, and sulfidic subaqueous clayey soil (Table 9-1, Appendix 1). The acid sulfate soil risk categorisation used in this study was based on a number of criteria (including the lime treatment category, the presence of MBO, peroxide pH, decrease in pH during incubation experiments) and indicated that the sites were predominantly high risk, with minor high risk present at site WL 1. The collection of water quality data was not part of this study.






Fitzpatrick *et al.* (2008a,e) also predicted the distribution of 14 subtypes of acid sulfate soil in the River Murray below Blanchetown (Lock 1) and the Lower Lakes for two water-level scenarios (i.e. pre-drought water level (+0.5 AHD) (Figure 2-3) and

February 2008 drought level (-0.5 AHD)) (Figure 2-4). The predicted distribution of acid sulfate soil types was made using bathymetry-, and soil and vegetation mapping in a Geographic Information System (GIS). However, field verification inspections have shown that the resolution of the spatial data used to underpin the map predictions were too coarse to predict the actual spatial variability of the acid sulfate soil subtypes (Fitzpatrick *et al.* 2008e). Further field work will assess the validity of the map units.

The MDBA has since funded a modified rapid assessment project to determine the likelihood of acid sulfate soil materials in the bank sediments of the lower Murray River between Wellington and Lock 1. Numerous sites had soil $pH_w < 4$ indicating sulfuric materials (Pers. Comm. Rob Kingham). The results of this study will be available shortly.








Subaqueous ASS under shallow water (< 2.5m)

-  Sulfidic subaqueous organic soils [Ak(p2)q]
-  Sulfidic subaqueous clayey soils [Ak(p2)q]
-  Sulfidic subaqueous sandy soils [Ak(p2)s]
-  Sulfidic subaqueous soils [Ak(p2)]
-  MBO subaqueous soils [Ak(m2)]

**Acid Sulfate Soils (ASS)
with water at
pre-drought levels**

**Waterlogged, saturated
& anaerobic ASS**

-  Sulfidic organic soils [Al(p2)]
-  Sulfidic vertosols [Bo(p2)]
-  Sulfidic hydrosols (hi prob) [Am(p2)]
-  Sulfidic hydrosols (low prob) [Bm(p2)]
-  MBO sulfidic hydrosols [Am(m2)]

**Drained, unsaturated
& aerobic ASS**





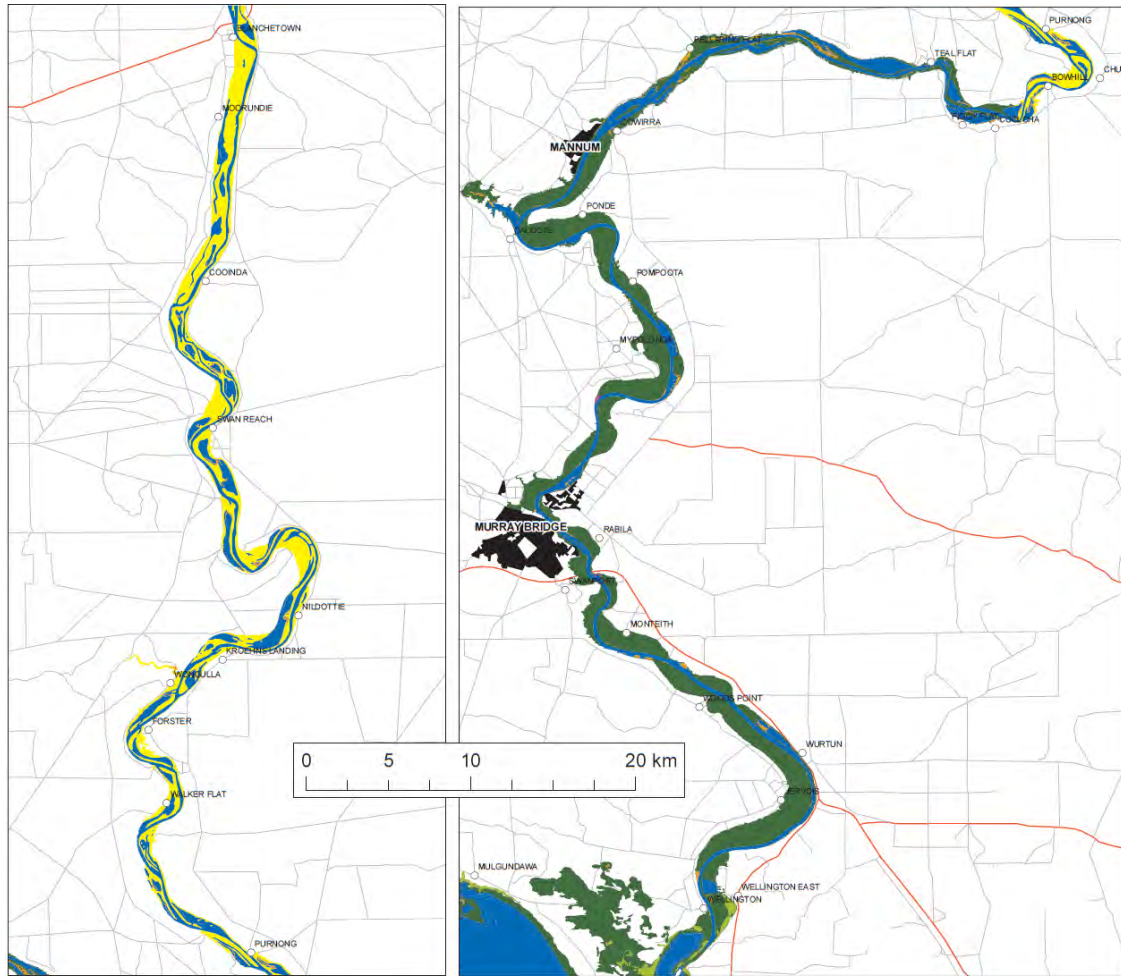





-  Sulfuric organic soils [Al(a1)]
-  Sulfuric vertosols [Ao(a1)]
-  Sulfuric hydrosols [Am(a1)]
-  MBO hydrosols (desiccation cracks) [Am(m2)d]

Figure 2-3: Predictive acid sulfate soil subtype maps of the river channel below Lock 1 at pre-drought water levels (i.e. +0.5 m AHD) (source: Fitzpatrick *et al.* 2008e).








Subaqueous ASS under shallow water (< 2.5m)

-  Sulfidic subaqueous organic soils [Ak(p2)o]
-  Sulfidic subaqueous clayey soils [Ak(p2)c]
-  Sulfidic subaqueous sandy soils [Ak(p2)s]
-  Sulfidic subaqueous soils [Ak(p2)]
-  MBO subaqueous soils [Ak(m2)]

**Acid Sulfate Soils (ASS)
with water level at -0.5
mAHD**

**Waterlogged, saturated
& anaerobic ASS**

-  Sulfidic organic soils [Al(p2)]
-  Sulfidic vertosols [Bo(p2)]
-  Sulfidic hydrosols (hi prob) [Am(p2)]
-  Sulfidic hydrosols (low prob) [Bm(p2)]
-  MBO sulfidic hydrosols [Am(m2)]

**Drained, unsaturated
& aerobic ASS**





-  Sulfuric organic soils [Al(a1)]
-  Sulfuric vertosols [Ao(a1)]
-  Sulfuric hydrosols [Am(a1)]
-  MBO hydrosols (desiccation cracks) [Am(m2)d]

Figure 2-4: Predictive acid sulfate soil subtype maps of the river channel below Lock 1 at drought water levels (i.e. -0.5 m AHD) (source: Fitzpatrick *et al.* 2008e).

2.2.1.2 Finnis River, Currency Creek, Black Swamp and Goolwa Channel

Fitzpatrick *et al.* (2009a,b) assessed the properties and extent of various subtypes of acid sulfate soils in the lower reaches of Finnis River, Currency Creek, Black Swamp and Goolwa Channel (Figure 2-5). A summary of the findings in this study is also presented in Fitzpatrick *et al.* (2009c). These water bodies are adjacent to Lake Alexandrina in the lower reaches of the River Murray, and were experiencing historically low water levels due to drought conditions at the time of sampling. A total of 12 transects were examined. The transects included 39 geographically well-distributed and locally representative soil profiles. The following standard methodologies were applied to classify the various subtypes of acid sulfate soils and non-acid sulfate soils to assess risk caused by drought conditions: (i) soil morphology, (ii) field pH testing, (iii) peroxide testing, (iv) acid-base accounting, (v) soil incubation and (vi) mineralogical analysis (using x-ray diffraction). A summary of the laboratory data including pH testing and acid-base accounting is presented in Appendix 1 (Table 9-3).

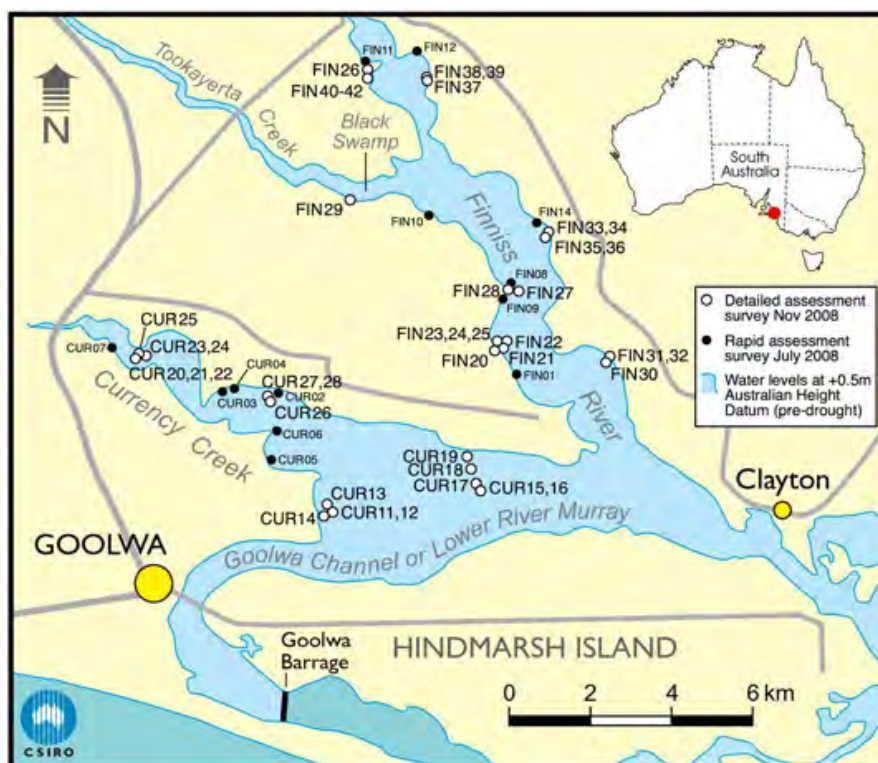


Figure 2-5: Locations of rapid and detailed assessment survey sites for Finnis River, Currency Creek, Black Swamp and Goolwa Channel (source: Fitzpatrick *et al.* 2009b).

Fitzpatrick *et al.* (2009a,b) found that more than half of the sites examined contained sulfuric materials ($\text{pH} < 4$). The remaining sites had significant potential for developing sulfuric materials if the water levels continue to drop. The pH_{FOX} values indicated that 70% of samples may have the potential to acidify to $\text{pH} < 2.5$ as a result of sulfide oxidation. The $\text{pH}_{\text{incubation}}$ (pH following incubation) data showed that 65% of samples were below $\text{pH} 4.0$, and would be characterised as hypersulfidic materials. Multiple layers were analysed at 32 sites and 18 of those sites contained a sulfuric material layer. The remaining 14 sites contained at least one hypersulfidic material layer indicating strong potential to acidify when exposed to air under moist conditions.

All samples had detectable sulfide concentrations (i.e. $\text{S}_{\text{CR}} \geq 0.01\% \text{ S}$) with a maximum S_{CR} of 4.32% S. All soil samples also had high sulfate concentrations exceeding $100 \text{ mg kg}^{-1} \text{ SO}_4$, and are therefore considered to have the potential to form monosulfidic materials if the soils were reflooded. The pH_{KCl} data showed that 63% of samples had a $\text{pH}_{\text{KCl}} < 6.5$, and therefore, by definition, contained zero ANC. Acid-base accounting calculations showed positive net acidity for 76% of samples (with a maximum net acidity of $2575 \text{ mole H}^+ \text{ tonne}^{-1}$), indicating that the majority of samples either contained existing acidity and/or have the potential to produce further acid upon oxidation. The presence of various iron hydroxysulfate minerals including sideronatrite, schwertmannite and jarosite/natrojarosite indicated oxidation of high concentrations of iron sulfides (principally pyrite) in the original soil materials.

The methodologies used in Fitzpatrick *et al.* (2009b) (i.e. peroxide testing, acid-base accounting, soil incubation) were combined to classify the acid sulfate soil types and determine an acid hazard class for each site. A summary of the type and prevalence of acid sulfate soil materials for each of the four areas examined is presented in Table 2-1.

Table 2-1: Acid sulfate soil material types counted by site occurrence (source: Fitzpatrick *et al.* 2009b).

Acid Sulfate Soil Material Type	Number of Sites and Percentage of Sites Accessed by Area				
	Finniss River	Currency Creek	Goolwa Channel	Black Swamp	Total
Sulfuric	8 (50%)	4 (67%)	6 (67%)	0	18 (56%)
Hypersulfidic	8 (50%)	2 (33%)	1 (11%)	1 (100%)	12 (38%)
Hyposulfidic ($S_{CR} \geq 0.10\%$)	0	0	0	0	0
Hyposulfidic ($S_{CR} < 0.10\%$)	0	0	2 (22%)	0	2 (6%)
Other acidic pH_w &/or $pH_{incubation}$ 4 – 5.5 soil materials	0	0	0	0	0
Other soil materials	0	0	0	0	0
Monosulfidic (observed)	0	0	0	0	0
Monosulfidic (potential)	16 (100%)	6 (100%)	9 (100%)	1 (100%)	32 (100%)

A summary of the acid hazard class based on the determination of the lime treatment category for each site is presented in Table 2-2. The acid hazard classification shows that more than 91% of sites assessed have a classification ranging from high to extra high, indicating a significant potential hazard. The general relationship between the acid sulfate soil types observed, the hazard type (i.e. acidification, metal mobilisation and deoxygenation) and the hazard condition (i.e. current, potential and none) is presented in Table 2-3. The sulfuric materials are identified as having a current risk of acidification and metal mobilisation, whereas the other soil types identified present a potential risk to the environment. The potential formation of monosulfides at all the sites examined is also identified as a potential deoxygenation risk.

Table 2-2: Summary of number of sites in each acid hazard class based on the lime treatment category (source: Fitzpatrick *et al.* 2009b).

Acid Hazard Class	Number of sites	Percentage of sites
No (N)	2	6
Low (L)	1	3
Medium (M)	0	0
High (H)	7	22
Very high(VH)	17	53
Extra high (XH)	5	16

Table 2-3: General relationship between acid sulfate soil material type and hazard condition (source: Fitzpatrick *et al.* 2009b).

Type of Acid Sulfate Soil Material	Hazard Type and Condition		
	Acidification	Metal Mobilisation	Deoxygenation
Sulfuric	current	current	none
Hypersulfidic	potential	potential	none
Hyposulfidic ($S_{CR} \geq 0.10\%$)	potential	potential	none
Monosulfidic (observed)	potential	current	current
Monosulfidic (potential)	potential	potential	potential
Hyposulfidic ($S_{CR} < 0.10\%$)	potential	potential	none
Other acidic (pH_W &/or $pH_{incubation}$) 4 to 5.5 soil materials	current or potential	current or potential	none
Other soil materials	none	none	none

Acid sulfate soil types in bold font were identified at sites in the Finniss River, Currency Creek, Black Swamp and Goolwa Channel.

The channel waters in Currency Creek and Finniss River were both alkaline (pH 7.8 and 8.9) at the time of sampling, with high SEC (specific electrical conductance) (18,388 and 23,591 $\mu S\ cm^{-1}$). Water quality data showed localised acidity in ponded and flowing water bodies (pH 3.3 - 3.8) in areas that had previously been identified as containing widespread sulfuric cracking clay soils. In some soil pits of dry river beds and wetlands of Currency Creek and Finniss River, the water present had pH values ranging from 3.4 to 3.9.

Fitzpatrick *et al.* (2009b) developed a series of conceptual toposequence models to gain a greater understanding of the temporal and spatial extent of the acid sulfate soil materials (e.g. Figure 2-6). Transects were located along a toposequence from dry inland areas to the main river channel. Predictive maps were developed depicting the occurrence of various acid sulfate soil subtypes for various scenarios including water levels at -0.5 m AHD, -1.0 m AHD, and -1.5 AHD. Approximately 2000 ha of sulfuric soils (pH < 4) occurred at a water level of -1.0 m AHD in the study area (Figure 2-7).

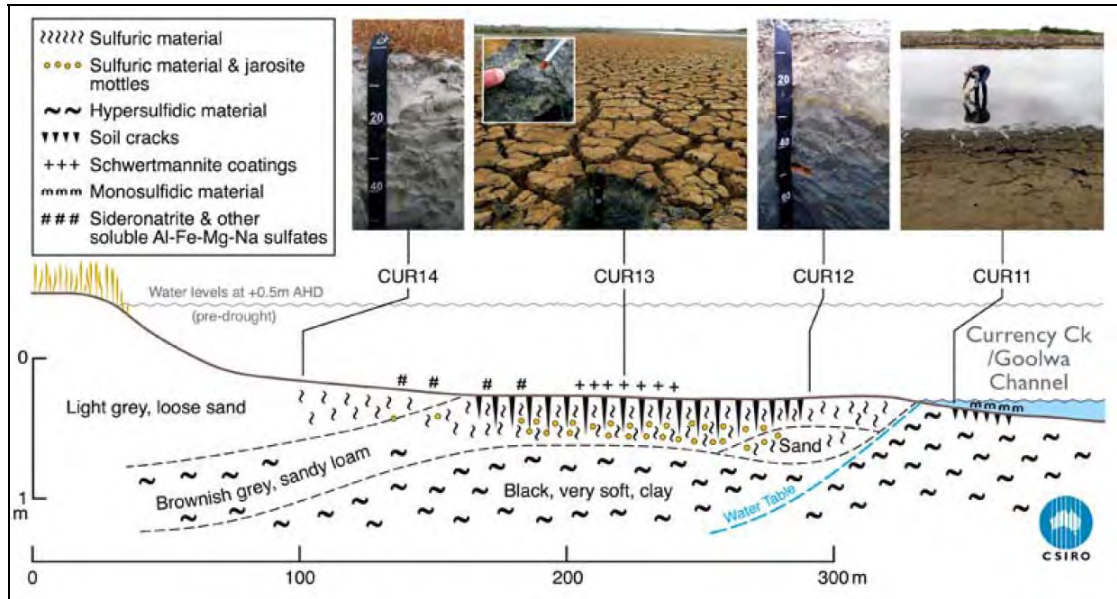


Figure 2-6: Conceptual toposequence model for sites CUR11 to 14, located on the western side of Goolwa Channel/Currency Creek (source: Fitzpatrick *et al.* 2009b).

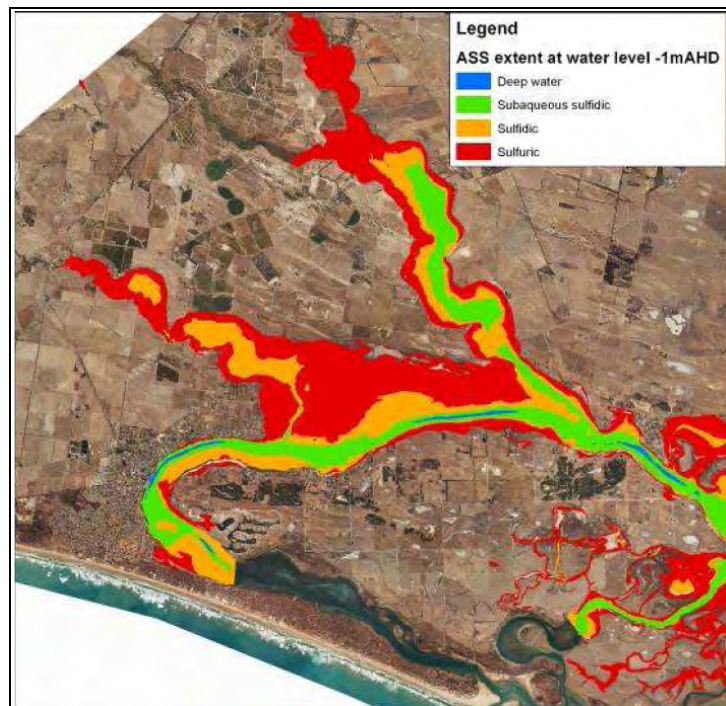


Figure 2-7: Map showing predicted occurrences of ASS Subtypes for Lake levels at -1.0 m AHD (based on Fitzpatrick *et al.* 2008e), which closely approximate the current distribution of sulfuric and sulfidic materials, verified from field work along 12 transects in late November 2008 (source: Fitzpatrick *et al.* 2009a).

Fitzpatrick *et al.* (2009b) also examined the mobilisation of acidity, nutrients and metals over a 24 hour period through the simulated rewetting of dried soils collected from Finniss River and Currency Creek with deionised water. The metal release was rapid and dissolved concentrations of many metals (i.e. Al, Cd, Co, Cu, Cr, Mn, Ni, V and Zn) greatly exceeded the ANZECC water quality guidelines (WQGs) for the protection of ecosystem health. For some metals (i.e. Al, Cd, Co, Cu, Cr, Ni and Zn) the concentrations were often > 100 times the WQGs values. The dissolved metal concentrations released from the soils into the surrounding water were generally significantly greater when the soil-water mixture had a pH < 5. Low concentrations of NO₃⁻ and PO₄³⁻ were released from the dried soils. Fitzpatrick *et al.* (2009b) also found that a greater concentration of metals was released from Finniss River soils than from Currency Creek soils.

2.2.1.3 Mundic Creek and Pike River systems

Shand *et al.* (2009) examined representative soil profiles from 27 sites in the Mundic Creek (16 sites) and Pike River (11 sites) system, on the eastern side of the Murray River near Renmark, to assess the potential impacts of acid sulfate soils. The channel systems examined in May 2008 included Mundic Creek, Pike River and Snake Creek (Figure 2-8). Three independent standard methodologies were applied to determine the acid sulfate soil risk, including peroxide pH testing, acid-base accounting and incubation experiments. Summaries of the laboratory data including pH testing and acid-base accounting data for all sites are presented in Appendix 1 (Table 9-4 and 9-5).

