



MURRAY-DARLING BASIN AUTHORITY

Detailed Assessment of Acid Sulfate Soils in the Murray–Darling Basin

Protocols for sampling, field characterisation,
laboratory analysis and data presentation

Version 1.3 (30 April 2010)

Title

Detailed Assessment of Acid Sulfate Soils in the Murray–Darling Basin: Protocols for sampling, field characterisation, laboratory analysis and data presentation

Compiled and edited by Gerard Grealish.

Contributing Authors:

Mr Glenn Atkinson, New South Wales Department of Climate Change and Water

Dr Darren Baldwin, Murray–Darling Freshwater Research Centre

Prof Richard Bush, Southern Cross University

Dr Rob Fitzpatrick, CSIRO Land and Water

Dr Paul Shand, CSIRO Land and Water

Prof Leigh Sullivan, Southern Cross University

Mr Bernie Powell, Queensland Department of Environment and Resource Management

Citation: Murray–Darling Basin Authority (2010). Detailed Assessment of Acid Sulfate Soils in the Murray–Darling Basin: Protocols for sampling, field characterisation, laboratory analysis and data presentation. MDBA Publication No. 57/10, 58 pp

Published by Murray-Darling Basin Authority
Postal Address GPO Box 1801, Canberra ACT 2601
Office location Level 4, 51 Allara Street, Canberra City
Australian Capital Territory

Telephone (02) 6279 0100 international + 61 2 6279 0100
Facsimile (02) 6248 8053 international + 61 2 6248 8053
E-Mail info@mdba.gov.au
Internet <http://www.mdba.gov.au>

For further information contact the Murray-Darling Basin Authority office on
(02) 6279 0100

This report may be cited as: Detailed Assessment of Acid Sulfate Soils in the Murray–Darling Basin:
Protocols for sampling, field characterisation, laboratory analysis and data presentation

MDBA Publication No. 57/10
ISBN (online) 978-1-921557-67-5

© Copyright Murray-Darling Basin Authority (MDBA), on behalf of the Commonwealth of Australia 2009.

This work is copyright. With the exception of photographs, any logo or emblem, and any trademarks, the work may be stored, retrieved and reproduced in whole or in part, provided that it is not sold or used in any way for commercial benefit, and that the source and author of any material used is acknowledged.

Apart from any use permitted under the *Copyright Act 1968* or above, no part of this work may be reproduced by any process without prior written permission from the Commonwealth. Requests and inquiries concerning reproduction and rights should be addressed to the Commonwealth Copyright Administration, Attorney General's Department, National Circuit, Barton ACT 2600 or posted at <http://www.ag.gov.au/cca>.

The views, opinions and conclusions expressed by the authors in this publication are not necessarily those of the MDBA or the Commonwealth. To the extent permitted by law, the MDBA and the Commonwealth excludes all liability to any person for any consequences, including but not limited to all losses, damages, costs, expenses and any other compensation, arising directly or indirectly from using this report (in part or in whole) and any information or material contained within it.

Australian Government Departments and Agencies are required by the *Disability Discrimination Act 1992* (Cth) to ensure that information and services can be accessed by people with disabilities. If you encounter accessibility difficulties or the information you require is in a format that you cannot access, please contact us.

ACKNOWLEDGEMENTS

This protocol document was compiled and edited by Gerard Grealish and is the culmination of the efforts of the numerous scientists and managers involved in the Murray–Darling Basin Acid Sulfate Soils Risk Assessment Project, especially members of the MDBA Acid Sulfate Soils Risk Assessment Advisory Group. Their contributions in developing this document are greatly appreciated, as is the valued input of Dr David Jones (Supervising Scientist Division, Department of the Environment, Water, Heritage and the Arts) in reviewing the draft protocol document. We would also like to thank Dr Stuart Simpson (CSIRO Land and Water, Sydney) and Mr Col Ahern (Queensland Acid Sulfate Soils Investigation Team, Department of Environment and Resource Management) for valuable contributions.

EXECUTIVE SUMMARY

This report outlines the protocols for conducting detailed assessment of acid sulfate soils (ASS) in the Murray–Darling Basin (MDB) under the Acid Sulfate Soils Risk Assessment Project, and is prepared primarily for assessments that are to be conducted in wetland areas. The detailed acid sulfate soil assessment consists of field sampling, field characterisation, laboratory analysis, data interpretation and reporting, and is conducted as a two-phase process (Phase 1 and Phase 2).