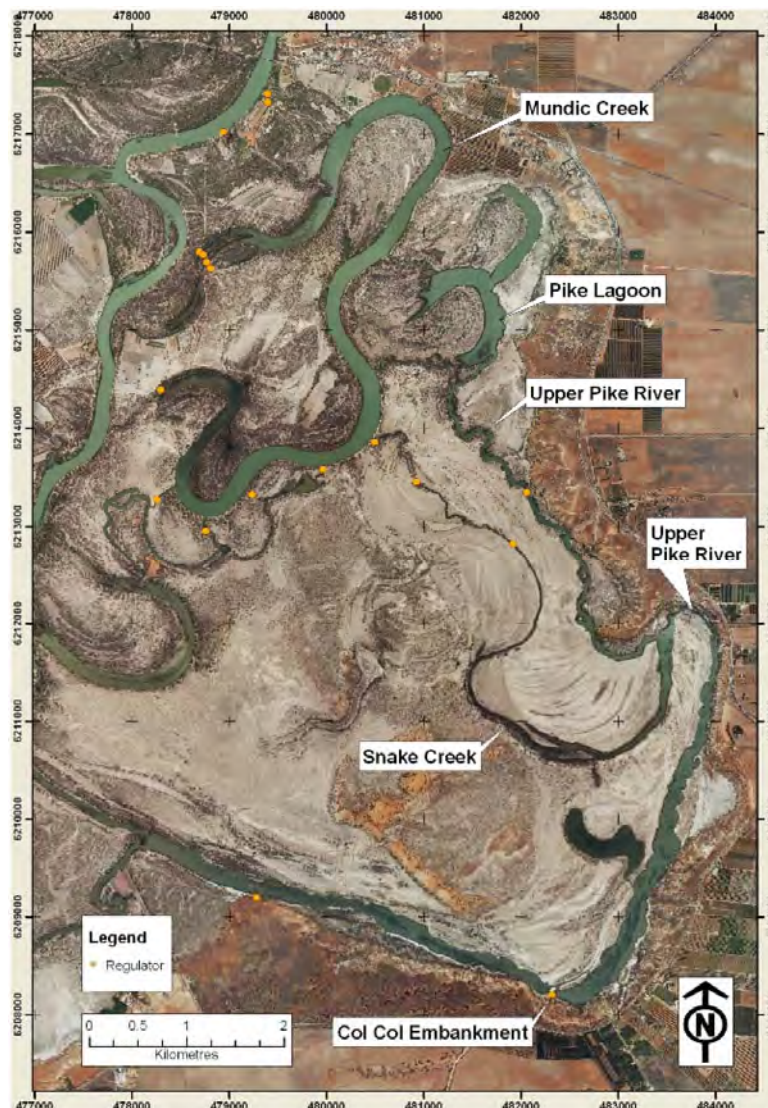


Figure 2-8: Map of Upper Pike system showing the main controlling structures (source: Shand *et al.* 2009).

Shand *et al.* (2009) found that sulfidic soil materials were present at all (except one) of the sites examined, although sulfuric materials (i.e. $\text{pH}_W < 4$) were not observed (Table 9-4, Appendix 1). Black gels (probably MBO) were observed in the more saline parts of the southern area of the complex. The pH_{FOX} values indicated that 35% of the samples may have the potential to acidify to $\text{pH} < 2.5$ as a result of sulfide oxidation. The $\text{pH}_{\text{incubation}}$ data showed that approximately 40% reached a final pH below 4.0 after incubation, and would therefore be characterised as hypersulfidic materials. Sulfidic soil materials (i.e. $\text{S}_{\text{CR}} \geq 0.01\% \text{ S}$) were observed in 88% of samples analysed with a S_{CR} ranging between < 0.01 and $0.58\% \text{ S}$ (Table 9-5, Appendix 1). The pH_{KCl} data showed that 90% of samples analysed had a $\text{pH}_{\text{KCl}} < 6.5$, and therefore contained zero ANC. Acid-base accounting calculations showed positive values for net acidity for 57 of the 60 samples analysed (i.e. $3 - 322 \text{ mole H}^+ \text{ tonne}^{-1}$), indicating that the majority of the samples contained existing acidity and may also have the potential to produce further acid upon oxidation.

The three methodologies used were combined to establish the acid sulfate soil acidification hazard for each site and an overall risk for each wetland (see Shand *et al.* 2009). A generalised risk assessment for the area was: moderate to high risk: Mundic Creek, Upper Pike River and Snake Creek; low to moderate risk: immediately upstream from Col Col and Salt Lake (unconnected to Mundic Creek). However, as suggested by Shand *et al.* (2009), even where the risk of development of sulfuric materials was moderate, there is significant potential for the pH to decrease to ~ 5 in many soil materials. At these pH values, there is still significant risk to the wetland ecosystems from acidity and subsequent release of trace metals if maintained for periods of time.

The surface water quality data collected at the time of sampling showed the pH varied between 6.8 and 9.6. The SEC of the surface waters was low at most sites (i.e. $\leq 541 \mu\text{S cm}^{-1}$), although a high SEC was observed at a couple of sites (i.e. $10,770 - 173,900 \mu\text{S cm}^{-1}$). Dissolved oxygen levels were relatively high at the majority of sites, ranging between 2.6 and 11.9 mg L^{-1} . The surface water sulfate concentration of the sites examined ranged between 3 and 208 mg L^{-1} .

2.2.2 Lower Loddon River and Burnt Creek, central Victoria

Thomas *et al.* (2009c) examined 69 soil and mineral samples collected from 35 locations which were representative of soil profiles found in the Loddon River (27 sites) and Burnt Creek (8 sites) area in central Victoria in December 2008. This study assessed current and potential environmental risk due to the presence of acid sulfate soils (Figure 2-9). Samples were usually collected along toposequence-based transects across the river or creek channel. Sites included the lowest point in the landscape, a moderately elevated site just above the normal flow level, and high elevated site above the normal flow level. The following standard methodologies were applied to classify the various subtypes of acid sulfate soils and non-acid sulfate soils to assess risk caused by the drought conditions including: (i) soil morphology, (ii) field pH, (iii) peroxide testing, (iv) acid-base accounting, (v) soil incubation and (vi) mineralogical analysis (using x-ray diffraction). A summary of the laboratory data including pH and acid-base accounting for all sites sampled are presented in Appendix 1 (Table 9-6 and 9-7).



Figure 2-9: Map of central Victoria showing areas assessed on the Lower Loddon River and Burnt Creek (source: Thomas *et al.* 2009c).

For sites sampled at the Loddon River, pH_W of the soil samples ranged between 3.8 and 9.0 (Table 9-6, Appendix 1). Only 3 of the 32 soil samples were classified as being sulfuric material (i.e. $\text{pH}_W < 4$ as a result of sulfide oxidation). The pH_{FOX} values ranged between 1.6 and 6.7. All soils showed a decrease in pH after treatment with peroxide, with the pH_{FOX} of 50% of the samples decreasing to less than 2.5. This decrease may be partly due to the presence of organic matter. The $\text{pH}_{\text{incubation}}$ data showed that 60% of samples were below pH 4.0. Sulfidic soil materials (i.e. $\text{S}_{\text{CR}} \geq 0.01\% \text{ S}$) were observed in 72% of samples analysed with a S_{CR} ranging between < 0.01 and $0.11\% \text{ S}$. Higher S_{CR} was usually observed at depth. The titratable actual acidity (TAA) for 90% of the samples was positive, indicating potential for acid release upon re-flooding of the dry sediments. The acid-base accounting data showed that the majority of soil materials had insufficient buffering capacity to neutralise either the acidity present or the potential acid produced from sulfide oxidation. The net acidity ranged between -103 and $168 \text{ mole H}^+ \text{ tonne}^{-1}$. The subaqueous soils in drainage channels appeared to contain monosulfidic materials (i.e. MBO). The soluble sulfate content exceeded the trigger value of 100 mg L^{-1} in all samples except one, indicating the formation of monosulfidic materials, which may be a potential hazard upon rewetting. The surface water at the time of sampling ranged between pH 3.9 and 6.9. The SEC of the surface waters ranged between 160 and $5,980 \mu\text{S cm}^{-1}$, with dissolved oxygen levels of between 0.7 and 12.2 mg L^{-1} .

At the Burnt Creek sites, the pH_W values of the soil materials ranged between 2.8 and 7.0 (Table 9-7, Appendix 1). Half of the soil samples (i.e. 5 sites) contained sulfuric materials (i.e. $\text{pH}_W < 4$ as a result of sulfide oxidation). The pH_{FOX} values ranged between 2.0 and 3.0. All soils showed a decrease in pH after treatment with peroxide, with pH_{FOX} of most samples decreasing to less than 2.5. The $\text{pH}_{\text{incubation}}$ data showed that most samples decreased to below pH 5.5. Sulfidic soil materials (i.e. $\text{S}_{\text{CR}} \geq 0.01\% \text{ S}$) were observed in most of the samples analysed (i.e. 80%), with a S_{CR} ranging between < 0.01 and $6.25\% \text{ S}$. The TAA for all samples was positive, indicating potential for acid release upon re-flooding of the dry sediments. The majority of the existing acidity was stored in sulfate salts at or near the surface. The acid-base accounting data showed that the net acidity was positive for all the soil materials analysed (with a maximum net acidity of $3930 \text{ mole H}^+ \text{ tonne}^{-1}$). The subaqueous soils in drainage channels appeared to contain monosulfidic materials (i.e. MBO). The soluble sulfate content exceeded the trigger value of 100 mg L^{-1} in all samples indicating the formation of monosulfidic materials, which may be a

potential hazard upon rewetting. The surface water at the time of sampling ranged between pH 2.8 and 6.9. The SEC of the surface waters ranged between 2,250 and 24,750 $\mu\text{S cm}^{-1}$, with dissolved oxygen levels of between 0.5 and 5.6 mg L^{-1} .

The identification of the presence of various iron and sulfate minerals, including natrojarosite, schwertmannite, lepidocrocite, goethite, sideronatrite, epsomite, hexahydrite and gypsum in both the Loddon River and Burnt Creek indicated the oxidation of high concentrations of iron sulfides (principally pyrite) in the original soil materials.

The methodologies used in this study (i.e. peroxide testing, acid-base accounting, soil incubation) were combined to classify and establish a risk category for the acid sulfate soil types. A summary of the type and prevalence of acid sulfate soil materials for the Loddon River and Burnt Creek is presented below in Table 2-4.

Table 2-4: Type and prevalence of acid sulfate soil materials for Loddon River and Burnt Creek (source: Thomas et al. 2009c).

Acid Sulfate Soil Material Type	Number of profiles (sites) and % of sites containing acid sulfate soil material	
	Loddon River	Burnt Creek
Sulfuric	8 (42%)	4 (100%)
Hypersulfidic	5 (26%)	0 (0%)
Hyposulfidic ($S_{CR} \geq 0.10\%$)	1 (5%)	0 (0%)
Monosulfidic (observed)	4 (21%)	2 (50%)
Monosulfidic (potential)	11 (100%)	2 (100%)
Hyposulfidic ($S_{CR} < 0.10\%$)	1 (5%)	0 (0%)
Other acidic (pH_w &/or $\text{pH}_{\text{incubation}} 4 - 5.5$)	2 (11%)	0 (0%)
Other soil materials	2 (11%)	0 (0%)

A summary of the risk categories for the various hazards associated with acid sulfate soil for the different soil landscapes and subtypes of acid sulfate soil identified is presented in Table 2-5. At the sites assessed in the Loddon River and Burnt Creek, the risk of soil acidification and subsequent metal mobilisation was considered to be high in streambed sediments, stream banks and mid-stream bars, particularly where sulfuric soils already exist. The risk of soil acidification was low in high banks and

terraces. Monosulfidic materials were found in ponds and moist stream beds and pose a deoxygenation and metal mobilisation hazard if disturbed. As discussed earlier, the risk of forming monosulfidic materials upon re-flooding under stagnant and low flow conditions was considered high.

Table 2-5: Risk categorisation for the various hazards associated with acid sulfate soil for soil landscapes and subtypes of acid sulfate soil identified (source: Thomas *et al.* 2009c).

Risk Class	Acidification	Metal mobilisation	De-oxygenation of water
Streambed Banks and bars High bank and terraces	High-Extremely High High-Very High Low	High High Low	Moderate-High Moderate Very Low
Sulfuric soil (sandy) Sulfidic soil Sulfidic subaqueous soil Sulfidic subaqueous clayey soil with MBO soil	High-Extremely High Moderate Low-moderate Moderate	High Moderate-High Moderate Moderate-High	Moderate Moderate High Extremely High
Hydrosol	Low	Low	Very Low

2.2.3 Channels associated with River Murray Locks 8 and 9 weir pools, New South Wales and Victoria

Shand *et al.* (2008) examined representative soil profiles from 11 wetlands and connecting stream sites associated with River Murray Locks 8 and 9 weir pools to assess the current and potential impacts of acid sulfate soils. The channels examined in February 2008 included Carr's Creek (Site 954), Cappits Creek (Site 1014), Walpolla Creek (Site 1026) and the Lower Darling Anabranh (Sites 220 and 3740) (Figure 2-10). Three independent standard methodologies were applied to determine the acid sulfate soil risk, including peroxide pH testing, acid-base accounting and ageing experiments. Summaries of the laboratory data including pH testing and acid-base accounting data for all channel sites are presented in Appendix 1 (Tables 9-8 - 9-10).



Figure 2-10: Location of the channel sampling sites including Carr's Creek (Site 954), Cappits Creek (Site 1014), Walpolla Creek (Site 1026) and Lower Darling Anabranh (Sites 220 and 3740) (source: Shand *et al.* 2008).

Shand *et al.* (2008) showed that sulfidic soil materials were present at each of the channel sites examined (Table 2-6). However, sulfidic soil material was only observed at depth at the Capitts Creek site (i.e. 130 – 140 cm). Sulfuric material (i.e. $\text{pH}_W < 4$) was only observed within the soil profile at Carr's Creek (8 – 24 cm), with a pH_W of 3.5. The pH_{FOX} values indicated that 38% of the channel samples may have the potential to acidify to $\text{pH} < 2.5$ as a result of sulfide oxidation. The $\text{pH}_{\text{Incubation}}$ data showed that only samples collected from Carr's Creek reached a final pH below 4.0 after incubation, and would therefore be characterised as hypersulfidic materials. Whilst sulfidic soil materials (i.e. $\text{S}_{\text{CR}} \geq 0.01\% \text{ S}$) were observed in many of the samples analysed, the amount of sulfide was generally low, with a maximum S_{CR} of 0.10% S (Table 9-9 and 9-10, Appendix 1). The pH_{KCl} data showed that 21 of the 22 channel samples analysed had a $\text{pH}_{\text{KCl}} < 6.5$, and therefore contained zero ANC. Therefore, acid-base accounting calculations showed positive values for net acidity for 21 of the 22 samples analysed (i.e. 1 - 78 mole H^+ tonne⁻¹), indicating that the majority of the samples contained existing acidity and may also have the potential to produce further acid upon oxidation.

Table 2-6: Summary of soil types identified in channel sediments (source: Shand *et al.* 2008).

Site	Site No.	Profile Depth (cm)	Soil Type
Carr's Creek	954/1	0 - 35	Sulfuric
	954/2	0 - 25	Sulfidic subaqueous
Capitts Creek	1014/1	0 - 25	Hydrosol
	1014/2	0 - 35	Hydrosol
	1014/3	0 -140	Sulfidic
Walpolla Creek	1026/1	0 - 30	Sulfidic subaqueous clay
	1026/2	0 - 20	Sulfidic subaqueous
Darling Anabranh	3740/1	0 - 30	Sulfidic subaqueous
	220/1	0 - 20	Sulfidic subaqueous clay

The three methodologies used were combined to establish the acid sulfate soil risk (i.e. the risk of the development of sulfuric materials) for each site (see Shand *et al.* 2008). The classification of each channel site according to risk was: (i) High risk - Carr's Creek, (ii) Moderate risk: Walpolla Creek and the Lower Darling Anabranh (Site 3740), and (iii) Low risk: Cappitts Creek and the Lower Darling Anabranh (Site 220). However, as suggested by Shand *et al.* (2008), even where the risk of development of sulfuric materials was moderate, there is significant potential for the pH to decrease to ~5 in many samples. There is still considerable risk to wetland

ecosystems from acidity and subsequent release of metals if a pH ~5 was maintained for significant periods of time.

The surface water quality data collected at the time of sampling showed the pH varied between 7.0 and 7.8. The SEC of the surface waters ranged between 177 and 321 $\mu\text{S cm}^{-1}$, with dissolved oxygen levels of between 5.4 and 8.3 mg L^{-1} . The surface water sulfate concentration in 10 of the wetlands examined ranged between 7.4 and 21 mg L^{-1} .

2.2.4 Salt Creek, south-west New South Wales

Fitzpatrick *et al.* (2008b,d) examined soil profiles and salts collected from Tareena Billabong (21 sites) and Salt Creek (8 sites) in south-west NSW in September 2007 to identify the presence of various subtypes of acid sulfate soils. The locations of sample sites at Salt Creek near to Tareena Billabong are shown in Figure 2-11. The methodologies used to classify the various subtypes of acid sulfate soils included soil morphology, field pH, peroxide testing, acid-base accounting and mineralogical analysis. Summaries of the laboratory data including pH and acid-base accounting data for all Salt Creek sites are presented in Appendix 1 (Table 9-11 and 9-12).



Figure 2-11: Location of sampling sites SC1-4 and SC7-8 at Salt Creek. Tareena Billabong is located on the right side of the image (source: Fitzpatrick *et al.* 2008b).

Fitzpatrick *et al.* (2008b,d) identified the presence of acid sulfate soils (including sulfidic subaqueous clayey and sulfidic cracking clay soils) at all sites examined at Salt Creek. None of the sites contained sulfuric materials ($\text{pH} < 4$), with the pH_w

values ranging between 4.8 and 8.1 (Table 9-11, Appendix 1). All soils showed a decrease in pH after treatment with peroxide, with pH_{FOX} values indicating that 47% of the samples may have the potential to acidify to $\text{pH} < 2.5$. Sulfidic soil materials (i.e. $\text{S}_{\text{CR}} \geq 0.01\% \text{ S}$) were observed in 87% of samples analysed, although the amount of sulfide was generally low, with a maximum S_{CR} of 0.05% S (Table 9-12, Appendix 1). The pH_{KCl} data showed that all samples analysed had a $\text{pH}_{\text{KCl}} < 6.5$, and therefore contained zero ANC. Therefore, acid-base accounting calculations showed positive values for net acidity for all samples, ranging between 2 and 33 mole H^+ tonne⁻¹. The findings indicated that acidification was more likely to be a serious problem if the Salt Creek river bed remained exposed. This is particularly important due to the low alkalinity of the river water, the soils adjacent to the creek and sediments in the creek bed. The collection of water quality data was not part of this study.

2.2.5 Edward-Wakool River system, New South Wales

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) (Figure 2-12). A series of control structures located throughout the area regulate the flow in the Edward-Wakool River system which flows into the River Murray near Swan Hill (Baldwin 2009). Sulfidic sediments have been observed in the main channel of the Wakool River, Niemur River (also known as Mallan Mallan Creek) and a number of associated creek systems (including Tuppal, Jimaringle, Cochran, Wyam and Merran Creeks) (e.g. Baldwin 2008a, 2009; Tulau 2009; Bush unpublished data). In the Wakool-Niemur River system between Deniliquin and Balranald, sulfuric and sulfidic sediments have been observed in incised channels that are associated with deep layers of MBO overlain with a halite crust (Tulau 2009). Extensive death and dieback of river red gums and black box was also often observed (Figure 2-13). However, at many sites within the Edward-Wakool River system, sulfidic sediments have been identified based on visual indicators, with limited data on reduced inorganic sulfur compounds. Further information on visual indicators of acid sulfate soils is presented in Section 3.4 (Table 3-2).

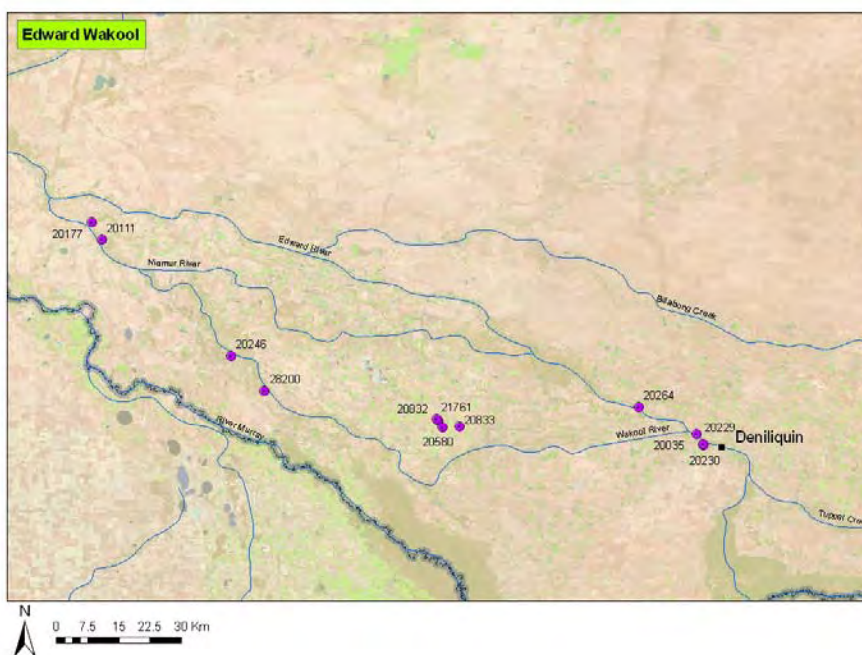


Figure 2-12: Map showing the ASSRAP priority acid sulfate soil assessment sites in the Edward-Wakool River system (source: MDBA unpublished).



Figure 2-13: A severely degraded acid sulfate soil site on Merran Creek on the Wakool River (source: Tulau 2009).

Many of the channel systems in the Edward-Wakool River system are highly saline, particularly in the western part of the system (Baldwin 2009). Baldwin (2008a) reported SEC ranging from $6,000 \mu\text{S cm}^{-1}$ in a partially filled reach of the Wakool River to over $100,000 \mu\text{S cm}^{-1}$ in a waterhole in Wyam Creek. The high salinities provide a source of sulfate essential for sulfide accumulation. Acidification of waterholes has also been reported in the Wakool River main channel, with pH levels as low as 2.9 (Baldwin 2009).

The concentration of reduced inorganic sulfur compounds has recently been measured in sediments collected from both the Wakool and Niemur Rivers (Bush unpublished data). Surface sediments were collected from four locations in the Wakool River and from two locations in the Niemur River (Table 9-13 and 9-14, Appendix 1). Low sulfide concentrations (i.e. $\leq 0.04\% \text{ S}_{\text{CR}}$) were observed in the channel sediments of both rivers at the time of sampling.

2.2.6 Talbragar River, central New South Wales

The Talbragar River is located near Dubbo in central NSW. Research undertaken on this river was one of the first studies to link elevated sulfate concentrations as a result of salinisation and the formation of sulfidic sediments in inland waterways of the MDB (Sullivan *et al.* 2002b, 2004, 2006b). Sullivan *et al.* (2002b) found monosulfide concentrations of up to approximately $35 \mu\text{mol S g}^{-1}$ ($\sim 0.1\% S_{AV}$) in freshwater sediments in the Talbragar River (Figure 2-14). An accumulation of acid-volatile sulfide (S_{AV}) was observed along the Talbragar River along with a general increase in sulfate concentration downstream from $\sim 10 \text{ mg L}^{-1}$ at Craboon to $\sim 25 \text{ mg L}^{-1}$, approximately 30 km downstream at Beni.