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

Phase 1 activities include:

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

Phase 2 investigations will only be conducted if the acid sulfate soil materials identified during Phase 1 are determined to be a priority concern at a wetland-scale, and if they are, they will then undergo further investigations to determine their nature and severity and the specific risks associated with the acid sulfate soil materials.

Phase 2 activities include:

- laboratory analysis (of soil)
- risk assessment
- interpretation and reporting.

This two-phase approach was developed in light of not knowing in advance how many sites in wetland areas will contain acid sulfate soil materials. To address this issue, Phase 1 will be conducted to conclusively identify the presence or absence of the various types of acid sulfate soil materials in each wetland. Phase 2 investigations will only commence when the results of the Phase 1 investigations have been completed and the need for further and more specific detailed risk assessment is determined, in order to reliably identify the nature and severity of the environmental risks posed by acid sulfate soil materials.

TABLE OF CONTENTS

Acknowledgements	ii
Executive Summary	iii
Table of Contents	iv
List of Figures	vi
List of Tables	vi
1 Introduction.....	1
1.1 Aim.....	1
1.2 Data Objectives	2
1.3 Background	9
1.4 Definitions of Acid Sulfate Soil Material	10
1.5 Framework for Defining and Assessing Hazard and Risk.....	12
1.6 Reporting of Findings	15
2 Quality Assurance and Quality Control.....	17
2.1 Site Selection and Sample Collection	17
2.2 Laboratory Analysis.....	17
2.3 Data Interpretation and Reporting of Findings	18
3 Detailed Assessment – Phase 1.....	19
3.1 Site Selection.....	19
3.1.1 Guidelines for Site Selection.....	21
3.2 Site and Profile Description	22
3.2.1 Occupational Health and Safety.....	22
3.2.2 Guidelines for Site and Profile Description	23
3.3 Sample Collection and Storage	24
3.3.1 Guidelines for Soil Sample Collection.....	24
3.3.2 Guidelines for Water Sample Collection	26
3.3.3 Guidelines for Sample Handling and Storage.....	29
3.4 Laboratory Analysis.....	29
3.4.1 Soil	30
3.4.2 Water.....	31
3.5 Identification of Acid Sulfate Soil Materials	32
3.6 Determining Priorities for Phase 2 Laboratory Analysis & Assessment	32
3.7 Interpretation and Reporting	34
4 Detailed Assessment – Phase 2.....	36
4.1 Laboratory Analysis.....	36
4.2 Risk Assessment	37
4.3 Interpretation and Reporting	37
5 References	39
Appendix 1: Screening Criteria for Selecting Detailed Assessment Study Areas	43
Appendix 2: Guidelines for Photographs and File Name Convention.....	44

Appendix 3: Australian Acid Sulfate Soil Identification Key	46
Appendix 4: Guidelines for pH _{incubation} Method	50
Appendix 5: Guidelines for Sulfur Species Suite Method – Acid Volatile Sulfur and Elemental Sulfur	52
Appendix 6: Guidelines for Rapid Metal Release Method	53
Appendix 7: Guidelines for Contaminant and Metalloid Dynamics Method	55
Appendix 8: Guidelines for Monosulfidic Formation Potential Method	56
Appendix 9: Guidelines for Mineral Identification by X-Ray Diffraction.....	57
Appendix 10: Guidelines for Geochemical Analysis by X-Ray Fluorescence Spectrometry	58

LIST OF FIGURES

Figure 3–1. Example of a transect approach to placement of sites in the different zones and the type of soil information that is captured.....	20
Figure 3–2. Example of a chip-tray sample showing the inside lid marked up adjacent to the soil sample collected to show soil morphology	26
Figure 3–3. Cross section diagram of a hydro-toposequence showing the sample labelling convention for an example wetland (12006).....	28
Figure A4–1. The same chip tray showing incubation of soil after (i) sampled in the field, (ii) ageing (incubation) for the minimum 8 weeks and (iii) ageing (incubation) at 10 weeks.	51

LIST OF TABLES

Table 1–1. Phase 1 data requirements – list of parameters, units of measurement, methods, method references, and objectives for conducting the test.....	3
Table 1–2. Phase 2 data requirements – list of parameters, units of measurement, methods, method references, and objectives for conducting the test.....	8
Table 1–3. Standardised table used to determine the consequence of a hazard occurring.	13
Table 1–4. Likelihood ratings for the disturbance scenario.	14
Table 1–5. Risk assessment matrix (Standards Australia/Standards New Zealand, 2004).....	15
Table 3–1. Study area size and suggested number of sites.	22
Table 3–2. Phase 1 report structure and information requirements.....	34
Table 4–1. Phase 2 report structure and information requirements.....	37
Table A3–1. Summary Soil Identification Key for acid sulfate soils.	47
Table A3–2. Soil Identification Key for acid sulfate soil subtypes.	48