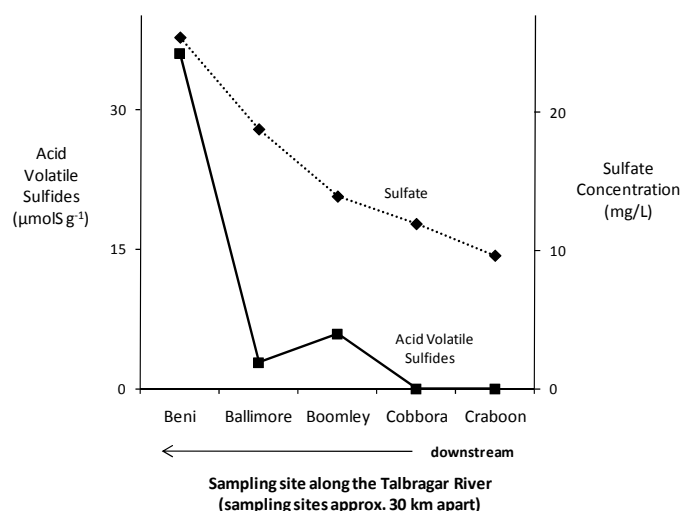


Figure 2-14: Acid-volatile sulfide content in sediments (26/02/02) and sulfate content of water in the Talbragar River (15/02/02) (source: Sullivan *et al.* 2002b).

The effect of the accumulated S_{AV} in the Talbragar sediments on the subsequent deoxygenation of the river channel during a flow event in early February 2002 is shown in Figure 2-15. The dissolved oxygen contents observed in parts of the Talbragar River (i.e. $< 4 \text{ mg L}^{-1}$) were low enough to cause a fish kill, and attributed to the downstream transport of the monosulfides (Sullivan *et al.* 2002a).

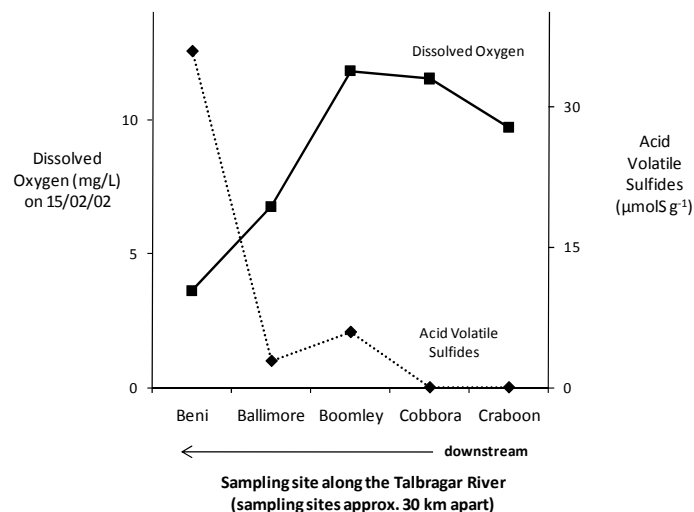


Figure 2-15: Acid-volatile sulfide content in sediments (26/02/02) and dissolved oxygen content of water in the Talbragar River (15/02/02) during the tail end of a flow event (source: Sullivan *et al.* 2002b).

In separate study undertaken in the Talbragar River in February/March 2004, monosulfide concentrations of up to 0.02% S_{AV} were observed (Table 9-15, Appendix 1) (Sullivan unpublished data). The reduced inorganic sulfur concentration in sediments at the time of this study ranged between <0.01 and 0.02% S_{CR} (Table 9-15, Appendix 1).

2.2.7 Irrigation channels, Queensland

In September/October 2008, a rapid assessment of acid sulfate soils in 200 inland wetland areas in the Queensland MDB was undertaken as part of the MDB ASSRAP (Biggs and King 2008). Although sulfidic sediments were not identified in any of the river and creek channels (Pers. comm. Andrew Biggs), irrigation infrastructure (i.e. sumps, excavations and channels) constructed into naturally saline subsoil was often found to provide suitable conditions for MBO formation (Biggs and King 2008). Visual evidence indicated that greater concentrations of 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). However, laboratory analytical data did not always support the field observation of MBO.

There is limited analytical data available on the presence of sulfidic sediments in irrigation channels in the Queensland MDB. Detailed chemical analyses were undertaken on surface sediments collected from 34 of the inland rapid assessment sites. Sulfidic sediments were identified at 21% of these sites, with sulfide concentrations ranging between 0.02 and 0.45% S_{CR} (Qld DERM unpublished data). The results showed the presence of sulfides within irrigation channels in the Talwood-Mungindi region and the Whyenbah channel (Figure 2-16 and 2-17). The sulfide concentrations in these channels ranged between 0.02 and 0.04% S_{CR} (Table 9-16, Appendix 1). However, earlier data collected in 2007 from irrigation channels in the Talwood-Mungindi region showed sulfide concentrations as high as 0.13% S_{CR} (Table 9-16, Appendix 1). Despite the visual evidence of MBO in both the Talwood-Mungindi region and Whyenbah channels in 2008, acid-volatile sulfides (AVS; a measure of iron monosulfide) were only detected in the Whyenbah channel (<0.01 - 0.11% S_{AV}) (Table 9-16, Appendix 1).

The sediments analysed from the Talwood-Mungindi region and Whyenbah channels had no or minimal existing acidity (i.e. < 10 mole H^+ tonne⁻¹). The acid-base accounting data showed negative net acidities for all the sulfidic sediments (Table 9-16, Appendix 1) as the ANC within the sediments were sufficient to neutralise the potential acidity produced from sulfide oxidation.



Figure 2-16: Map showing the rapid assessment sampling locations in the irrigation channels in the Talwood-Mungindi region, Queensland.



Figure 2-17: Map showing the rapid assessment sampling locations in the Whybah channels, Queensland.

The rapid assessment data showed that the sites sampled in the irrigation channels in the Talwood-Mungindi region exceeded the ASSRAP trigger values (see Table 3-1 in Section 3.2) for soil and water SEC, soil pH and surface water sulfate (Table 9-17, Appendix 1). Sites sampled in the Whyenbah channel exceeded the trigger values for soil SEC and surface water sulfate (Table 9-17, Appendix 1).

2.2.8 Summary of the reported distribution of reduced inorganic sulfur compounds in channels in the Murray-Darling Basin

This desktop assessment identifies the known distribution of reduced inorganic sulfur compounds in the MDB. A summary of the reported reduced inorganic sulfur concentrations in channels systems in the MDB is presented in Table 2-7. The approximate location of where reduced inorganic sulfur compounds have been reported in channel sediments in the MDB is presented in Figure 2-18. Additional data for sites which were not presented as case studies in Section 2.2 is also included in Appendix 1.

The main findings of this desktop assessment are presented below.

- There is currently limited reported data on the presence of reduced inorganic sulfur compounds in river and channel sediments within the MDB (Table 2-7).
- The presence of reduced inorganic sulfur compounds in river and creek channels is highly variable and has largely been reported in the Murray catchment (Figure 2-18) where most detailed studies have been undertaken.
- Generally, the greatest concentration of reduced inorganic sulfur compounds in river and creek channels was observed within the Lower River Murray floodplains, SA.
- The highest reduced inorganic sulfur concentration of 6.25% S_{CR} was identified in sulfidic sediments at Burnt Creek, Vic.
- Visual observations suggest that sulfidic materials are widespread in the Edward-Wakool River system, although only low concentrations of reduced inorganic sulfur compounds have been measured at a few sites (i.e. $\leq 0.04\%$ S_{CR}).
- There are limited data available on the distribution of MBO materials, despite substantial visual evidence of their presence. Elevated S_{AV} concentrations were identified in the Talbragar River ($\sim 0.1\%$ S_{AV}), Picaminy Creek (0.33% S_{AV}) and in various irrigation channels (up to 0.54% S_{AV}) (Table 2-7).
- The potential formation of monosulfides was identified at several sites due to the presence of elevated sulfate concentrations (i.e. $> 100 \text{ mg kg}^{-1} \text{ SO}_4$) in the channel sediments (e.g. Fitzpatrick *et al.* 2009b; Thomas *et al.* 2009c).

- Irrigation channels were often observed to have elevated sulfide concentrations. However, data from irrigation channels in Queensland (i.e. Talwood-Mungindi region and Whyenbah irrigation channels) indicate there is sufficient ANC to neutralise all the potential acidity.
- Acid-base accounting data has shown that the net acidity within channel systems is highly variable, with many sites containing sufficient net acidity to represent a significant potential hazard if disturbed.
- Sullivan *et al.* (2002b) showed a relationship between sulfate in the water column and sediment sulfide concentration in the Talbragar River. The sulfide concentrations were also sufficient to result in deoxygenation within the river system.
- Where water quality data was available, many sites which had reduced inorganic sulfur compounds present had high SEC (i.e. $> 2,000 \mu\text{S cm}^{-1}$). However, this was not always the case, and may be due to temporal variations in salinity.
- A range of acid sulfate soil materials have been identified in channel systems within the MDB including sulfuric, hypersulfidic, hyposulfidic and monosulfidic materials.
- A range of acid sulfate soil subtypes (e.g. sulfidic cracking clay soil, sulfuric cracking clay soil, and sulfidic subaqueous clayey soil) have also been identified in the MDB.
- The potential hazards identified in this assessment if reduced inorganic sulfur compounds present were to be disturbed included: acidification, metal mobilisation and deoxygenation.
- Thomas *et al.* (2009c) found greater hazard of acidification and subsequent metal mobilisation from acid sulfate soil materials identified in streambed sediments, stream banks and mid-stream bars than in high banks and terraces.

Table 2-7: Summary of the concentration of reduced inorganic sulfur compounds in channel sediments in the MDB.

State	River/Creek	Reduced inorganic sulfur concentrations (%S _{CR} , %S _{AV})	Reference
South Australia	River Murray below Blanchetown (Lock 1)	0.02 – 0.18% S _{CR}	Fitzpatrick <i>et al.</i> (2008e)
	Finniss River	<0.01 – 1.71% S _{CR}	Fitzpatrick <i>et al.</i> (2009b)
	Currency Creek	<0.01 – 1.49% S _{CR}	
	Black Swamp	0.03 – 0.96% S _{CR}	
	Goolwa Channel	<0.01 – 4.32% S _{CR}	
	Mundic Creek	<0.01 – 0.32% S _{CR}	Shand <i>et al.</i> (2009)
Pike River	<0.01 – 0.58% S _{CR}		
Snake Creek	0.02 – 0.03% S _{CR}		
South Australia	Dishers Creek, near Renmark	0.08 – 0.45% S _{CR} <0.01 – 0.08% S _{AV}	Sullivan (unpublished data)
	Lower Loddon River	0.00 – 0.11% S _{CR}	Thomas <i>et al.</i> (2009c)
Victoria	Burnt Creek	0.00 – 6.25% S _{CR}	
Victoria	Walpolla Creek	<0.01 – 0.07% S _{CR}	Shand <i>et al.</i> (2008)
Victoria	Butlers Creek	0.01 – 0.02% S _{CR}	Baldwin (2008b)
Victoria	Picaminy Creek, Kerang	0.49% S _{CR} 0.33% S _{AV}	Sullivan (unpublished data)
	Irrigation channels, Kerang	0.46 – 0.74% S _{CR} 0.32 – 0.54% S _{AV}	Sullivan (unpublished data)
New South Wales	Carr's Creek	0.01 – 0.10% S _{CR}	Shand <i>et al.</i> (2008)
	Cappits Creek	<0.01 – 0.01% S _{CR}	
	Darling Anabranh	<0.01 – 0.05% S _{CR}	
	Salt Creek	<0.01 – 0.05% S _{CR}	Fitzpatrick <i>et al.</i> (2008d)
	Wakool River	<0.01 – 0.04% S _{CR} <0.01% S _{AV}	Bush (unpublished data)
	Niemur River	0.01 – 0.03% S _{CR} <0.01% S _{AV}	Bush (unpublished data)
	Washpen Creek ¹	≤ 0.01 – 0.04% S _{CR}	Baldwin <i>et al.</i> (2008)
	Talbragar River	0.00 – 0.02% S _{CR} <0.01 – ~0.1% S _{AV}	Sullivan (unpublished data) Sullivan <i>et al.</i> (2002b)
	Irrigation channel, Scenic Hill, Griffith	0.57% S _{CR} 0.24% S _{AV}	Sullivan (unpublished data)
	Irrigation channels, Hanwood	0.11 – 0.13% S _{CR} 0.07 – 0.13% S _{AV}	Sullivan (unpublished data)
Queensland	Irrigation channels, Talwood-Mungindi region	<0.02 – 0.13% S _{CR} <0.01% S _{AV}	Qld DERM (unpublished data)
	Whyenbah irrigation channel	0.02 – 0.04% S _{CR} <0.01 – 0.11% S _{AV}	Qld DERM (unpublished data)

¹ Disconnected from the Euston Weir pool, River Murray.

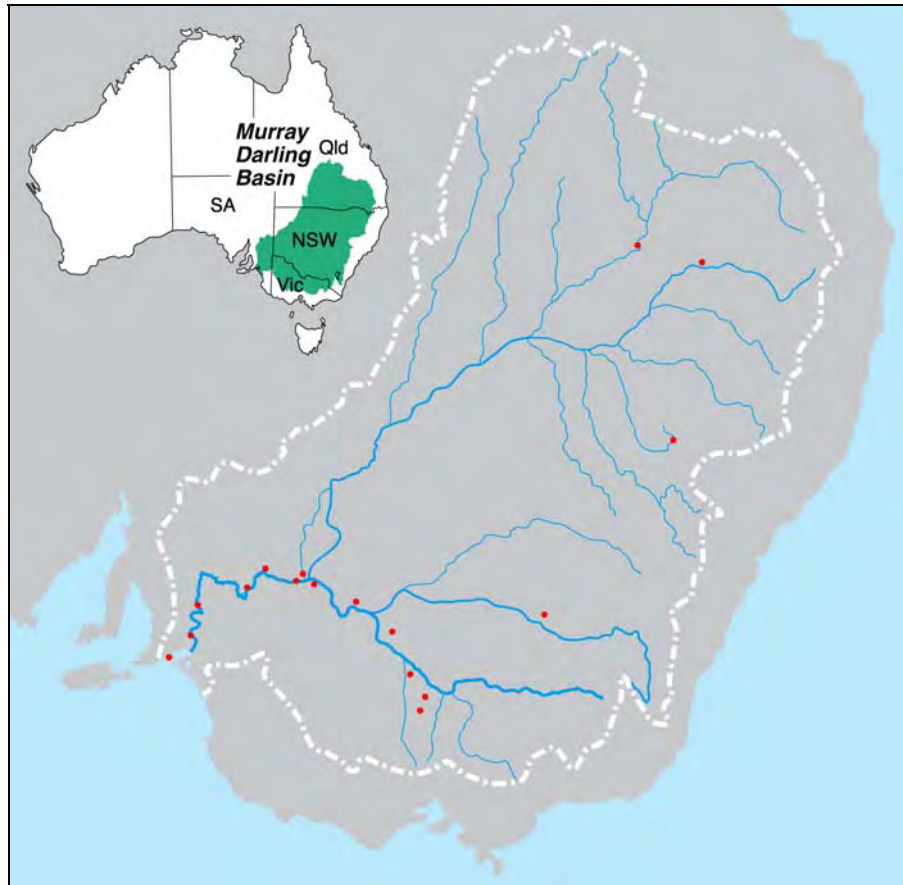


Figure 2-18: Map showing the geographical distribution of reduced inorganic sulfur compounds reported in channel sediments in the MDB.

During the literature search phase of this project, additional potential sources of reduced inorganic sulfur concentration data were identified. However, the sources of information were not available in the timeframe of this study. The sources of additional data include:

- An MDBA-funded modified rapid assessment project to determine the likelihood of acid sulfate soil materials in the bank sediments of the lower Murray River between Wellington and Lock 1. Numerous sites were found with soil pH < 4 indicating sulfuric materials (Pers. Comm. Rob Kingham). This project was undertaken by the South Australian Murray-Darling Basin Natural Resources Management Board (SA MDB NRMB) with support from CSIRO Land and Water. The results of this project are being compiled by the SA Department of Environment and Heritage and should be available shortly.

- Currently, 96 priority wetlands within the Basin are undergoing a detailed acid sulfate soil assessment as part of the ASSRAP. A small number of creek and channel systems (e.g. Talwood-Mungindi region, Queensland; Bet Bet Creek, Victoria) were selected for detailed assessment on the basis of a high likelihood of acid sulfate soil materials being present (Pers. Comm. Rob Kingham).
- A detailed acid sulfate soil assessment funded by the MDBA is currently being undertaken by Southern Cross GeoScience and the NSW Department of Environment, Climate Change and Water in the Edward-Wakool River system.
- The Department of the Environment, Water, Heritage and the Arts (DEWHA) Joint Steering Committee on Acid Sulfate Soils is in the process of completing a report entitled "*National guidance for the management of acid sulfate soils in inland aquatic ecosystems*" which may provide some additional sources of information (DEWHA In press).
- Professor Leigh Sullivan is compiling unpublished data he has collected for a book chapter on sulfidic sediments in channels in the MDB. The relevant unpublished data is included in this report.

3. FURTHER INFORMATION INDICATING THE POTENTIAL PRESENCE OF REDUCED INORGANIC SULFUR COMPOUNDS IN CHANNEL SYSTEMS

3.1 Atlas of Australian acid sulfate soils

The Atlas of Australian Acid Sulfate Soils is a web-based hazard assessment tool that provides information on the distribution and properties of acid sulfate soils across Australia (Fitzpatrick *et al.* 2008c). It is estimated that inland acid sulfate soils occupy approximately 160,000 km² of Australia (Fitzpatrick *et al.* 2008c). The atlas provides four classes of probability of occurrence, four levels of confidence relating to the quality of the data source, and up to 10 additional descriptors (e.g. Figure 3-1) (Fitzpatrick *et al.* 2008c). This hazard assessment tool is regularly updated and is available on the Australian Soil Resource Information System (ASRIS: <http://www.asris.csiro.au>).

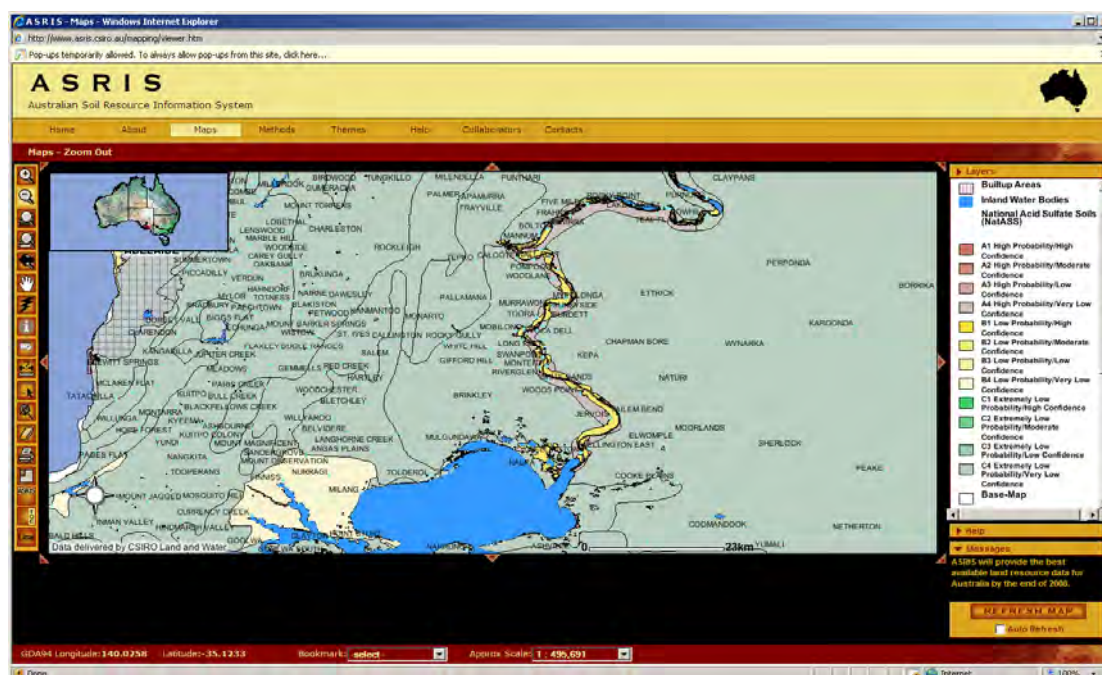


Figure 3-1: Atlas of Australian acid sulfate soils showing the likelihood of acid sulfate soils in the Lower River Murray (source: ASRIS; <http://www.asris.csiro.au>).

3.2 Water quality data

Water quality data, particularly parameters such as salinity and sulfate, have been used as an indicator for the occurrence of sulfidic sediments in freshwater environments in the absence of sediment data in the MDB. For example, Baldwin *et al.* (2007) developed a protocol using water quality parameters to assess the potential occurrence of sulfidic sediments in wetlands at levels that could cause ecological damage. Using data collected from 81 wetlands in the MDB (Hall *et al.* 2006a,b), potential indicators of sulfidic sediments included elevated salinity in the overlying water ($> 1750 \mu\text{S cm}^{-1}$) or sediment ($> 400 \mu\text{S cm}^{-1}$) and high sulfate levels in the water column ($> 10 \text{ mg L}^{-1}$).

In developing the protocol, Baldwin *et al.* (2007) found that five out of the six wetlands assessed with $\text{SEC} > 1750 \mu\text{S cm}^{-1}$ were characterised as sulfidic. The sixth wetland had an elevated peroxide oxidisable sulfur level, indicating the potential for developing sulfidic sediments. However, as SEC in surface waters and sometimes shallow groundwaters are subject to change over time, particularly as a result of rainfall, a SEC below this threshold is not necessarily indicative of the absence of sulfidic sediments. Baldwin *et al.* (2007) also found that six out of nine wetlands with an average soil salinity of $> 400 \mu\text{S cm}^{-1}$ (in a 1:5 sediment: water extract) were classified as being sulfidic, while two others had elevated peroxide oxidisable sulfur levels, indicating the potential for developing sulfidic sediments.

Hall *et al.* (2006b) observed that reduced inorganic sulfur concentrations in sediments was positively correlated with sulfate concentration of the overlying water column in the inland wetlands examined. Nine out of 12 wetlands with average sulfate concentrations $> 10 \text{ mg L}^{-1}$ had or probably contained sulfidic sediments (Baldwin *et al.* 2007). This sulfate concentration is consistent with other studies on inland sediments where sulfidic sediments have been observed (e.g. Sullivan *et al.* 2002b), although further research is required to define the precise sulfate concentration. Sulfidic sediments are also highly likely to occur where the surface water pH in the wetland was < 4.0 and/or a soil pH < 4.5 . The pH is only useful at locations where some sulfide oxidation has occurred and the buffering capacity of the soil and surrounding waters has been exceeded.

The thresholds for water identified by Baldwin *et al.* (2007) were used to develop the screening criteria for selecting detailed acid sulfate soils assessment study areas for the ASSRAP (Table 3-1). The soil sulfate concentration (in a 1:5 soil:water extract) was also included in the screening criteria. MDBA (2010) stated a water soluble sulfate content of $\geq 100 \text{ mg L}^{-1}$ (in a 1:5 soil:water extract) in dry soils would result in sulfate concentrations of $> 10 \text{ mg L}^{-1}$ in overlying water bodies as a result of inundation, although the nature of this relationship is probably more complicated.

Table 3-1: 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).

Parameter	Trigger value	Action recommended	Priority
pH soil*	<4	Detailed assessment	Extreme
	4 – 5.5	Detailed assessment	Moderate
	>5	No further assessment	N/A
pH water	<5.5	Detailed assessment	High
	5.5 – 6.5	Detailed assessment	Moderate
	>6.5	No further assessment	N/A
Electrical conductivity soil (1:5)	$>1000 \mu\text{S cm}^{-1}$	Detailed assessment	High
	$400 - 1000 \mu\text{S cm}^{-1}$	Detailed assessment	Moderate
	$<400 \mu\text{S cm}^{-1}$	No further assessment	N/A
Electrical conductivity water	$>5000 \mu\text{S cm}^{-1}$	Detailed assessment	High
	$1750 - 5000 \mu\text{S cm}^{-1}$	Detailed assessment	Moderate
	$<1750 \mu\text{S cm}^{-1}$	No further assessment	N/A
Sulfate soil	$>500 \text{ mg L}^{-1}$	Detailed assessment	High
	$100 - 500 \text{ mg L}^{-1}$	Detailed assessment	Moderate
	$<100 \text{ mg L}^{-1}$	No further assessment	N/A
Sulfate water	$>50 \text{ mg L}^{-1}$	Detailed assessment	High
	$10 - 50 \text{ mg L}^{-1}$	Detailed assessment	Moderate
	$<10 \text{ mg L}^{-1}$	No further assessment	N/A

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

It is important to recognise that the trigger values indicated in Table 3-1 are only screening criteria. Locations with a high priority may not have suitable conditions for sulfide formation due to additional factors such as insufficient organic carbon or prolonged anoxic conditions.

An examination of the salinity data collected from selected water quality monitoring stations throughout the MDB in 1994-95 show only a few sites (i.e. Campaspe River, Loddon River and Barr Creek) exceeded the salinity trigger value of $1750 \mu\text{S cm}^{-1}$ (MDBC 2009). However, at some sites, there may be a significant variation in salinity with depth in the channel. Salinity-dependent stratification (often referred to as a halocline) is known to occur in freshwater bodies following groundwater incursions (Nielsen *et al.* 2003). The presence of haloclines may play an important role in the formation of sulfides in freshwater environments, although further research is required to show their importance. A halocline may become a barrier to the movement of oxygen from the surface, which may eventually lead to anoxia (Nielsen *et al.* 2003). Sulfidic sediments may rapidly form under these anoxic conditions in the presence of sulfate, organic matter and iron. Groundwater quality data, particularly from piezometers close to channels, and may provide a useful source of information in determining the likely areas of sulfide formation within channel systems.

Surface water and groundwater sulfate concentrations are most likely the most useful parameter in determining the presence of reduced inorganic sulfur compounds within channels in the MDB. This is particularly important in areas where there are multiple sources of sulfate, such as agricultural chemicals. Additional water quality parameters such as nutrient and dissolved oxygen concentrations may also be useful in predicting the potential presence of reduced inorganic sulfur compounds within channels. Elevated nutrient concentrations may lead to the development of algal blooms, and provide a source of organic matter for sulfide formation (see Section 3.3). Low dissolved oxygen levels following increases in flow may possibly indicate the presence of MBO materials in the channel. However, deoxygenation may also occur as a result of many other unrelated processes (see Section 4.2.3).

Surface water quality data is available at numerous sites in the MDB (e.g. Figure 3-2). However, water quality data may not be as useful in determining the potential locations of sulfidic sediments as was found with wetland systems. The water quality in channel systems is usually subject to greater variations compared to wetland systems. In addition, some parameters are only measured on an infrequent basis (e.g. quarterly).

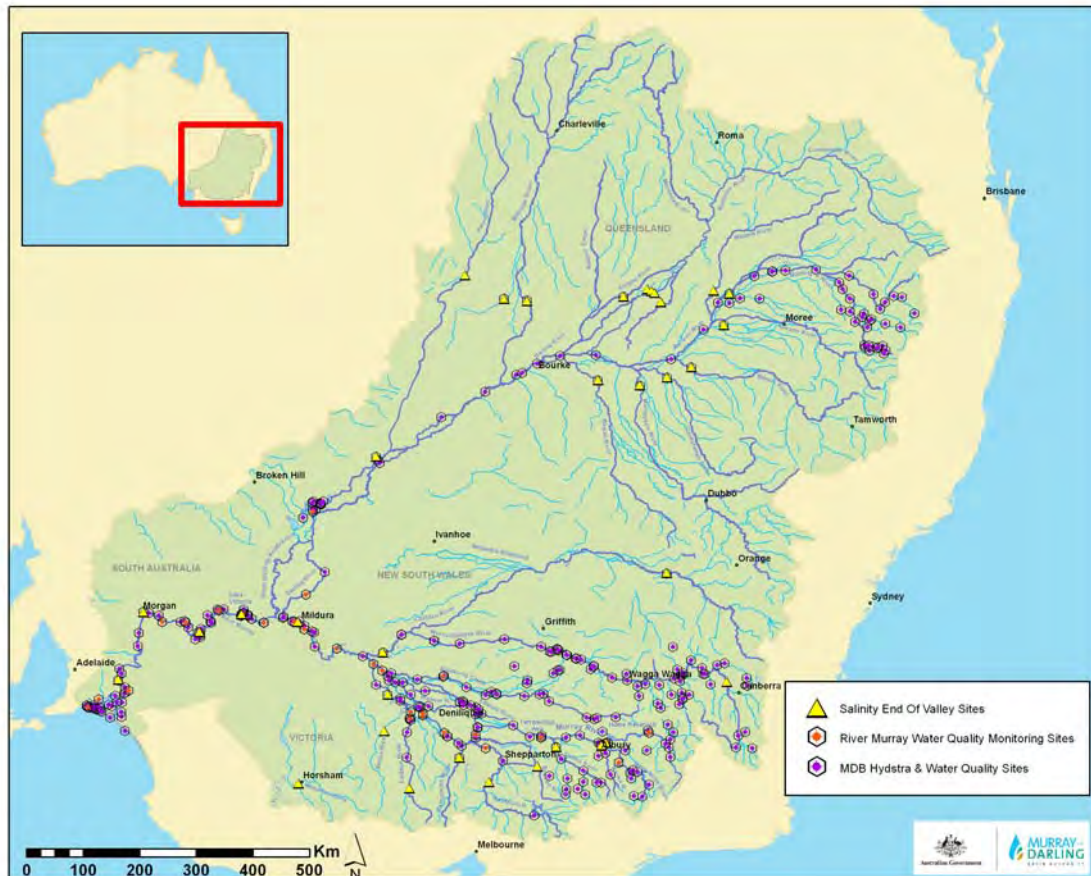


Figure 3-2: Locations of selected water quality monitoring stations in the MDB. The spatial representations of monitoring locations are indicative only and may not represent the actual location (source: MDBA).

Baldwin *et al.* (2007) also identified that sulfidic sediments were likely to occur if the wetland receives municipal waste water, irrigation return water or water from a salt interception scheme.

3.3 Algal Blooms

The supply of metabolisable organic matter is an essential factor in the formation of sulfides. Its presence is necessary for sulfate reduction to occur and is an important limiting factor for microbial reduction of ferric iron. In environments where the supply of sulfate is not limiting, the presence of organic matter has often been identified as the limiting factor (e.g. Berner 1984). Eutrophication (i.e. the enrichment of waters with nutrients) and the subsequent development of algal blooms provides an ideal source of organic matter for sulfide formation, MBO materials in particular. The increase in water clarity and nutrient release as a consequence of salinisation has been implicated in the formation of significant blooms of cyanobacteria (e.g. Nielsen *et al.* 2003). An indication of the areas within the MDB prone to algal blooms is given in Figure 3-3.

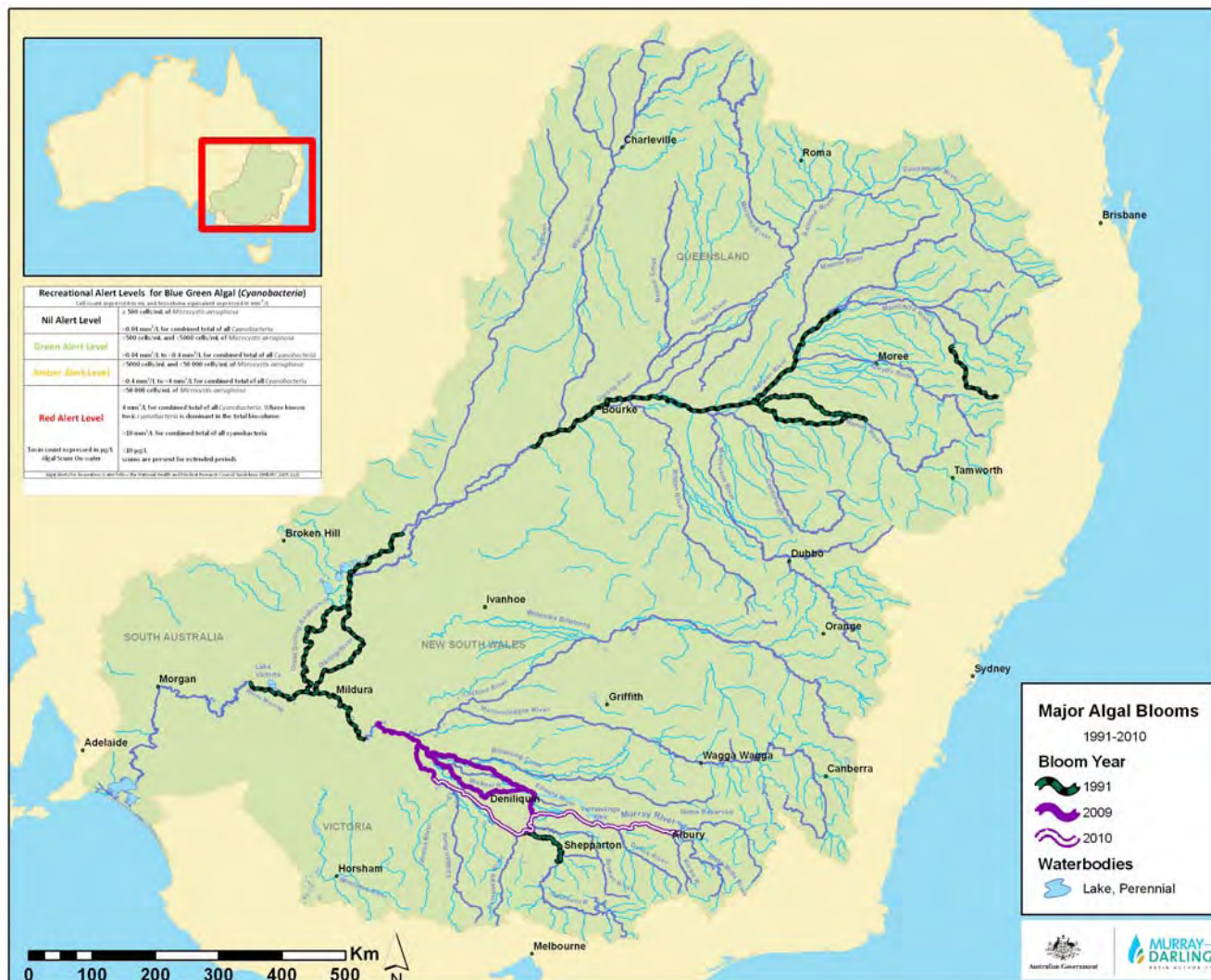


Figure 3-3: Sites of major algal blooms in the MDB from 1991 to present. The spatial representations of algal bloom locations are indicative only and may not represent the actual location (source: MDBA).

3.4 Landscape information

Landscape information from sources such as geological maps and remote sensing images may be used to interpolate and extrapolate between and beyond site data to predict the distribution of sulfidic sediments. For example, high resolution digital photography (ADS40), Light Detection And Ranging (LiDAR) high resolution elevation data, radiometrics, soil landscape and land systems maps, and salinity discharge maps are all essential data (Pers. comm. Mitch Tulau). However, the coverage for some datasets is not comprehensive in the MDB. For example, Figure 3-4 shows the high resolution digital photography (ADS40) coverage for New South Wales.

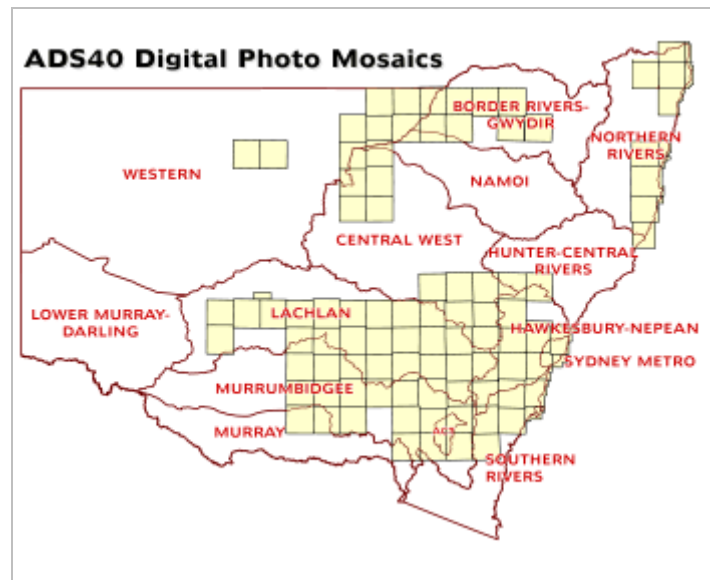


Figure 3-4: Map showing the high resolution digital photography (ADS40) coverage for New South Wales (source: Pers. comm. Mitch Tulau).

Aerial assessments using key visual indicators have been used as an initial assessment technique to identify potential areas that may contain sulfidic sediments. An aerial assessment was undertaken along the Darling River corridor from Bourke to Wentworth in western New South Wales to ascertain the likelihood of acid sulfate soils (Ralph and Baldwin 2009). This aerial assessment supplemented the MDBA acid sulfate soil risk rapid assessment program and was undertaken for setting priorities for potential on-ground rapid assessment. The key visual indicators used in

this study included marked discolouration of the channel bed, banks or wetlands (i.e. the presence of yellow/red tinges and/or seepage zones, and/or white scalds or salt efflorescences, and/or black pugging in grey or light coloured sediments) and the presence of dead and/or dying riparian or wetland vegetation.

A list of soil, water and vegetation indicators that are suggestive of acid sulfate soils in coastal environments is presented in Table 3-2. These indicators are also directly applicable in inland environments.

Table 3-2: List of soil, water and vegetation indicators that are suggestive of the presence of coastal acid sulfate soils (source: DEC 2009).

SOIL TYPE	INDICATORS
<p>Potential Acid Sulfate Soil (PASS)</p>	<p>Soil characteristics</p> <ul style="list-style-type: none"> • Waterlogged soils – unripe muds (soft, sticky and can be squeezed between fingers, blue grey or dark greenish grey mud with a high water content), silty sands or sands (mid to dark grey) or bottom sediments (dark grey to black e.g. iron monosulfide “black oozes”) possibly exposed at sides and bottom of drains, cuttings or in boreholes • Peat or peaty soils • Coffee rock horizons • A sulfurous smell e.g. hydrogen sulfide or ‘rotten egg’ gas • Soil pH_F >4 and commonly neutral • Soil pH_{FOX} <3, with large unit change from pH_F to pH_{FOX}, together with volcanic reaction to peroxide <p>Water characteristics</p> <ul style="list-style-type: none"> • waterlogged soils • water pH usually neutral but may be acidic • oily looking iron bacterial surface scum (the similar appearances of iron bacterial scum and a hydrocarbon slick can be differentiated by disturbing the surface with a stick -- bacterial scum will separate if agitated whereas a hydrocarbon slick will adhere to the stick upon removal) <p><i>NB: Caution should be taken when inspecting highly altered landscapes in the field (e.g. where inert fill has been placed over ASS material, dredge spoil, etc). Soil, water and landscape indicators may be masked by past landscape and drainage modifications and this should be taken into consideration when determining borehole locations.</i></p> <p>Vegetation characteristics</p> <ul style="list-style-type: none"> • dominant vegetation is tolerant of salt, acid and/or waterlogging conditions e.g. mangroves, salt couch, <i>Phragmites</i> (a tall acid tolerant grass species), swamp-tolerant reeds, rushes, paperbarks (<i>Melaleuca spp.</i>) and swamp oak (<i>Casuarina spp.</i>)
<p>Actual Acid Sulfate Soil (AASS)</p>	<p>Soil characteristics</p> <ul style="list-style-type: none"> • presence of corroded shell • sulfurous smell e.g. hydrogen sulfide or ‘rotten egg’ gas • any jarositic horizons or substantial iron oxide mottling in surface encrustations or in any material dredged or excavated and left exposed • field pH_F < 4 (when field pH_F >4 but <5 this may indicate some existing acidity and other indicators should be used to confirm presence or absence) <p>Water characteristics</p> <ul style="list-style-type: none"> • water of pH <5.5 (and particularly below 4.5) in surface water bodies, drains or groundwater (this is not a definitive indicator as organic acids may contribute to low pH in some environments such as <i>Melaleuca</i> swamps) • unusually clear or milky blue-green water flowing from or within the area (aluminium released by ASS acts as a flocculating agent) • extensive iron stains on any drain or pond surfaces, or iron-stained water and ochre deposits • oily looking bacterial surface scum (differentiated from a hydrocarbon slick of similar appearance as described for PASS) <p>Vegetation characteristics</p> <ul style="list-style-type: none"> • dead, dying, stunted vegetation* • scalded or bare low-lying areas* • poor vegetation regrowth in previously disturbed areas <p>Infrastructure</p> <ol style="list-style-type: none"> 1. corrosion of concrete and/or steel structures* (including foundations, fences, masonry/brick walls, pipes) <p><i>* May also be due to excessive salinity or to salinity in combination with AASS.</i></p>

4. HAZARD AND ECOLOGICAL RISK OF REDUCED INORGANIC SULFUR COMPOUNDS

A framework for defining and assessing the hazard and risk has recently been developed for acid sulfate soil materials in priority wetlands in the MDB (MDBA 2010). The same framework will be used to assess the environmental hazard and indicate the overall risk of reduced inorganic sulfur compounds in channels in the MDB.

This chapter will cover the following three areas as outlined in the adopted framework:

- defining and assessing acid sulfate soil materials (Section 4.1),
- defining and assessing hazards (Section 4.2), and
- defining and assessing risk (Section 4.3).

4.1 Defining and assessing acid sulfate soil materials

Acid sulfate soil materials have been defined by Sullivan *et al.* (2008b, 2009b) to include:

- sulfidic,
- hypersulfidic,
- hyposulfidic,
- sulfuric material, and
- monosulfidic.

A full explanation of each of the terms used above is given in Section 1.3.2.

4.2 Defining and assessing hazards

As described previously, reduced inorganic sulfur compounds are generally stable under reducing conditions. However, on exposure to the atmosphere as a result of drought or disturbance, the acidity produced from oxidation can impact on water quality, crop production, and corrode concrete and steel structures (Dent 1986). In addition to 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), high concentrations of Al and Fe (Ferguson and Eyre 1999; Ward *et al.* 2002), and the release of other trace metals (Preda and Cox 2001; Sundström *et al.* 2002; Burton *et al.* 2008; Simpson *et al.* 2008; Sullivan *et al.* 2008a). The mobilisation of sulfidic sediments may also result in the release of nutrients into the water column (Sullivan *et al.* 2008a).

While problems associated with the oxidation of pyrite are well documented (Dent 1986; Sammut *et al.* 1996), the oxidation of potentially large amounts of monosulfides that occur in MBOs in acid sulfate soil landscapes is a relatively new issue (Sullivan and Bush 2000; Sullivan *et al.* 2002a; Bush *et al.* 2004). Unlike pyrite, which is relatively stable, iron monosulfides are extremely reactive over a wide range of pH, may rapidly deoxygenate surface waters and cause severe acidification (Sullivan and Bush 2000; Sullivan *et al.* 2002a). Recent laboratory studies have shown that MBO from the Lower Lakes region of South Australia were capable of causing complete and rapid deoxygenation of water upon mobilisation (Sullivan *et al.* 2008a). Sullivan *et al.* (2008a) also showed that the mobilisation of these MBO materials resulted in high concentrations of a wide range of contaminants including Al, Mn, NH_4^+ and NO_3^- .

The general relationship between acid sulfate soil type, hazard type (i.e. acidification, metal mobilisation and deoxygenation) and hazard condition (i.e. current, potential and none) is presented in Table 4-1. These hazards may present a 'current' risk to the environment where the hazard has been measured or observed, or present a 'potential' risk where laboratory analyses of the soil properties indicates that a hazard is likely to eventuate if environmental conditions are changed (Fitzpatrick *et al.* 2009b).

Table 4-1: General relationship between acid sulfate soil material type and hazard condition (source: Fitzpatrick *et al.* 2009b).

Type of Acid Sulfate Soil Material	Hazard Type and Condition		
	Acidification	Metal Mobilisation	Deoxygenation
Sulfuric	current	current	none
Hypersulfidic	potential	potential	none
Hyposulfidic ($S_{CR} \geq 0.10\%$)	potential	potential	none
Monosulfidic (observed)	potential	current	current
Monosulfidic (potential)	potential	potential	potential
Hyposulfidic ($S_{CR} < 0.10\%$)	potential	potential	none

The following sub-sections examine the hazards associated with reduced inorganic sulfur compounds and include:

- contemporary accumulation of sulfides (Section 4.2.1),
- deoxygenation hazard (Section 4.2.2),
- accumulation and release of contaminants (Section 4.2.3),
- acidification hazard (Section 4.2.4), and
- additional potential hazards (Section 4.2.5).

4.2.1 Contemporary accumulation of sulfides

The formation and accumulation of iron sulfide minerals is a microbially driven process (Figure 4-1) that requires the following conditions: a supply of sulfate, reducing conditions with sulfate-reducing bacteria, a supply of organic matter and iron rich sediments (Berner 1984; Dent 1986). The sedimentary sulfur cycle is closely linked with carbon diagenesis (Vairavamurthy *et al.* 1995), and the supply of organic matter is an important limiting factor for microbial sulfate and ferric iron reduction. However, in freshwater systems the availability of sulfate is usually the main limiting factor to sulfate reduction and the formation of sulfides in benthic sediments (Berner 1984).

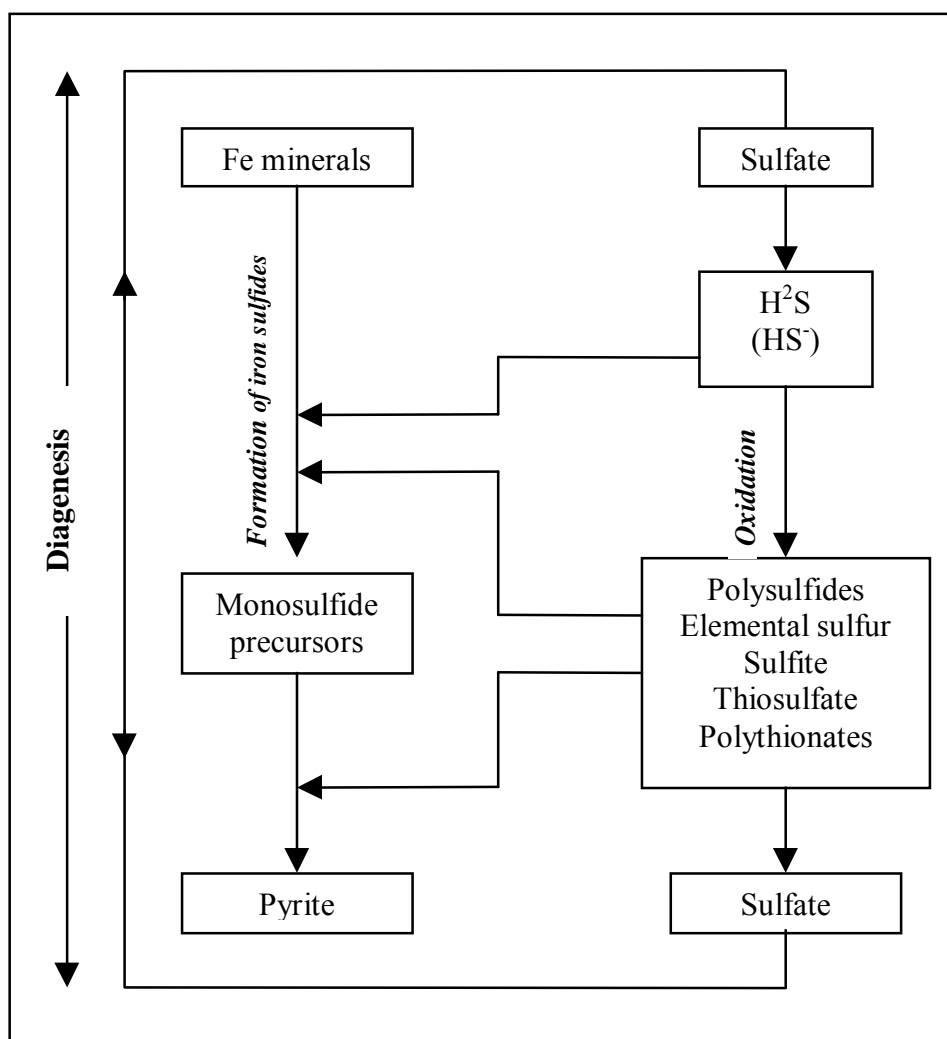


Figure 4-1: Schematic diagram showing the biogeochemical formation of iron sulfide minerals (after Vairavamurthy *et al.* 1995).

The findings of this study have shown suitable conditions for the accumulation of sulfides, including highly reactive monosulfides, in river, creek and irrigation channels in the MDB (Table 2-7). Significant changes to the hydrology of regulated sections of the MDB system due to higher weir pool levels, and the chemistry of channel systems, particularly as a result of increased salinity inputs, has led to the accumulation of sulfidic sediments within some channel systems. A build up of sulfides in sediments is usually minimised under natural wetting and drying cycles. The mobilisation or rewetting of these sulfidic sediments may have adverse effects on water quality within the channel and downstream. The main hazards resulting from the disturbance of sulfidic sediments include deoxygenation, contaminant mobilisation and/or acidification. These hazards will be discussed further in the following sub-sections.

Dissolved sulfide may also accumulate in the water column under reducing conditions (Morse *et al.* 1987) and is highly toxic to aquatic organisms. The ANZECC guideline freshwater trigger value for sulfide for the protection of 95% of species is $1 \mu\text{g S L}^{-1}$ (expressed as un-ionised H_2S) (ANZECC/ARMCANZ 2000). Dissolved sulfide is particularly prone to accumulate within channel systems where stratification occurs. For example, salt-dependent stratification may eventually lead to anoxic conditions (see Section 3.2) and the formation of sulfide in the water column.

4.2.2 Deoxygenation hazard

The ANZECC guidelines for aquatic ecosystems recommends a dissolved oxygen concentration of greater than 85% saturation for lowland rivers (ANZECC/ARMCANZ 2000). Native fish and other large aquatic organisms require a dissolved oxygen concentration of least 2 mg L^{-1} to survive, but may become stressed below $4 - 5 \text{ mg L}^{-1}$ (Hladyz and Watkins 2009).

The deoxygenation of surface waters may occur when MBO is mobilised into the water column, with severe deoxygenation occurring within minutes of mobilisation (Sullivan and Bush 2002; Sullivan *et al.* 2002a). This rapid rate of deoxygenation indicates that the chemical oxidation of MBO is largely responsible for consuming the dissolved oxygen in the water column. However, MBO also contains high concentrations of organic matter which also consumes oxygen as it is decomposed by microbes. Recent laboratory studies have shown the mobilisation of MBO collected from the Lower Lake region caused complete and rapid deoxygenation in the water column, even in relatively dilute suspension:water ratios (Sullivan *et al.* 2008a). The deoxygenation behaviour was strongly related to the acid-volatile sulfide (S_{AV}) concentration.

Burton *et al.* (2006a) have described the oxidation dynamics of MBO. A summary of the changes in sulfur speciation (i.e. pyrite, S_{AV} , elemental sulfur and sulfate) and pH during MBO oxidation is shown in Figure 4-2. The complete oxidation of MBO is a two-step process, with each step consuming oxygen (Equations 4.1 – 4.3) (Figure 4-3). The first step is an initial rapid chemical reaction of iron monosulfide minerals with oxygen, forming iron oxides and elemental sulfur. This oxidation step does not affect pH and is therefore non-acidifying. The second step occurs after a few days delay to allow for the accumulation of necessary sulfur-oxidising microbes that are required for the oxidation of elemental sulfur. The oxidation of elemental sulfur is responsible for the extreme acidification associated with MBO oxidation. Elevated elemental sulfur concentrations have recently been reported in channel sediments associated with acid sulfate soils (Burton *et al.* 2006b; Ward *et al.* 2009, in press).

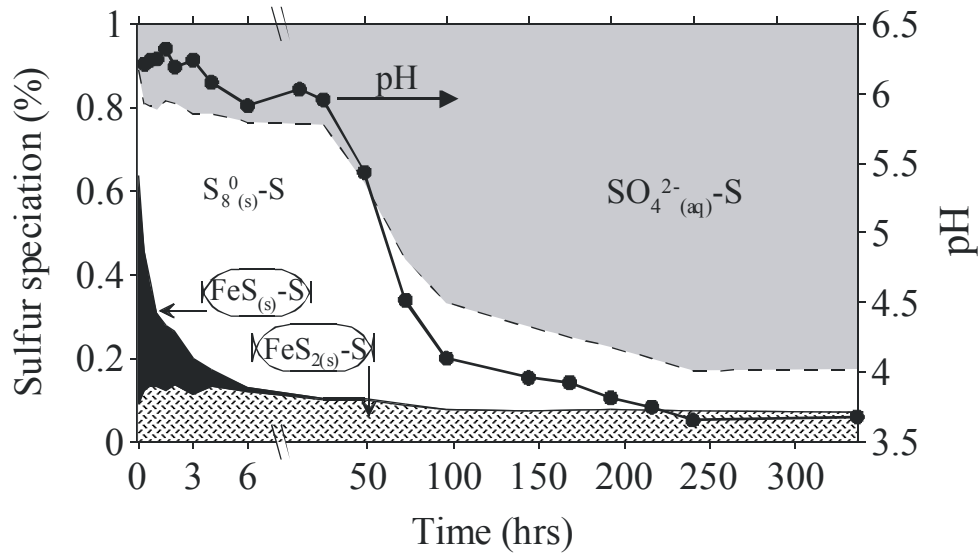


Figure 4-2: Changes to the sulfur speciation (pyrite, S_{AV} , elemental sulfur, sulfate) and pH during oxidation of MBO (source: Burton *et al.* 2006a).

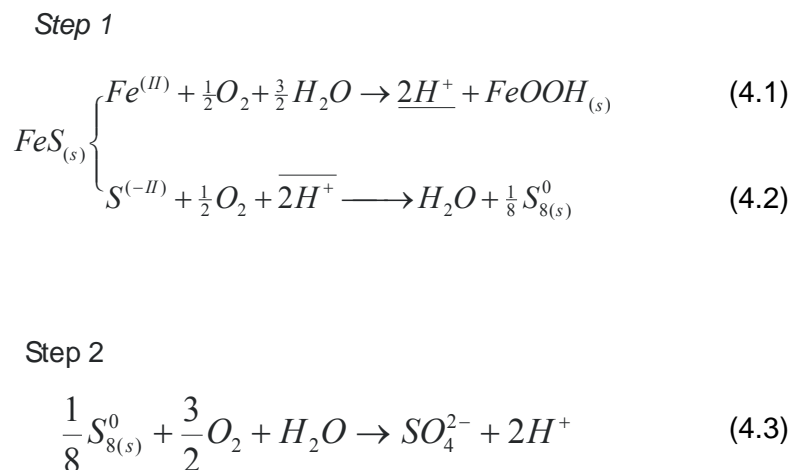


Figure 4-3: Summary of the two-step reaction process for the oxidation of MBO (source: Burton *et al.* 2006a).

Deoxygenation of surface waters, often referred to as blackwater events, are natural events in lowland river systems, and may occur during flood events when elevated levels of dissolved organic carbon leached from leaf litter is decomposed by microbes (Baldwin *et al.* 2001; Howitt *et al.* 2007). As microbes decompose dissolved organic carbon, dissolved oxygen is consumed faster than it can be replenished. However, it is currently impossible to differentiate between deoxygenation caused by MBO oxidation and that by organic matter decomposition

without chemical analysis during the deoxygenation event. At least two fish kills in the Edward-Wakool River system during the summer in 2009 were attributed to deoxygenation events (Hladyz and Watkins 2009). The contribution of MBO oxidation to these deoxygenation events is currently unknown.

Data on the presence of MBO in channel systems in the MDB is currently limited to studies referenced in Table 2-7. MBO has often been identified based on visual inspections rather than quantified by chemical analysis. However, this study has shown high concentrations of iron monosulfide (up to 0.54% S_{AV}) in channel systems within the MDB (Table 2-7), and many of the reported MBO represent a significant deoxygenation hazard if disturbed.

Some of the deoxygenation risk factors associated with wetlands containing reduced inorganic sulfur compounds are also applicable to channel systems (Lamontagne *et al.* 2004). These factors include:

- potential for natural causes or management actions to resuspend sediments,
- suspended sediment load,
- sediment sulfide concentration and form,
- water column residence time,
- sulfide reaction rates,
- salinity, and
- critical dissolved oxygen levels for target species.

4.2.3 Accumulation and release of contaminants

Contaminant mobilisation to surface water and groundwater may occur following the rewetting or mobilisation of sulfidic sediments. Numerous studies have shown that sulfide oxidation and associated acidification may contribute to the release of Fe, Al, As and other trace metals (e.g. Aström 1998; Appleyard *et al.* 2006; Burton *et al.* 2006a, 2008). Trace metals are commonly associated with iron sulfides (Huerta-Diaz and Morse 1992; Morse and Arakaki 1993), and the occurrence of iron monosulfide is known to control the bioavailability of many metals (Di Toro *et al.* 1992; Chapman *et al.* 1998; Simpson *et al.* 2005). Acidification may also result in dissolution of minerals within the sediment leading to metal release. For example, it is well known that acidity formed during sulfide oxidation can react with aluminosilicate clay minerals and result in the liberation of dissolved Al and metal ions (van Breemen 1973). Many other metals and metalloids in addition to Fe can form sulfide minerals, which are released upon oxidation.

Disturbance and oxidation can potentially result in the rapid release of toxic concentrations of MBO associated metals to surrounding surface waters (Burton *et al.* 2006a). Burton *et al.* (2006a) demonstrated a rapid release of metals to the water column on oxidation due to the highly reactive nature of the iron sulfides. This process can result in metal concentrations far exceeding ANZECC water quality trigger values, even where total metal concentrations in an MBO are below the threshold guidelines.

The toxic effects of metals on biota can be both a direct toxicological impact or an indirect chronic impact due to the bioaccumulation of metals and transfer within the food web (DOW 2009). Metal speciation plays a vital role in metal bioavailability, which is influenced by various water quality variables including pH, hardness, alkalinity, dissolved organic carbon and salinity (Stauber *et al.* 2008).

There is limited data currently available on the mobilisation of contaminants from sulfidic sediments in the MDB. Recent studies have demonstrated the potential release of metals and nutrients following rewetting or mobilisation of sulfidic sediments from the lower River Murray and the Lower Lakes region of the MDB (e.g. Simpson *et al.* 2008, 2010; Sullivan *et al.* 2008a, 2009a; Fitzpatrick *et al.* 2009b). The laboratory inundation of sulfuric soil materials from the Lower Lakes led to

chemical reduction of iron minerals and caused mobilisation of high concentrations of metals (i.e. Al, As, Cu, Mn, Ni, Ag, Cd, Cr, Co) and nutrients (i.e. NH_4^+ and NO_3^-) (Sullivan *et al.* 2008a). The mobilisation of MBO from the Lower Lakes region resulted in high concentrations of Al, Mn, NH_4^+ and NO_3^- in the water column (Sullivan *et al.* 2008a). Simpson *et al.* (2010) found that rewetting dried soils with River Murray water resulted in rapid metal release and the dissolved concentrations of many metals in their experiments exceeded the Australian water quality guidelines, despite trace metal concentrations in most soils being at background levels. Further information on the mobilisation of contaminants from sediments collected from Finniss River and Currency Creek following rewetting is given in Section 2.2.1.2.

4.2.4 Acidification hazard

The ANZECC guidelines for aquatic ecosystems recommend a surface water pH > 6.5 (ANZECC/ARMCANZ 2000). If left undisturbed and inundated, sediments containing reduced inorganic sulfur compounds generally pose little or no threat of acidification. Acidification occurs when sediments containing reduced inorganic sulfur compounds are exposed to air. These compounds react with oxygen to form sulfuric acid. Where the amount of acid produced is greater than the buffering capacity of the sediments and overlying water, acidification of soil, surface water and groundwater may occur.

A number of oxidation reactions of reduced inorganic sulfur compounds (principally pyrite) may take place to produce acidity (e.g. Equations 1.1 and 1.2). The oxidation of iron monosulfides and subsequently, elemental sulfur, is largely responsible for the acidification of MBO materials (see Figure 4-2). In addition, a range of secondary minerals (including jarosite, natrojarosite, sideronatrite and schwertmannite) may also form as oxidation products and act as stores of acidity that may be released upon rewetting (Ahern *et al.* 2004; Fitzpatrick and Shand 2008b).

The effects of acid discharge into aquatic environments have been reported by many authors (e.g. Sammut *et al.* 1993; 1996), and include:

- fish kills,
- the onset of fish disease (e.g. epizootic ulcerative syndrome, also known as 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),
- loss of habitat and spawning areas,
- clarification of water, resulting in increased water temperatures, and
- smothering of benthos by iron flocs.

Lamontagne *et al.* (2004) identified the acidification risk factors associated with wetlands containing reduced inorganic sulfur compounds, and include:

- quantity of sulfide present,
- form of sulfide (pyrite vs. monosulfides),
- carbonate content of the sediments,
- clay content (texture) of the sediments,
- volume and alkalinity of the receiving water body, and
- wetting-drying regime of the wetland.

The acidification risk factors identified for wetlands within the MDB are directly applicable to channelised systems. The presence of sulfuric sediments ($\text{pH} < 4$) is also an additional acidification risk factor. In channel systems, the flow velocity within channels is also an important risk factor in determining whether mobilisation and subsequent acidification could potentially occur.

Acid sulfate soil action criteria indicating the need for an acid sulfate soil management plan have been developed for coastal acid sulfate soils based on soil texture, sulfide content (i.e. S_{CR} concentration) and mass of soil that will be disturbed (Table 4-2) (Dear *et al.* 2002). A higher criterion is given for clay materials which are expected to have a greater buffering capacity than sandy materials. However, these action criteria may not reflect the acidification hazard, as some soil materials may also have a high concentration of existing acidity and/or ANC. The potential acidification hazard of an acid sulfate soil material is often determined using an acid-base accounting approach which takes account of these factors (Ahern *et al.* 2004). A summary of the acid-base accounting approach is given in Appendix 2.

A summary of the reduced inorganic sulfur concentrations and the calculated net acidities for channels reported to contain reduced inorganic sulfur compounds is presented in Table 4-3. The net acidities were found to be highly variable within channel system sediments in the MDB. High net acidities were observed in some channel sediments, particularly in the Lower Murray River floodplain, Lower Loddon River and Burnt Creek. The high net acidities largely reflect the elevated reduced inorganic sulfur concentrations in the channels at these sites. However, acid-base accounting calculations show negative net acidities for sediments within Queensland irrigation channels despite appreciable sulfides due to the high sediment ANC.

Certain factors may result in an over-estimate of the ANC used in the acid-base accounting approach. For example, ANC may not be readily or rapidly available (e.g. locked up in shells) or surface coatings may limit the neutralising ability and reactivity of carbonate minerals (Ahern *et al.* 2004).

Table 4-2: Acid sulfate soil action criteria indicating the need for an acid sulfate soil management plan based on soil texture range, chromium reducible sulfur (S_{CR}) concentration and mass of soil that will be disturbed (source: Dear *et al.* 2002).

Texture range	S_{CR} (%)	
	<1000 t disturbed soil	>1000 t disturbed soil
Coarse: Sands to loamy sands	0.03	0.03
Medium: Sandy loams to light clays	0.06	0.03
Fine: Medium to heavy clays	0.10	0.03

As discussed in Section 2.2, a combination of standard methodologies are often applied in addition to acid-base accounting to assess the acidification hazard, including field pH, peroxide testing, soil incubation and mineralogical analysis. Many of the case studies presented in this study showed sulfuric materials (pH < 4), which present a significant acidification hazard upon rewetting. These materials were widespread within channel systems in the MDB (see Sections 2.2.1 - 2.2.3). Peroxide testing and soil incubation also identified that many channel sediments within the MDB have the potential to acidify to pH < 4 as a result of sulfide oxidation (see Sections 2.2.1 – 2.2.4). Mineralogical analysis has shown the presence of sulfide oxidation products including jarosite, natrojarosite, sideronatrite and schwertmannite in channel systems which may release acidity upon rewetting (see Sections 2.2.1 and 2.2.2).

Table 4-3: Summary of reduced inorganic sulfur concentrations and calculated net acidities in channel sediments in the MDB.

State	River/Creek	Reduced inorganic sulfur Concentrations (%S _{CR} , %S _{AV})	Net Acidity (mole H ⁺ tonne ⁻¹)	
			Min.	Max
South Australia	River Murray below Blanchetown (Lock 1)	0.02 – 0.18% S _{CR}	-24	352
	Finniss River	<0.01 – 1.71% S _{CR}	-2,070	1,088
	Currency Creek	<0.01 – 1.49% S _{CR}	-40	976
	Black Swamp	0.03 – 0.96% S _{CR}	25	606
	Goolwa Channel	<0.01 – 4.32% S _{CR}	-2,277	2,575
	Mundic Creek	<0.01 – 0.32% S _{CR}	-46	233
	Pike River	<0.01 – 0.58% S _{CR}	-51	322
Victoria	Snake Creek	0.02 – 0.03% S _{CR}	13	24
	Dishers Creek, near Renmark	0.08 – 0.45% S _{CR} <0.01 – 0.08% S _{AV}	n.a.	n.a.
	Lower Loddon River	0.00 – 0.11% S _{CR}	-103	168
	Burnt Creek	0.00 – 6.25% S _{CR}	7	3,930
	Walpolla Creek	<0.01 – 0.07% S _{CR}	6	65
	Butlers Creek	0.01 – 0.02% S _{CR}	10	28
New South Wales	Picaminy Creek, Kerang	0.49% S _{CR} 0.33% S _{AV}	n.a.	n.a.
	Irrigation channels, Kerang	0.46 – 0.74% S _{CR} 0.32 – 0.54% S _{AV}	n.a.	n.a.
	Carr's Creek	0.01 – 0.10% S _{CR}	8	78
	Cappits Creek	<0.01 – 0.01% S _{CR}	-69	23
	Darling Anabranh	<0.01 – 0.05% S _{CR}	1	39
	Salt Creek	<0.01 – 0.05% S _{CR}	2	33
	Wakool River	<0.01 – 0.04% S _{CR} <0.01% S _{AV}	n.a.	n.a.
	Niemur River	0.01 – 0.03% S _{CR} <0.01% S _{AV}	n.a.	n.a.
	Washpen Creek ¹	≤ 0.01 – 0.04% S _{CR}	21	58
Queensland	Talbragar River	0.00 – 0.02% S _{CR} <0.01 – ~0.1% S _{AV}	n.a.	n.a.
	Irrigation channel, Scenic Hill, Griffith	0.57% S _{CR} 0.24% S _{AV}	n.a.	n.a.
	Irrigation channels, Hanwood	0.11 – 0.13% S _{CR} 0.07 – 0.13% S _{AV}	n.a.	n.a.
	Irrigation channels, Talwood-Mungindi region	<0.02 – 0.13% S _{CR} <0.01% S _{AV}	-52	-181
	Whyenbah irrigation channel	0.02 – 0.04% S _{CR} <0.01 – 0.11% S _{AV}	-254	-641

¹ Disconnected from the Euston Weir pool, River Murray. n.a.: data not available.

4.2.5 Additional potential hazards

Additional potential hazards associated with reduced inorganic sulfur compounds include the production of malodours (SO₂, H₂S, organo-S compounds), noxious gases and dust (Lamontagne *et al.* 2006; MDBA 2010). In areas where significant MBO formation occurs, this material may coat surface sediments and reduce habitat available to benthic invertebrates (Lamontagne *et al.* 2003). High rates of sulfate reduction can also increase phosphorus availability for algae and could possibly lead to the development of algal blooms (Lamontagne *et al.* 2003).

Lamontagne *et al.* (2003) also identified the accumulation of radionuclides as a potential environmental hazard associated with sulfidic sediments in the MDB. In addition to Fe, other metals (including uranium) can form mineral deposits in the presence of reduced inorganic sulfur. Therefore, there is the possibility that the accumulation of sulfidic materials can also lead to the accumulation of radionuclides in some areas.

4.3 Defining and assessing risk

Risk is a measure of both the consequences of a hazard occurring, and the likelihood of its occurrence (MDBA 2010). According to the National Environment Protection Measures (NEPM), risk is defined as *"the probability in a certain timeframe that an adverse outcome will occur in a person, a group of people, plants, animals and/or the ecology of a specified area that is exposed to a particular dose or concentration of a hazardous agent, i.e. it depends on both the level of toxicity of hazardous agent and the level of exposure"* (NEPC 1999).

In the framework presented by MDBA (2010), a series of standardised tables were provided to define and assess risk. The tables determine the consequence of a hazard occurring (Table 4-4), and a likelihood rating for the disturbance scenario for each hazard (Table 4-5). These two factors are then combined in a risk assessment matrix to determine the level of risk (Table 4-6).

Table 4-4 determines the level of consequence of a hazard occurring, ranging from insignificant to extreme, and primarily takes account of the environmental and water quality impacts, both to the waterway and downstream impacts.

Table 4-4: Standardised table used to determine the consequences of a hazard occurring (source: MDBA 2010).

Descriptor	Definition
Extreme	Irreversible damage to waterway values and/or waters downstream; localised species extinction; permanent loss of water supplies
Major	Long-term damage to waterway values and/or waters downstream; significant impacts on listed species; significant impacts on water supplies
Moderate	Short-term damage to waterway values and/or waters downstream; short-term impacts on species
Minor	Localised short-term damage to waterway values and/or waters downstream; temporary loss of water supplies
Insignificant	Negligible impact on waterway values and/or waters downstream; no detectable impacts on species

Table 4-5 determines the likelihood (i.e. probability) of disturbance for each hazard, ranging from rare to almost certain. This requires an understanding of the nature and severity of the materials (including the extent and net acid generating potential) as well as contributing factors influencing the risk (MDBA 2010). Examples of disturbance include: (i) rewetting of acid sulfate soil materials after oxidation, (ii) acid sulfate soil materials that are currently inundated and may be oxidised, or (iii) acid sulfate soil materials that are currently inundated and may be dispersed by flushing (e.g. scouring flows) (MDBA 2010). As mentioned previously, the consequence of a hazard occurring and the likelihood rating for the disturbance scenario for each hazard are then ranked using a standardised risk assessment matrix (Table 4-6).

Table 4-5: Likelihood ratings for the disturbance scenario (source: MDBA 2010).

Descriptor	Definition
Almost certain	Disturbance is expected to occur in most circumstances
Likely	Disturbance will probably occur in most circumstances
Possible	Disturbance might occur at some time
Unlikely	Disturbance could occur at some time
Rare	Disturbance may occur only in exceptional circumstances

Table 4-6: Risk assessment matrix (source: Standards Australia / Standards New Zealand 2004).

Likelihood category	Consequences category				
	Extreme	Major	Moderate	Minor	Insignificant
Almost certain	Very High	Very High	High	High	Medium
Likely	Very High	High	High	Medium	Medium
Possible	High	High	High	Medium	Low
Unlikely	High	Medium	Medium	Low	Low
Rare	High	Medium	Medium	Low	Low

Legend

- Very High: Very High Risk - immediate action recommended.
- High: High Risk - senior management attention needed.
- Medium: Medium Risk - management action may be recommended. Agency responsible must be specified.
- Low: Low Risk - manage by routine procedures.

The pathway to exposure of the various hazards outlined in this study is dependent on both natural processes (e.g. droughts and floods) and a variety of management decisions (e.g. water management regime). The risk framework outlined highlights the need for primary data. Although a number of potential hazards associated with reduced inorganic sulfur compounds have been identified, this desktop assessment has revealed that a thorough assessment of risk on a basin scale is not possible with the data currently available.

4.4 Potential impacts of climate change

The potential impacts of climate change on the MDB are not yet fully assessed. However, the earlier predictions are for warmer conditions, an increasing proportion of rainfall to occur from heavy falls and increasing occurrence of drought in many regions. All of these factors may have an impact on either the accumulation of sulfides within channels or their potential exposure and oxidation through desiccation, or mobilisation by floodwaters. Specific land management factors such as water extraction, water capture and drainage will also affect how climate change may impact the sediments within channels.

4.4.1 Drought

The effects of prolonged drought on the oxidation and acidification of sulfidic sediments have been examined for agricultural areas (e.g. Wilson *et al.* 1999). Drought can exert its greatest impact on already hydrologically stressed river landscapes. Exposure of unoxidised sulfidic soils by extreme drought is an emerging concern in drought prone regions. In their natural state, sulfidic sediments are characteristically waterlogged, and drought has rarely been considered a significant threat. However, water capture and irrigation have reduced the environmental flows, particularly at critically dry periods. The vulnerability of drying out water bodies that currently prevent subaqueous sulfidic soil materials from oxidising is largely unknown. With higher temperatures, increasing evaporative losses, less rainfall and greater demand on water resources under a changing climate, subaqueous sulfidic sediments that are currently protected by natural water bodies will become increasingly susceptible to exposure by drought.

An insight to the potential scale of drought triggered acid sulfate soil impacts is currently provided in the lower MDB. Drought has lowered lake water levels, exposing thousands of hectares of sulfidic shoreline and lake-bed sediments in the Lower Lakes region (Fitzpatrick *et al.* 2008a). These sediments are beginning to oxidise and acidify. Climate change predicts a greater occurrence of drought, however, the vulnerability of subaqueous acid sulfate soils and potential consequences to water quality have not been systematically assessed.

4.4.2 Floods

Biogeochemical processes occurring in channels exert a controlling influence on water quality (Burton *et al.* 2006d). Catastrophic fish kills as a result of extreme deoxygenation and/or acidification can result from large flood events (Bush *et al.* 2004; Sammut *et al.* 1996; Johnston *et al.* 2004). In isolation, it would seem reasonable to expect that an increase in the frequency of flood events will increase the environmental and agronomic impact from sulfides within channels. However, there are a range of other factors that may contribute to the magnitude of floodwater impacts, such as the abundance of MBO in channels and seasonality. Deoxygenation is known to be far more intense during summer floods due to the more rapid decomposition of floodplain vegetation (Johnston *et al.* 2004). A consideration of how contaminants accumulate in the soil profile and how MBO materials accumulate in channels between floods, and the influence of seasonality is required to begin to understand how future climate change may affect flood induced impacts in acid sulfate soil landscapes. In addition, higher flow flood events leading to increased volumes of water and increased flushing as a consequence of climate change would also potentially affect the impacts.

Our scientific understanding of the chemical, biological and hydrological processes of sulfidic sediments within channel systems suggests that climate change will have an impact on these materials. However, advancing our understanding of these impacts will require new science that integrates the influence of climate change on the parameters which govern sulfide accumulation and oxidation. This is a critical and emerging frontier for acid sulfate soil research.

5. MANAGEMENT OPTIONS AVAILABLE

Where waterways are impacted by sulfidic sediments, a range of management options are available. In coastal acid sulfate soil landscapes, the management options include avoidance, prevention of oxidation, oxidation and leaching, removal of pyritic material, and neutralisation (White and Melville 1993; Ahern *et al.* 1998; Dear *et al.* 2002). However, applying management principles that are relevant to coastal acid sulfate soil management such as avoiding disturbing acid sulfate soils, may not be possible in inland systems as strategies, such as avoidance, may not be under our control (Warren 2010).

Baldwin and Fraser (2009) recently summarised the management options for inland waterways impacted by sulfidic sediments. The main strategies included minimising the formation of sulfidic sediments (such as reducing the salt load or re-instating more natural flow regimes), rehabilitation of impacted waterways (including inundation and/or neutralisation), or isolation of the acidified water body from the surrounding environment for wetland systems.

A national guidance document on the management of inland acid sulfate soil landscapes titled “*National guidance for the management of acid sulfate soils in inland aquatic ecosystems*” is about to be released (DEWHA In press). The national guidance document provides a hierarchy of management options for managing acid sulfate soils in inland aquatic ecosystems including:

1. *Minimising the formation of acid sulfate soils in inland aquatic ecosystems.*
2. *Preventing oxidation of acid sulfate soils, if they are already present in quantities of concern or controlled oxidation to remove acid sulfate soils if levels are a concern but the water and soil has adequate neutralising capacity.*
3. *Controlling or treating acidification if oxidation of acid sulfate soils does occur.*
4. *Protecting connected aquatic ecosystems/other parts of the environment if treatment of the directly affected aquatic ecosystem is not feasible.*

In some instances it may not be practical or even sensible to undertake any active intervention (for example in a pond used as part of a salt interception scheme), in which case the management objective is:

5. *Limited further intervention.*

The possible activities associated with each management objective is summarised in Table 5-1. Further information on each management option is provided in detail in the national guidance document.

Table 5-1: Summary of management objectives and possible activities (source: DEWHA In press).

Management objective	Activities
Minimising the formation of acid sulfate soils in inland aquatic ecosystems	<p>Reduce secondary salinisation through:</p> <ul style="list-style-type: none"> • lowering saline water tables • maintaining the freshwater lens between saline groundwater and the aquatic ecosystem • stopping the delivery of irrigation return water • Incorporating a more natural flow regime
Preventing oxidation of acid sulfate soils or controlled oxidation to remove acid sulfate soils	<p>Preventing oxidation:</p> <ul style="list-style-type: none"> • Keep the sediments covered by water • Avoid flow regimes that could re-suspend sediments <p>Controlled oxidation:</p> <ul style="list-style-type: none"> • Assess whether neutralising capacity of the sediments and water far exceeds the acidity produced by oxidation • Assess the risk of deoxygenation and metal release. <p>Monitor intervention and have a contingency plan to ensure avoidance of these risks.</p>
Controlling or treating acidification	<ul style="list-style-type: none"> • Neutralise water column and/or sediments by adding chemical ameliorants • Add organic matter to promote bioremediation by micro-organisms • Use stored alkalinity in the ecosystem
Protecting adjacent or downstream environments if treatment of the affected aquatic ecosystem is not feasible	<ul style="list-style-type: none"> • Isolate the site • Neutralise and dilute surface water • Treat discharge waters by neutralisation or biological treatment
Limited further intervention	<ul style="list-style-type: none"> • Assess risk • Communicate with stakeholders • Undertake monitoring • Assess responsibilities and obligations and take action as required

6. FUTURE RESEARCH ON CHANNELISED SYSTEMS IN THE BASIN

The findings of this desktop assessment have shown there are still significant knowledge gaps in determining the extent and risk of sulfidic sediments in channelised systems in the MDB. To assess the hazard and risk associated with sulfide accumulations within channels of the MDB will require new fundamental knowledge on the landscape factors and geochemical processes that affect the accumulation and properties of these materials. There is a considerable depth of knowledge on reduced inorganic sulfur accumulations in coastal landscapes, but the processes, impacts and options available for management are not directly applicable to inland settings. To progress an understanding of the environmental hazards and development of appropriate management response for the MDB will require new knowledge in the following areas:

1. Specific data on the linkages between the spatial occurrence of reduced inorganic sulfur accumulations within channels to geomorphic and hydro-geophysical attributes. Integration of site specific geomorphic data is required to develop landscape models for the purpose of spatial extrapolation of reduced inorganic sulfur accumulations across the channelised systems in the MDB.
2. Field based site specific assessments to characterise the properties of sulfur compounds and sulfidic sediments in the channel and water column of rivers and creeks of the MDB.
3. The development of an appropriate sampling strategy for assessing the spatial extent and magnitude of sulfidic sediments in inland channels.
4. Field and laboratory studies to establish the kinetics and reaction pathways of sulfidic sediment accumulation in channels of the MDB, with a focus on determining the main biogeochemical drivers for sulfidisation and geophysical constraints to their accumulation.

5. Field and laboratory studies to establish the kinetics and reaction pathways of oxidation of this material in order to quantify the risks posed by their scour and mobilisation to water quality.
6. Studies to identify potential management opportunities/interventions that minimise the formation, disturbance or impacts of sulfidic sediments in the main channel of rivers and creeks of the MDB.
7. Specific detailed assessment of the potential impacts of climate change and water management to the environmental risk from sulfides within channels.
8. Further investigation into the fate of mobilised and precipitated metals within channels.
9. A greater understanding of benthic chemical changes in channel systems, particularly in the long-term.

7. CONCLUSIONS AND RECOMMENDATIONS

- This desktop assessment on the distribution and environmental risk of reduced inorganic sulfur compounds in river and creek channels in the MDB has shown that while there is an increasing awareness of the presence of reduced inorganic sulfur compounds in wetlands in MDB, there are significant knowledge gaps in determining both the extent and risk of sulfidic sediments in channelised systems.
- Elevated sulfate concentrations have been suggested as potential drivers for contemporary sulfide accumulations in channels. Further data specifically on sulfate concentration and trends in channels will be required to clarify this potential factor.
- There is not enough data on reduced inorganic sulfur compounds in the MDB to draw strong conclusions on the level of hazard or risk it poses on a basin wide perspective. There are a lot of visual records of suspected compounds, in particular MBOs, but without proper testing for monosulfides it is difficult to say whether this is evidence of reduced inorganic sulfur compounds.
- From the available data there are some areas within the MDB that have an acute problem. It is reasonable to suggest that the issue may not be a priority across the entire basin, but will be in a few priority locations. It is apparent from the existing data that reduced inorganic sulfur compounds are highly variable across the entire basin as well as within individual wetland systems.
- We know from our understanding of sulfides in other landscapes that the formation and disturbances of these compounds can have significant impact upon water quality and aquatic life.
- We need more information in order to assess the risk and hazard of reduced inorganic sulfur compounds in channels at a basin level. In particular we do not have sufficient understanding of reduced inorganic sulfur compounds within the MDB landscape to predict where they will form and at what magnitude.

- There is insufficient information available to assess the relative risk posed by these sediments (based on their likelihood of occurrence and potential impacts) when compared to other risks to water resources and water-dependent ecosystems already identified in the MDB.

The broad recommendation from this study is:

- We need a greater understanding of reduced inorganic sulfur compounds in river and creek channels within the MDB landscape. We have an understanding of sulfides in other landscapes (i.e. coastal estuaries, wetlands and salt marshes), but will require new primary data to establish a fundamental understanding of the processes and controls on sulfur accumulation in the MDB. There is insufficient data to assess the direct applicability of knowledge on sulfur cycling from other well studied systems such as coastal and marine environments.

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APPENDICES

APPENDIX 1: LABORATORY ANALYTICAL SOIL DATA

Table 9-1: Table showing pH data, acid sulfate soil materials, classification, S_{CR}, lime calculation and risk for Murray River below Blanchetown (Lock 1) (source: Fitzpatrick *et al.* 2008e).

Method/ Sample	Depth	pH _w	pH _{FOX}	¹ ASS materials (all profile)	² ASS classification (and ³ code)	⁴ S _{CR}	⁵ Lime Calculation kg CaCO ₃ /tonne DW	⁶ ASS Risk (all profile)
WL 1.1	0-10	6.7	1.8	Sulfidic	Sulfidic subaqueous clayey soil – sandy (1.2)	0.086	4	H
WL 1.2	10-30	7.0	2.6			0.024	2	
WL 1.3	30-50	6.9	2.3			0.028	2	
WL 1.4	50-70	6.7	2.2			0.096	5	
WL 2.1	0-5	7.15	2.13	Sulfidic	Sulfidic cracking clay soil (3.2)	0.046	3	VH
WL 2.2	5-25	6.84	3.21			0.043	2	
WL 2.3	25-40	7.52	6.54			0.047	-2	
WL 5.1	Crust			Sulfuric	Sulfuric cracking clay soil (3.3)			VH
WL 5.2	Crust							
WL 5.3	0-1	2.54	1.02			0.069	26	
WL 5.4	1-5	2.65	1.51			0.054	19	
WL 5.5	5-20	2.75	1.21			0.180	24	
WL 5.6	20-50	3.8	1.7			0.044	14	
WL 5.7	50-70	5.2	2.2			0.043	5	
WL 5.8	70-90					0.029	3	
WL 5.9	90-110	6.1	2.3					
MOR 3.4	1-10	4.94	3	Sulfidic	Sulfidic cracking clay soil (3.2)	0.139	8	VH
MOR 3.5	10-30	5.02	3.23			0.087	6	
MOR 3.6	30-50	5.14	3.78					
MOR 3.7	50-70	5.52	3.63					
MOR 4.1	0-5	5.38	2.64	Sulfidic	Sulfidic cracking clay soil (3.2)			VH
MOR 4.2	5-20	5.29	3.37			0.028	3	
MOR 7.1	0-10	4.97	2.78	Sulfidic	Sulfidic subaqueous clayey soil (1.2)	0.155	8	VH

¹ Sulfuric and Sulfidic (Appendix 1); Hyposulfidic (pH_{Incubation} or pH_{FOX} decreases to pH 4-5)

² See classification in Table 13.

³ See classification key code in Table 12.

⁴ Reduced Inorganic sulfur (% chromium reducible S; S_{CR}). This measures the reduced sulfur in the sample that potentially can oxidise to sulfuric acid.

⁵ Lime needed to neutralise acidity, based on net acidity/alkalinity, which includes a 1.5 times safety factor (Negative values have sufficient excess ANC and should not need additional lime) and interpretation from Dear *et al.*, (2002; page 8).

⁶ ASS Risk categorisation is based on a number of criteria, including mainly the five lime treatment categories: N = No treatment (no lime); L=Low level treatment; M = Medium level treatment, H = High level treatment, VH = Very high level treatment, XH = Extra High level treatment: based on data presented in Table 13. Additional criteria include the presence of MBO, peroxide pH, decrease in pH during incubation experiments.

Table 9-2: Selected sulfur-based acidity and acid neutralising capacity analyses and calculations for Murray River below Blanchetown (Lock 1) (source: Fitzpatrick *et al.* 2008e).

Sample No	Texture Class ^a	pH _{KCl} ^b	S _{CR} ^c %	CaCO ₃ ^d %	Net Acidity mole H ⁺ /tonne ^e	Lime Calculation ^f kg CaCO ₃ /tonne DW
MOR 3.4		5.41	0.139	<0.05	102	8
MOR 3.5		4.99	0.087	<0.05	80	6
MOR 4.2		4.97	0.028	<0.05	45	3
MOR 7.1		5.25	0.155	<0.05	105	8
WL 1.1	Medium	5.52	0.086	0.00	59	4
WL 1.2	Medium	5.19	0.024	0.00	28	2
WL 1.3	Coarse	5.63	0.028	0.00	24	2
WL 1.4	Medium	5.39	0.096	0.00	68	5
WL 2.1	Coarse	5.65	0.046	0.00	34	3
WL 2.2	Fine	6.50	0.043	0.01	25	2
WL 2.3	Medium	7.41	0.047	0.40	-24	-2
WL 5.3	Medium	3.24	0.069	0.00	352	26
WL 5.4	Medium	3.24	0.054	0.00	254	19
WL 5.5	Medium	3.33	0.180	0.00	324	24
WL 5.6	Medium	3.80	0.044	0.00	181	14
WL 5.7	Fine	4.56	0.043	0.00	64	5
WL 5.8	Fine	5.02	0.029	0.00	40	3
WL 5.10	Fine	5.32	0.040	0.00	45	3

^a Texture Class: coarse = sands to loamy sands; medium = sandy loams to light clays; fine = medium to heavy clays and silty clay

^b pH_{KCl}: pH measured in 1M KCl. Samples with pH values greater than 6.5 have no residual acidity.

^c Reduced Inorganic sulfur (% chromium reducible S; S_{CR}). This measures the reduced sulfur in the sample that potentially can oxidise to sulfuric acid. Classification is as potential acid sulfate material if: coarse S_{CR} ≥ 0.03% or 19 mole H⁺/t; medium S_{CR} ≥ 0.06%S or 37 mole H⁺/t; fine S_{CR} ≥ 0.1%S or 62 mole H⁺/t).

^d % ANC: This is termed acid neutralising capacity (ANC) and is presented as CaCO₃ equivalents.

^e This is based on potential acidity derived from % S_{CR}.

^f Lime needed to neutralise acidity, based on net acidity/alkalinity. Includes a 1.5 times safety factor. Negative values have sufficient excess ANC and should not need additional lime.

Table 9-3: Laboratory soil data summary including pH testing and acid-base accounting for Finniss River, Currency Creek, Black Swamp and Goolwa Channel samples (source: Fitzpatrick *et al.* 2009b).

Parameter	Description	Units	Minimum	Median	Maximum	No. of Samples
EC	Electrical conductivity	mS/cm	<0.01	5	756	119
pH _w	pH in water		2.00*	5.80	8.60	119
pH _{FOX}	pH after peroxide treatment		1.00	1.87	7.59	119
pH _{incubation}	pH after ageing 20 weeks		1.00	3.00	7.90	119
pH _{KCl}	pH in KCl		2.89	5.45	9.48	119
Sulfate		mg SO ₄ / kg	112	2700	109650	119
TAA	Total actual acidity	mole H ⁺ / tonne	0	6	2420	119
ANC	Acid neutralising capacity as %CaCO ₃	mole H ⁺ / tonne	0	0	3563	119
S _{CR}	Cr-reducible sulfur	mole H ⁺ / tonne	3	89	2696	119
NA	Net acidity; retained acidity not included	mole H ⁺ / tonne	-2277	72	2575	119
Lime Calculation	Calculated, with a 1.5 safety factor	kg CaCO ₃ / tonne	-171	5	193	119

*Several salt efflorescences, surface precipitates and sandy surface materials adjacent to streamlines in wetlands near Wally's Landing (e.g. FIN 26 sites), which underwent rewetting from rainfall events in May 2009 measured pH levels of 0.5 to 1.3 in the field and laboratory.

Table 9-4: pH of field soils in water (pH_w), after treatment with hydrogen peroxide (pH_{Fox}) and after incubating for 16 weeks (pH_{aging}) for Mundic Creek (Pike 1-15), Salt Lake (Pike 16), Pike River (Pike 17-23), Snake Creek (Pike 24) and Col Col area (Pike 25-27) (source: Shand *et al.* 2009).

Site/Sample No	Upper depth	Lower depth	¹ pH _w	² pH _{Fox}	³ pH _{aging}
PIKE 1.1	0	15	6.1	1.8	3.9
PIKE 1.2	15	30	5.7	1.8	3.9
PIKE 1.3	30	60	6.4	2.7	4.5
PIKE 2.1	0	5	6.2	1.8	3.9
PIKE 2.2	5	45	6.1	2.9	3.9
PIKE 2.3	45	60	5.7	3.5	4.0
PIKE 3.1	0	10	6.4	2.3	3.9
PIKE 3.2	10	25	6.5	2.7	3.9
PIKE 4.1	0	15	6.1	1.9	3.9
PIKE 4.2	15	25	6.2	2.5	4.0
PIKE 5.1	0	15	6.4	2.0	3.0
PIKE 5.2	15	30	6.1	3.4	3.0
PIKE 6.1	40	80	na	na	
PIKE 7.1	0	5	5.9	3.0	4.0
PIKE 7.2	5	15	5.9	3.9	5.0
PIKE 7.3	15	30	5.4	3.6	4.0
PIKE 8.1	0	8	6.9	2.7	4.5
PIKE 8.2	8	25	6.3	4.8	5.0
PIKE 9.1	0	10	6.6	6.1	5.0
PIKE 9.2	10	25	6.6	6.2	4.0
PIKE 10.1	0	15	6.6	2.0	3.3
PIKE 10.2	15	90	6.9	5.7	4.0
PIKE 11.1	0	8	6.3	2.3	3.9
PIKE 11.2	8	20	6.7	3.2	4.0
PIKE 11.3	20	30	5.6	3.7	4.0
PIKE 12.1	0	5	5.9	1.5	3.9
PIKE 12.2	5	30	6.7	2.5	3.9
PIKE 13.1	0	8	5.6	1.7	3.9
PIKE 13.2	8	23	5.9	2.0	3.9
PIKE 14.1	0	3	6.4	2.4	3.9
PIKE 14.2	3	5	6.5	2.4	4.2
PIKE 14.3	5	30	6.0	2.5	3.9
PIKE 15.1	0	5	6.1	2.5	3.6
PIKE 15.2	5	20	6.6	3.4	4.0
PIKE 16.1	0	1.5	salt efflorescence		
PIKE 16.2	1.5	4	6.8	4.4	5.0
PIKE 16.3	4	20	5.7	3.8	4.5
PIKE 16.4	20	40	4.7	2.9	2.5
PIKE 17.1	0	10	7.2	1.8	3.6
PIKE 17.2	10	25	7.7	2.4	6.5
PIKE 17.3	25	50	7.5	6.4	4.2
PIKE 18.1	0	10	6.9	2.6	4.0
PIKE 18.2	10	25	7.3	5.9	3.9
PIKE 19.1	0	12	6.4	2.1	4.0
PIKE 19.2	12	30	6.4	5.1	4.0
PIKE 20.1	0	12	5.8	2.4	4.5
PIKE 20.2	12	30	6.5	5.0	4.0
PIKE 21.1	0	15	5.9	1.9	3.6
PIKE 21.2	15	25	6.5	2.8	4.0
PIKE 22.1	0	15	6.0	2.8	5.0
PIKE 22.2	15	40	6.0	3.1	5.0
PIKE 23.1	0	10	6.7	2.4	3.3
PIKE 23.2	10	30	6.7	2.6	3.3
PIKE 23.3	30	40	6.9	5.1	4.2
PIKE 24.1	0	5	6.2	2.3	3.9
PIKE 24.2	5	25	7.1	3.3	4.5
PIKE 25.1	0	5	7.4	7.1	6.5
PIKE 25.2	5	25	7.1	6.8	5.8
PIKE 26.1	0	8	7.4	7.2	4.0
PIKE 26.2	8	30	6.7	6.8	4.5
PIKE 27.1	0	3	7.2	6.0	4.0
PIKE 27.2	3	20	6.1	4.3	4.7

Notes:

¹ pH_w values were obtained using field moist samples to which water was added to form a slurry which approximates, on a weight basis, 1:1 of soil to water, respectively. The mixture was shaken regularly and allowed to equilibrate at room temperature (about 20°C) for at least one hour.

² pH_{Fox} values were obtained using field moist soil and treating the sample with 30% hydrogen peroxide (pH adjusted to about 5, see Ahern *et al.* 2004) until reaction ceased and the mixture cooled to room temperature. The final mixture approximated a 1:2 slurry.

³ pH_{aging} is the pH of the soil, measured after incubation in chip trays, using pH strips after a period of at least 16 weeks.

Table 9-5: Acid-base accounting data for Mundic Creek (Pike 1-15), Salt Lake (Pike 16), Pike River (Pike 17-23), Snake Creek (Pike 24) and Col Col area (Pike 25-27) (source: Shand et al. 2009).

Sample Site	Depth (cm)	Moisture Content (%)	pH _{KCl} (TAA)	Titrate Actual Acidity (TAA) (mole H ⁺ /tonne (to pH 6.5))	Reduced Inorganic Sulfur (% Cr reducible S) %S _{CR} (note 2)	Reduced Inorganic Sulfur (S _{CR}) (mole H ⁺ /tonne)	ANCBT (%CaCO ₃)	a-ANCE (mole H ⁺ /tonne)	NET ACIDITY Chromium Suite (mole H ⁺ /tonne (based on %S _{CR}))	LIME CALCULATION Chromium Suite (kg CaCO ₃ /tonne DW (includes 1.5 safety factor))
Method			23A	23F	22B	a-22B	19A2	a-19A2	note 5	note 5
PIKE 1.1	0-15	62.9	4.92	24	0.118	74	0.00	0	98	7
PIKE 1.2	15-30	49.4	4.61	34	0.125	78	0.00	0	112	8
PIKE 1.3	30-60	44.9	4.76	30	0.095	59	0.00	0	89	7
PIKE 2.1	0-15	56.6	5.28	18	0.111	69	0.00	0	87	7
PIKE 2.2	15-45	50.1	5.06	27	0.075	47	0.00	0	73	6
PIKE 2.3	45-60	42.8	5.02	28	0.036	22	0.00	0	50	4
PIKE 3.1	0-10	54.8	5.01	22	0.074	46	0.00	0	68	5
PIKE 3.2	10-25	53.9	4.94	33	0.093	58	0.00	0	91	7
PIKE 4.1	0-15	52.8	5.32	12	0.111	69	0.00	0	81	6
PIKE 4.2	15-25	21.8	5.42	12	0.022	14	0.00	0	26	2
PIKE 5.1	0-15	49.2	5.33	13	0.088	55	0.00	0	68	5
PIKE 5.2	15-30	27.5	5.46	10	0.043	27	0.00	0	37	3
PIKE 7.1	0-5	45.8	5.01	25	0.038	24	0.00	0	49	4
PIKE 7.2	5-15	31.9	5.11	24	0.015	9	0.00	0	33	2
PIKE 7.3	15-30	31.7	4.87	28	0.011	7	0.00	0	35	3
PIKE 8.1	0-8	55.3	5.52	14	0.024	15	0.00	0	29	2
PIKE 8.2	8-25	74.3	5.47	12	0.012	7	0.00	0	19	1
PIKE 9.1	0-10	31.3	5.75	8	0.005	3	0.00	0	11	1
PIKE 9.2	30-40	31.2	5.61	11	0.003	2	0.00	0	13	1
PIKE 10.1	0-15	78.5	5.61	31	0.324	202	0.00	0	233	17
PIKE 10.2	50-90	29.3	5.93	4	0.014	9	0.00	0	13	1
PIKE 11.1	0-8	57.7	5.37	21	0.135	84	0.00	0	105	8
PIKE 11.2	8-20	28.3	5.31	17	0.014	9	0.00	0	26	2
PIKE 11.3	20-30	26.6	5.34	16	0.006	4	0.00	0	20	1
PIKE 12.1	0-5	46.8	5.22	15	0.148	92	0.00	0	107	8
PIKE 12.2	5-30	30.5	5.38	11	0.023	14	0.00	0	25	2
PIKE 13.1	0-8	48.7	5.04	17	0.135	84	0.00	0	101	8
PIKE 13.2	8-23	33.4	5.24	11	0.099	62	0.00	0	73	5
PIKE 14.1	0-3	22.5	5.66	1	0.006	4	0.00	0	5	0
PIKE 14.2	3-5	19.7	5.43	3	0.010	6	0.00	0	9	1
PIKE 14.3	5-30	21.1	5.50	2	0.008	5	0.00	0	7	1
PIKE 15.1	0-5	18.5	6.05	0	0.013	8	0.00	0	8	1
PIKE 15.2	5-20	20.1	6.41	0	0.014	9	0.00	0	9	1
PIKE 16.2	1.5-4	29.8	7.18	0	0.158	99	0.62	123	17	1
PIKE 16.3	4-20	25.9	6.54	0	0.012	7	0.40	80	-46	-3
PIKE 16.4	20-40	20.7	5.75	6	0.012	7	0.00	0	13	1
PIKE 17.1	0-8	47.8	6.06	3	0.512	319	0.00	0	322	24
PIKE 17.2	8-25	32.7	6.62	0	0.234	146	0.58	115	69	5
PIKE 17.3	25-50	29.1	6.46	0	0.073	46	0.00	0	46	3
PIKE 18.1	0-10	50.3	5.68	7	0.181	113	0.00	0	120	9
PIKE 18.2	10-25	31.0	6.28	1	0.072	45	0.00	0	46	3
PIKE 19.1	0-10	55.5	5.17	16	0.107	67	0.00	0	83	6
PIKE 19.2	10-30	30.1	5.46	15	0.012	7	0.00	0	22	2
PIKE 20.1	0-12	51.3	5.26	16	0.087	54	0.00	0	70	5
PIKE 20.2	12-30	30.0	5.69	11	0.026	16	0.00	0	27	2
PIKE 21.1	0-15	53.3	5.17	18	0.095	59	0.00	0	77	6
PIKE 21.2	15-25	30.4	5.38	19	0.030	19	0.00	0	38	3
PIKE 22.1	0-15	33.3	5.31	15	0.012	7	0.00	0	22	2
PIKE 22.2	15-40	28.7	5.15	16	0.012	7	0.00	0	23	2
PIKE 23.1	0-10	52.3	5.66	9	0.088	55	0.00	0	64	5
PIKE 23.2	10-30	63.3	5.68	10	0.154	96	0.00	0	106	8
PIKE 23.3	30-40	35.4	6.23	2	0.046	29	0.00	0	31	2
PIKE 24.1	0-5	44.2	5.56	6	0.029	18	0.00	0	24	2
PIKE 24.2	5-25	22.4	5.78	3	0.016	10	0.00	0	13	1
PIKE 25.1	0-10	24.5	7.38	0	0.011	7	0.44	87	-51	-4
PIKE 25.2	10-25	22.4	6.20	1	0.004	2	0.00	0	3	0
PIKE 26.1	0-8	43.2	7.22	0	0.195	122	0.96	191	-6	0
PIKE 26.2	8-30	30.5	5.37	8	0.005	3	0.00	0	11	1
PIKE 27.1	0-3	48.5	6.89	0	0.579	361	0.71	142	267	20
PIKE 27.2	3-25	31.3	5.79	6	0.025	16	0.00	0	22	2

NOTES

- All analysis is Dry Weight (DW) - samples dried and ground immediately upon arrival
- Samples analysed by SPOCAS method 23 (i.e. Suspension Peroxide Oxidation Combined Acidity & sulfate) and 'Chromium Reducible Sulfur' technique (Scr - Method 22B)
- Methods from Ahern, CR, McEneaney AE, Sullivan LA (2004). *Acid Sulfate Soils Laboratory Methods Guidelines*. QLD DNRME.
- Bulk density was determined immediately on arrival to laboratory (in situ bulk density is preferred)
- ABA Equation: Net Acidity = Potential Sulfidic Acidity (i.e. Scr or Sox) + Actual Acidity + Retained Acidity - measured ANC/FF
- For Texture: coarse = sands to loamy sands; medium = sandy loams to light clays; fine = medium to heavy clays and silty clays
- CRS, TAA and ANC are NATA certified but other SPOCAS segments are currently not NATA certification
- Results at or below detection limits are replaced with '0' for calculation purposes
- Projects that disturb >1000 tonnes of soil, the ≥0.03% S classification guideline would apply

Table 9-6: Summary of laboratory analysis of soil samples including pH and acid-base accounting for the Loddon River (source: Thomas *et al.* 2009c).

Parameter	Units	Minimum	Median	Maximum	¹ n
² pH _w	pH	3.82	6.26	9.03	32
³ pH _{FOX}	pH	1.55	2.59	6.74	32
⁴ pH _{field}	pH	2.2	3.9	5.0	12
⁵ pH _{incubation}	pH	2.5	4.0	7.0	43
⁶ EC _{field}	dS m ⁻¹	0.04	0.1	2.28	9
⁷ pH _{KCl}	pH	3.39	4.91	8.62	32
⁸ TAA	mole H ⁺ tonne ⁻¹	0	27.4	120.0	32
SO ₄	mg kg ⁻¹ SO ₄	80.7	833	10125	32
⁹ S _{CR}	%S	0	0.018	0.108	32
¹⁰ ANC	%CaCO ₃	0	0	0.806	32
¹¹ Net Acidity	mole H ⁺ tonne ⁻¹	-103	54.5	168	32

¹n: number of samples. ²pH_w: pH water. ³pH_{FOX}: pH after peroxide treatment. ⁴pH_{field}: pH measured in field with pH strips (detailed assessment). ⁵pH_{incubation}: pH measured on chip tray samples kept moist for 19 weeks. ⁶EC_{field}: electrical conductivity measured on top soil layer (rapid assessment). ⁷pH_{KCl}: pH in KCl. ⁸TAA: total actual acidity pH_{KCl}. ⁹S_{CR}: chromium reducible sulfur. ¹⁰ANC: acid neutralising capacity. ¹¹Net acidity does not include retained acidity.

Table 9-7: Summary of laboratory analysis of soil samples including pH and acid-base accounting for Burnt Creek (source: Thomas *et al.* 2009c).

Parameter	Units	Minimum	Median	Maximum	¹ n
² pH _w	pH	2.83	4.68	6.99	10
³ pH _{FOX}	pH	1.95	2.41	3.00	10
⁴ pH _{field}	pH	1.9	4.4	6.5	12
⁵ pH _{incubation}	pH	2.5	3.6	6.5	17
⁶ EC _{field}	dS m ⁻¹	0.18	0.36	5.50	9
⁷ pH _{KCl}	pH	2.84	4.6	6.22	10
⁸ TAA	mole H ⁺ tonne ⁻¹	2.61	42.4	878	10
SO ₄	mg kg ⁻¹ SO ₄	303	2805	47700	10
⁹ S _{CR}	%S	0	0.023	6.25	10
¹⁰ ANC	%CaCO ₃	0	0	0	10
¹¹ Net Acidity	mole H ⁺ tonne ⁻¹	7.01	66.3	3930	10

¹n: number of samples. ²pH_w: pH water. ³pH_{FOX}: pH after peroxide treatment. ⁴pH_{field}: pH measured in field with pH strips (detailed assessment). ⁵pH_{incubation}: pH measured on chip tray samples kept moist for 19 weeks. ⁶EC_{field}: electrical conductivity measured on top soil layer (rapid assessment). ⁷pH_{KCl}: pH in KCl. ⁸TAA: total actual acidity pH_{KCl}. ⁹S_{CR}: chromium reducible sulfur. ¹⁰ANC: acid neutralising capacity. ¹¹Net acidity does not include retained acidity.

Table 9-8: pH of field soils in water (pH_w) and after treatment with hydrogen peroxide (pH_{Fox}) for Carr's Creek (Site 954), Cappits Creek (Site 1014), Walpolla Creek (Site 1026) and Darling Anabranch (Sites 220 and 3470) (source: Shand *et al.* 2008).

Site/Sample No	Upper depth	Lower depth	pH water	pH peroxide
220/1.1	0	2	6.2	3.3
220/1.2	2	15	6.9	5.8
220/1.3	15	20	7.4	6.3
954/1.1	0	2	5.2	2.0
954/1.2	2	8	5.1	2.2
954/1.3	8	24	3.5	1.5
954/1.4	24	35	5.3	3.2
954/2.1	0	2	5.6	2.5
954/2.2	2	10	6.2	2.1
954/2.3	10	25	6.6	2.3
1014/1.1	0	5	7.0	4.3
1014/1.2	5	25	7.4	7.4
1014/2.1	0	3	6.9	4.5
1014/2.2	3	25	7.3	6.8
1014/2.3	25	35	7.2	6.8
1014/3.1	0	10	4.3	2.8
1014/3.2	50	60	4.4	3.0
1014/3.3	130	140	7.0	5.8
1026/1.1	0	3	5.8	2.4
1026/1.2	3	10	6.2	2.2
1026/1.3	10	30	6.8	4.4
1026/2.1	0	5	5.4	2.6
1026/2.2	5	20	7.7	5.7
3740/1.1	0	2	6.0	2.1
3740/1.2	2	5	7.0	2.0
3740/1.3	5	30	7.3	1.8

Notes:

1) pH_w values were obtained using field moist samples to which water was added to form a slurry which approximates, on a weight basis, 1:2 of soil to water, respectively. The mixture was shaken regularly and allowed to equilibrate at room temperature (about 25C) for at least one hour.

2) pH_{Fox} values were obtained using field moist soil and treating the sample with 30% hydrogen peroxide (pH adjusted to about 5, see Ahern *et al.* 2004) until reaction ceased and the mixture cooled to room temperature. The final mixture also approximated a 1:2 slurry.

Table 9-9: Acid-base accounting data for Carr's Creek (Site 954), Cappits Creek (Site 1014), Walpolla Creek (Site 1026) and Darling Anabranh (Site 3470) (source: Shand *et al.* 2008).

Sample Site	Depth (cm)	Moisture Content (%)	pHKCl (TAA)	Titrateable Actual Acidity (TAA) mole H ⁺ /tonne	Reduced Inorganic Sulfur (% Cr reducible S)	Reduced Inorganic Sulfur (Scr) mole H ⁺ /tonne	ANCBT (%CaCO ₃)	a-ANCE mole H ⁺ /tonne	NET ACIDITY Chromium Suite mole H ⁺ /tonne	LIME CALCULATION Chromium Suite kg CaCO ₃ /tonne DW
954 2.1	0-2	31.9	5.41	4.51	0.006	3.74	0.00	0	8	1
954 2.2	2-10	28.3	5.14	8.11	0.01	6.24	0.00	0	14	1
954 2.3	10-25	47.0	5.87	23.89	0.101	62.99	0.07	14	78	6
1014/1.1	0-5	31.8	7.04	0.00	<0.005	0.00	0.52	104	-69	-5
1014/1.2	5-25	24.1	5.95	3.85	<0.005	0.00	0.00	0	4	0
1014-2.1	0-3	35.9	5.02	11.56	<0.005	0.00	0.00	0	12	1
1014-2.2	3-25	28.0	5.63	4.34	<0.005	0.00	0.00	0	4	0
1014-2.3	25-35	31.4	5.86	3.13	<0.005	0.00	0.00	0	3	0
1014-3.1	0-10	3.4	4.41	23.13	<0.005	0.00	0.00	0	23	2
1014-3.2	50-60	8.7	4.64	18.79	<0.005	0.00	0.00	0	19	1
1014-3.3	130-140	20.6	5.43	7.71	0.005	3.12	0.00	0	11	1
1026/1.1	0-3	59.2	5.30	19.08	0.059	36.80	0.00	0	56	4
1026/1.2	3-10	53.1	4.91	21.46	0.051	31.81	0.00	0	53	4
1026/1.3	10-30	33.4	4.99	19.08	0.073	45.53	0.00	0	65	5
1026/2.1	0-5	26.9	4.97	8.59	<0.005	0.00	0.02	4	6	0
1026/2.2	5-20	22.0	5.06	9.54	0.015	9.36	0.04	8	14	1
3470-1.1	0-2	44.0	5.43	4.34	0.03	18.71	0.00	0	23	2
3470-1.2	2-5	37.6	5.09	12.05	0.03	18.71	0.00	0	31	2
3470-1.3	5-30	35.7	5.04	10.60	0.046	28.69	0.00	0	39	3

NOTES – Analyses by the Environmental Analysis Laboratory, Southern Cross University:
 1 - All analysis is Dry Weight (DW) - samples dried and ground immediately upon arrival
 2 - Samples analysed by SPOCAS method 23 (i.e. Suspension Peroxide Oxidation Combined Acidity & sulfate) and 'Chromium Reducible Sulfur' technique (Scr - Method 22B)
 3 - Methods from Ahern, CR, McElnea AE, Sullivan LA (2004). *Acid Sulfate Soils Laboratory Methods Guidelines*. QLD DNRME.
 4 - Bulk density was determined immediately on arrival to laboratory (in situ bulk density is preferred)
 5 - ABA Equation: Net Acidity = Potential Sulfidic Acidity (i.e. Scr or Sox) + Actual Acidity + Retained Acidity - measured ANC/FF
 6 - For Texture: coarse = sands to loamy sands; medium = sandy loams to light clays; fine = medium to heavy clays and silty clays
 7 - CRS, TAA and ANC are NATA certified but other SPOCAS segments are currently not NATA certification
 8 - Results at or below detection limits are replaced with '0' for calculation purposes
 9 - Projects that disturb >1000 tonnes of soil, the ≥0.03% S classification guideline would apply
 (Classification of potential acid sulfate material if: coarse Scr≥0.03%S or 19mole H⁺/t; medium Scr≥0.06%S or 37mole H⁺/t; fine Scr≥0.1%S or 62mole H⁺/t)

Table 9-10: Acid-base accounting data for Darling Anabranh (Site 220) (source: Shand *et al.* 2008).

Sample Site	Depth (cm)	Moisture Content (%)	pHKCl (TAA)	Titrateable Actual Acidity (TAA) mole H ⁺ /tonne	Reduced Inorganic Sulfur (% Cr reducible S)	Reduced Inorganic Sulfur (Scr) mole H ⁺ /tonne	ANCBT (%CaCO ₃)	a-ANCE mole H ⁺ /tonne	NET ACIDITY Chromium Suite mole H ⁺ /tonne	LIME CALCULATION Chromium Suite kg CaCO ₃ /tonne DW
				(to pH 6.5)	%Scr (note 2)				(based on %Scr)	(includes 1.5 safety factor)
Method			23A	23F	22B	a- 22B	19A2	a-19A2	note 5	note 5
220-1.1	0-2	45.7	5.19	5.78	0.015	9.36	0.00	0	15	1
220-1.2	2-15	34.2	5.49	6.26	0.009	5.61	0.00	0	12	1
220-1.3	15-20	33.8	5.70	0.00	0.002	1.25	0.00	0	1	0

NOTES – Analyses by the Environmental Analysis Laboratory, Southern Cross University:
 1 - All analysis is Dry Weight (DW) - samples dried and ground immediately upon arrival
 2 - Samples analysed by SPOCAS method 23 (i.e. Suspension Peroxide Oxidation Combined Acidity & sulfate) and 'Chromium Reducible Sulfur' technique (Scr - Method 22B)
 3 - Methods from Ahern, CR, McElnea AE, Sullivan LA (2004). *Acid Sulfate Soils Laboratory Methods Guidelines*. QLD DNRME.
 4 - Bulk density was determined immediately on arrival to laboratory (in situ bulk density is preferred)
 5 - ABA Equation: Net Acidity = Potential Sulfidic Acidity (i.e. Scr or Sox) + Actual Acidity + Retained Acidity - measured ANC/FF
 6 - For Texture: coarse = sands to loamy sands; medium = sandy loams to light clays; fine = medium to heavy clays and silty clays
 7 - CRS, TAA and ANC are NATA certified but other SPOCAS segments are currently not NATA certification
 8 - Results at or below detection limits are replaced with '0' for calculation purposes
 9 - Projects that disturb >1000 tonnes of soil, the ≥0.03% S classification guideline would apply
 (Classification of potential acid sulfate material if: coarse Scr≥0.03%S or 19mole H⁺/t; medium Scr≥0.06%S or 37mole H⁺/t; fine Scr≥0.1%S or 62mole H⁺/t)

Table 9-11: pH of soils in water (pH_w) and after treatment with hydrogen peroxide (pH_{Fox}) (Ahern *et al.* 2004) for sites sampled at Salt Creek (source: Fitzpatrick *et al.* 2008d).

Sample No.	Upper Depth (cm)	Lower Depth (cm)	pH water	pH hydrogen peroxide
SC1.1	0	10	6.97	2.04
SC1.2	10	20	6.84	2.2
SC1.3	20	30	6.36	4.48
SC2.1	10	30	6.54	1.93
SC3.2	0	5	8.13	4.77
SC5.1	0	5	4.8	2.5
SC5.2	5	20	5.5	1.9
SC5.3	20	40	6.5	2.0
SC5.4	40	70	7.2	2.8
SC6.2	1	10	5.0	1.8
SC6.3	10	50	5.1	2.6
SC6.4	50	70	7.9	1.9
SC7.1	0	5	6.4	2.5
SC7.2	5	20	5.9	2.4
SC7.3	20	40	6.0	2.5
SC8.1	0	2	6.0	2.6
SC8.2	2	30	5.7	3.9

Table 9-12: Selected sulfur-based acidity and acid neutralising capacity analyses and calculations for sites sampled at Salt Creek (source: Fitzpatrick *et al.* 2008d).

Sample No	Texture Class ^a	Est. Bulk Density t/m ³	pH _{KCl} ^b	S _{cr} ^c %	CaCO ₃ ^d %	Net Acidity ^e mole H ⁺ /tonne	Lime Calculation ^f kg CaCO ₃ /tonne DW
SC 1.1	Medium	0.64	5.65	0.028	0.00	25	2
SC 1.2	Medium	0.76	5.16	0.021	0.00	27	2
SC 1.3	Fine	1.01	5.37	0.003	0.00	12	1
SC 2.1	Coarse	1.35	5.94	0.047	0.00	33	2
SC 5.1	Coarse	1.01	5.49	0.016	0.00	17	1
SC 5.2	Coarse	1.17	6.01	0.025	0.00	18	1
SC 5.3	Coarse	1.33	5.94	0.016	0.00	13	1
SC 5.4	Medium	1.25	5.62	0.007	0.00	11	1
SC 6.2	Coarse	1.41	5.88	0.013	0.00	12	1
SC 6.3	Coarse	1.43	6.13	<0.005	0.00	2	0
SC 7.1	Coarse	1.07	6.11	0.006	0.00	7	1
SC 7.2	Coarse	1.02	5.74	0.01	0.00	10	1
SC 7.3	Medium	1.37	5.66	0.005	0.00	9	1
SC 8.1	Fine	0.76	5.72	0.014	0.00	15	1
SC 8.2	Fine	1.22	4.98	0.005	0.00	22	2

^aTexture Class: coarse = sands to loamy sands; medium = sandy loams to light clays; fine = medium to heavy clays and silty clay. ^bpH_{KCl}: pH measured in 1M KCl. Samples with pH values greater than 6.5 have no residual acidity.

^cReduced Inorganic sulfur (% chromium reducible S; S_{cr}). This measures the reduced sulfur in the sample that potentially can oxidise to sulfuric acid. Classification is as potential acid sulfate material if: coarse S_{cr} ≥ 0.03% or 19mole H⁺/t; medium S_{cr} ≥ 0.06%S or 37mole H⁺/t; fine S_{cr} ≥ 0.1%S or 62mole H⁺/t). Thought pH had to fall below 4 or 4.5 for it be an ASS ?

^d% ANC: This is termed acid neutralising capacity (ANC) and is presented as CaCO₃ equivalents.

^eThis is based on potential acidity derived from % S_{cr}.

^fLime needed to neutralise acidity, based on net acidity/alkalinity. Includes a 1.5 times safety factor. Negative values have sufficient excess ANC and should not need additional lime.

Table 9-13: Summary of laboratory sulfide data for Wakool River collected in 2009 (source: Bush unpublished data).

Site	Sample No.	S _{AV} (%)	S _{CR} (%)
Glenmore Hole	Pool	<0.005	0.02
	T1	<0.005	0.01
	T2	<0.005	0.01
	T3	<0.005	0.01
	T4	<0.005	0.02
Coonamite Bridge	Pool	<0.005	0.01
	T1	<0.005	0.04
	T2	<0.005	0.01
	T3	<0.005	0.01
	T4	<0.005	0.01
Bryans	Pool	<0.005	0.04
	T1	<0.005	0.03
	T2	<0.005	0.02
	T3	<0.005	0.01
	T4	<0.005	0.01
Merran Junction	Pool	<0.005	0.03

Table 9-14: Summary of laboratory sulfide data for the Niemur River collected in 2009 (source: Bush unpublished data).

Site	Sample No.	S _{AV} (%)	S _{CR} (%)
Site 1	1a	<0.005	0.01
	1b	<0.005	0.01
	2a	<0.005	0.01
	2b	<0.005	0.01
	3a	<0.005	0.01
	3b	<0.005	0.03
	4a	<0.005	0.03
	4b	<0.005	0.01
Site 2	1a	<0.005	0.02
	1b	<0.005	0.02
	2a	<0.005	0.03
	2b	<0.005	0.02
	3a	<0.005	0.02
	3b	0.007	0.02

Table 9-15: Summary of laboratory data including soil pH, soil electrical conductivity (EC) and sulfide levels in channels sampled in February/March 2004 in the Murray-Darling Basin (source: Sullivan unpublished data).

Site (Depth)	pH (1:5 water)	EC (1:5 water) (dS m ⁻¹)	S _{CR} (%)	S _{AV} (%)
Dishers (0-10 cm)	8.45	28.70	0.19	0.078
Dishers Creek A (10-30 cm)	8.43	5.51	0.08	<0.005
Dishers Creek B (10-30 cm)	8.31	6.82	0.45	0.032
Picaminy Creek, Kerang	8.73	2.86	0.49	0.327
Kerang irrigation channel 1	7.18	0.58	0.58	0.540
Kerang irrigation channel 2	8.16	1.73	0.70	0.324
Kerang irrigation channel 3	8.25	1.53	0.74	0.417
Kerang irrigation channel 4	7.80	4.26	0.46	0.351
Beni, Talbragar River	8.95	0.30	0.02	0.022
Ballimore, Talbragar River	8.12	0.39	0.02	0.008
Boomley, Talbragar River	8.85	0.28	0.01	<0.005
Cobbora, Talbragar River	7.52	0.54	<0.01	<0.005
Craboon, Talbragar River	8.21	0.30	<0.01	<0.005
Scenic Hill Grit, Griffith	8.34	0.24	0.57	0.243
Hanwood Grit, Hanwood	8.03	0.41	0.11	0.069
Little Rd Grit, Hanwood	7.71	0.67	0.13	0.134

Table 9-16: Summary of laboratory data for Talwood-Mungindi region and Whyenbah channels in Queensland (source: Qld DERM unpublished data).

Site	MDBA Wetland ID	Date Sampled	Depth (m)	¹ EC (dS/m)	² pH _w	³ pH _{KCl}	⁴ TAA (mole H ⁺ /tonne)	⁵ CRS (%S _{CR})	⁶ ANC (%CaCO ₃)	⁷ Net Acidity (mole H ⁺ /tonne)	⁸ AVS (%S _{AV})	Total Carbon (%C)	Sulfate (mg SO ₄ /kg)
Irrigation channel, Talwood-Mungindi region	80051	23-Sep-08	0.00-0.05	6.53	7.9	7.7	0	0.03	1.50	-181	<0.005	1.33	3810
Irrigation channel, Talwood-Mungindi region	80052	23-Sep-08	0.03-0.11	3.66	7.8	6.8	0	<0.02	0.80	-	<0.005	0.62	3210
Irrigation channel, Talwood-Mungindi region	80053	23-Sep-08	0.10-0.30	4.89	7.8	7.1	0	<0.02	0.90	-	<0.005	0.45	3900
Irrigation channel, Talwood-Mungindi region	-	30-Jul-07	0.00-0.02	36.30	7.7	7.6	0	<0.02	0.80	-	-	0.46	-
Irrigation channel, Talwood-Mungindi region	-	30-Jul-07	0.02-0.10	6.88	6.2	5.5	<10	<0.02	<0.5	-	-	0.35	-
Irrigation channel, Talwood-Mungindi region	-	30-Jul-07	0.02-0.10	14.00	7.5	7.4	0	0.03	0.90	-101	-	0.71	-
Irrigation channel, Talwood-Mungindi region	-	30-Jul-07	0.10-0.20	17.40	7.2	6.9	0	0.07	0.80	-63	-	0.69	-
Irrigation channel, Talwood-Mungindi region	-	14-Mar-07	0.00-0.10	7.56	7.7	7.6	0	0.13	1.00	-52	-	0.80	-
Irrigation channel, Talwood-Mungindi region	-	14-Mar-07	0.00-0.10	6.76	7.6	7.4	0	0.03	0.90	-101	-	0.64	-
Whyenbah channel	80127	30-Oct-08	0.00-0.05	0.45	8.2	8.2	0	0.02	2.00	-254	0.005	1.65	-
Whyenbah channel	80128	30-Oct-08	0.00-0.08	0.39	8.2	8.1	0	0.04	5.00	-641	0.114	1.41	-

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

Table 9-17: Summary of acid sulfate soils rapid assessment data for Talwood-Mungindi region and Whyenbah channels in Queensland (source: MDBA unpublished data).

Site	MDBA Wetland ID	Date Sampled	Soil pH*	Soil EC (dS/m)	Water pH (field)	Water EC (field) (dS/m)	Water EC (lab) (dS/m)	Water Sulfate (mg SO ₄ /kg)
Irrigation channel, Talwood-Mungindi region ¹	80051	23-Sep-08	4.0 - 7.4	1.46 - 3.42	7.95	8.10	7.68	498
Irrigation channel, Talwood-Mungindi region ¹	80052	23-Sep-08	4.8 - 7.3	0.74 - 6.72	8.67	18.50	18.49	1968
Irrigation channel, Talwood-Mungindi region ¹	80053	23-Sep-08	4.5 - 7.1	0.37 - 12.20	6.75	5.27	3.29	219
Whyenbah channel ²	80127	30-Oct-08	6.9 - 7.7	0.20 - 1.40	8.60	1.22	1.22	448
Whyenbah channel ³	80128	30-Oct-08	6.2 - 8.1	0.27 - 0.43	9.10	1.07	1.08	431

Triggers Exceeded: ¹EC soil: high; EC water high; pH soil: moderate; Sulfate water: high. ²EC soil: high; Sulfate water: high. ³EC soil: moderate; Sulfate water: high. * As determined by both in-field measurements and subsequent analysis of samples collected in chip-trays.

Table 9-18: Summary of laboratory data including pH and acid-base accounting for Butlers Creek (source: Baldwin 2008b).

Sample	Texture	pH (1:5 water)	S _{CR} (%)	TAA (mole H ⁺ tonne ⁻¹)	ANC (mole H ⁺ tonne ⁻¹)	Net Acidity based on S _{CR} (mole H ⁺ tonne ⁻¹)
1	Fine	5.04	0.017	16	24	10
2	Fine	4.91	0.012	21	0	28
3	Fine	4.84	0.014	18	5	23

Table 9-19: Summary of laboratory data including pH and acid-base accounting for Washpen Creek, NSW (source: Baldwin *et al.* 2008).

Sample	Texture	S _{CR} (%)	TAA (mole H ⁺ tonne ⁻¹)	Net Acidity based on S _{CR} (mole H ⁺ tonne ⁻¹)
1	Medium	0.036	15	38
2	Fine	0.012	27	34
3	Fine	0.018	46	57
4	Medium	<0.005	21	21
5	Fine	0.026	41	58
6	Medium	0.038	14	38

APPENDIX 2: ACID-BASE ACCOUNTING METHODOLOGY

Acid-base accounting 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 (Sullivan *et al.* 2001, 2002c). The standard acid-base accounting approach applicable to acid sulfate soil from Ahern *et al.* (2004) is:

$$\text{Net Acidity} = \text{Potential Sulfidic Acidity} + \text{Existing Acidity} - \text{Acid Neutralising Capacity/Fineness Factor}$$

An explanation of the components of this acid-base accounting approach is given below.

- **Potential Sulfidic Acidity (PSA):** The Potential Sulfidic Acidity is most easily and accurately determined by assessing the Chromium Reducible Sulfur. This method was developed specifically for analysing acid sulfate soil materials (Sullivan *et al.* 2000) to assess their Potential Sulfidic Acidity (PSA). This is also known as the 'acid generation potential' (AGP). The method is also described in Ahern *et al.* (2004), which includes the chromium reducible sulfur (S_{CR} : Method Code 22B) and its conversion to PSA.
- **Existing Acidity:** This is the sum of Actual Acidity and Retained Acidity (Ahern *et al.* 2004). Titratable Actual Acidity (TAA) is a measure of the actual acidity in acid sulfate soil materials that has already been oxidised. TAA measures the sum of both soluble and exchangeable acidity. The Retained Acidity is the acidity 'stored' in minerals such as jarosite, schwertmannite and other hydroxysulfate minerals. While these minerals are stable under acidic conditions, acidity can be released under altered environmental conditions. The methods for determining both TAA and Retained Acidity are given by Ahern *et al.* (2004).
- **Acid Neutralising Capacity (ANC):** Soils with pH > 6.5 may potentially have ANC in the form of (usually) carbonate minerals, primarily of calcium, magnesium and sodium carbonates. The carbonate minerals present are estimated by titration, and alkalinity present is expressed in calcium carbonate (CaCO_3) equivalents. Any acid sulfate soil material with a pH < 6.5 has a zero ANC (Ahern *et al.* 2004). The methods for determining ANC are given by Ahern *et al.* (2004).
- **Fineness Factor (FF):** This is defined by Ahern *et al.* (2004) as "a factor applied to the ANC 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 soils they may provide little effective ANC when exposure to acid may result in the formation of surface crusts (iron oxides or gypsum), preventing or slowing further neutralisation reactions. The use of the "Fineness Factor" also applies to those naturally occurring alkalinity sources in soil materials as measured by the ANC methods.

***APPENDIX 3: SUMMARY OF ACID SULFATE SOIL RAPID
ASSESSMENT SITES IN RIVER AND CREEK CHANNELS
WITHIN THE MURRAY-DARLING BASIN***

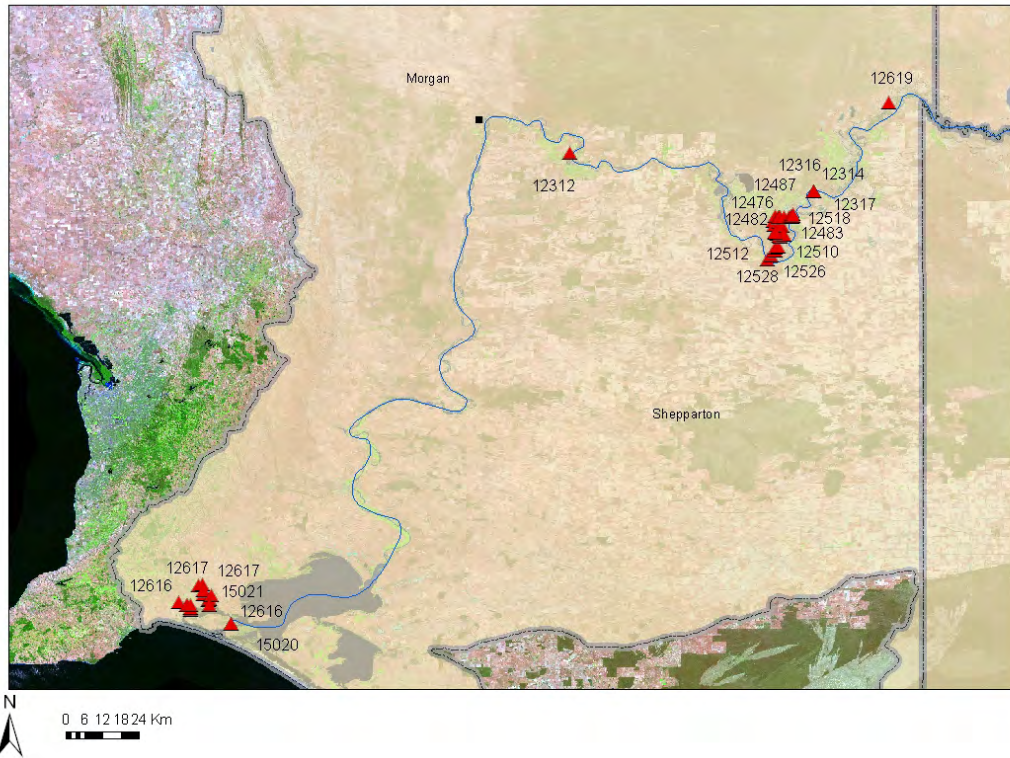


Figure 9-1: Map showing the acid sulfate soil rapid assessment sites in river and creek channels in South Australia (source: MDBA).

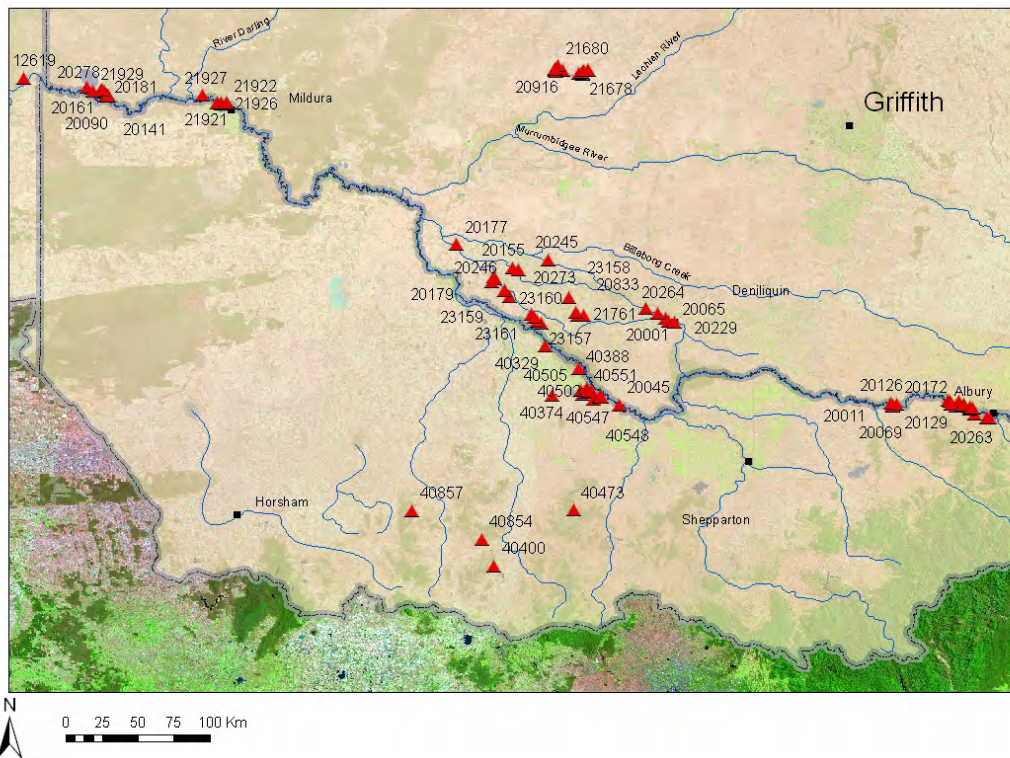


Figure 9-2: Map showing the acid sulfate soil rapid assessment sites in river and creek channels in Victoria (source: MDBA).

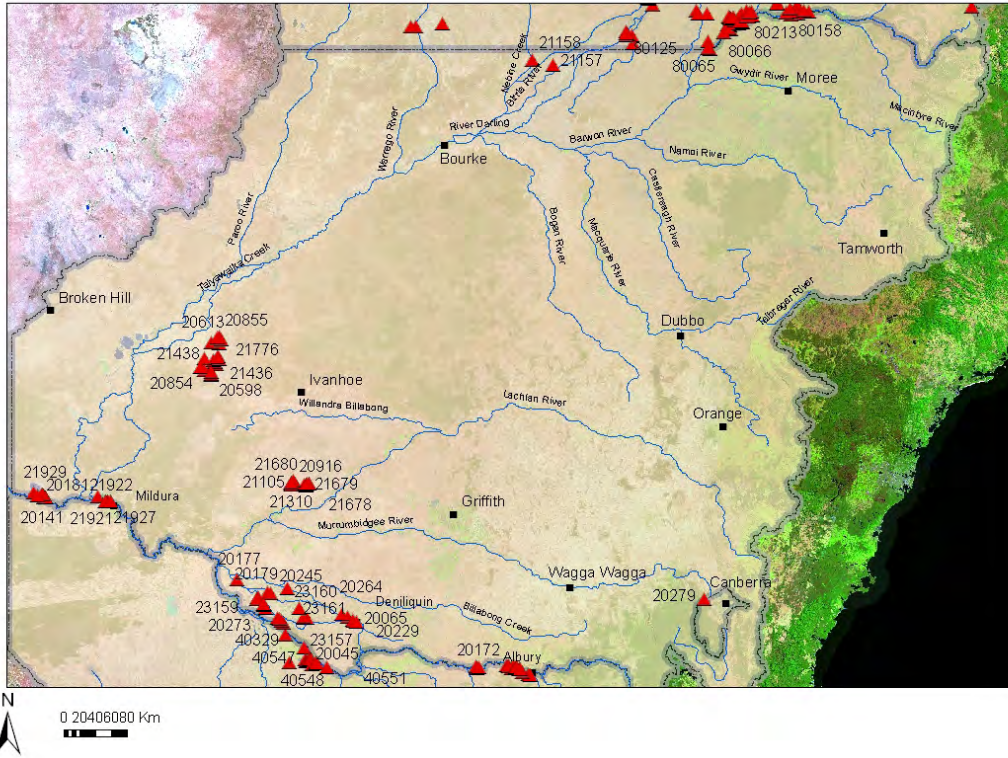


Figure 9-3: Map showing the acid sulfate soil rapid assessment sites in river and creek channels in New South Wales (source: MDBA).

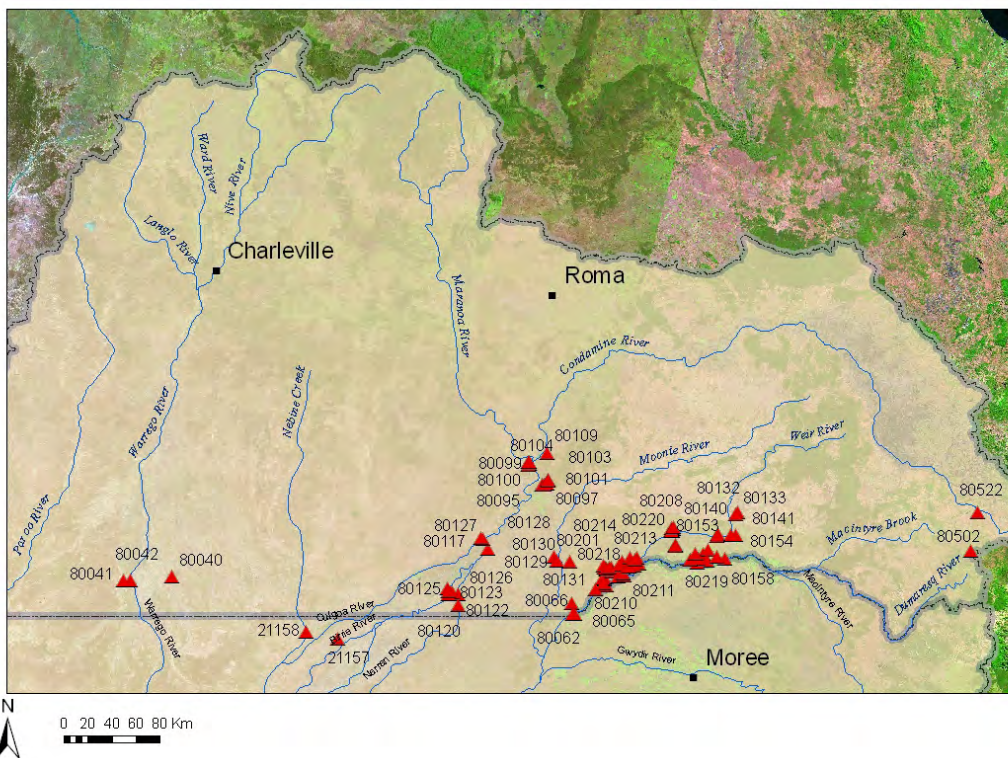


Figure 9-4: Map showing the acid sulfate soil rapid assessment sites in river and creek channels in Queensland (source: MDBA).