1 Introduction

This report outlines the protocols for conducting detailed assessment of acid sulfate soils (ASS) in the Murray–Darling Basin (MDB) under the Acid Sulfate Soils Risk Assessment Project, and is prepared primarily for assessments that are to be conducted in wetland areas. The detailed acid sulfate soil assessment consists of field sampling, field characterisation, laboratory analysis, data interpretation and reporting, that is conducted as a two-phase process (Phase 1 and Phase 2).

- Phase 1 investigations determine whether or not acid sulfate soil materials are present (or absent) for the study area, and provide characterisation of the properties and types of acid sulfate soil materials.
- Phase 2 investigations will only be conducted if the acid sulfate soil materials identified during Phase 1 are determined to be a priority concern at a wetland-scale, and if they are, they will then undergo further investigations to determine their nature and severity and the specific risks associated with the acid sulfate soil materials.

This two-phase approach was developed in light of not knowing in advance how many sites in wetlands will contain acid sulfate soil materials. To address this issue, Phase 1 will be conducted to conclusively identify the presence or absence of the various types of acid sulfate soil materials in each wetland. Phase 2 investigations will only commence when the results of the Phase 1 investigations have been completed and the need for further and more specific detailed risk assessment is determined, in order to reliably identify the nature and severity of the environmental risks posed by acid sulfate soil materials present and allow identification of broad acid sulfate soil management options.

Acid sulfate soils are those soils containing iron sulfide minerals (e.g. Pons 1973; Fanning 2002) that form naturally when sulfate in the water is converted to sulfide by bacteria. These soils may either contain sulfuric acid (sulfuric material), or have the potential to form sulfuric acid (sulfidic material), or cause de-oxygenation (monosulfidic material), or release contaminants when the sulfide minerals are exposed to air (oxygen).

This protocol document has been prepared with key input from the Scientific Reference Panel of the Murray–Darling Basin Acid Sulfate Soil Risk Assessment Project and other acid sulfate soil specialists and is tailored to meet the requirements of this project. We acknowledge that information in other guidelines and manuals (Ahern *et al.* 1998; Ahern *et al.* 2004; Simpson *et al.* 2008; DEC 2009) were used in the development of this protocol document and further information can be obtained about acid sulfate soils from these other materials.

1.1 Aim

The aim of this protocol document is to provide the rationale and define a set of data requirements that will be used to conduct acid sulfate soil assessments in the Murray–Darling Basin under the Acid Sulfate Soil Risk Assessment Project.

The Murray–Darling Basin covers a large area and detailed acid sulfate soil assessments may be conducted by many different groups for the Acid Sulfate Soil Risk Assessment Project. The purpose of this protocol document is to provide a set of standard operating procedures and guidelines to be used in the assessment to ensure standardisation of methodology, comparability and scientific integrity of the data results. The data results will be interpreted to

determine the nature and severity of acid sulfate soils and to provide information that will be used to guide planning and management decisions.

1.2 Data Objectives

To achieve these aims, a range of tests were identified by the Scientific Reference Panel of the Murray–Darling Basin Acid Sulfate Soil Risk Assessment Project for consideration in these protocols. Through a process of evaluation and conducting of assessment work for selected study areas, a final set of tests were recommended for inclusion and these are prescribed in this protocol document. The detailed assessment involves comprehensive analysis using a set of established and tested field and laboratory methods to determine the presence (or absence) and extent of acid sulfate soils and associated problems, including potential for acidification, metal mobilisation and de-oxygenation.

The mandatory data requirements, their objectives for obtaining the results, and methods are summarised for Phase 1 assessment in Table 1–1 and for Phase 2 assessment in Table 1–2. Details of the tests are discussed in the following sections. Phase 1 involves field work, collection of soil and water samples, laboratory analysis, interpretation and reporting of data. Phase 2 involves laboratory analysis (only on samples that meet the selection criteria) and the interpretation and reporting of results.

Table 1–1. Phase 1 data requirements – list of parameters, units of measurement, methods, method references, and objectives for conducting the test.

Parameter	Units	Method or Method Code	Method Reference	Objective
Site and Profile Description				
Site identification number	Unique numeric code	Unique code	Sequence provided by client	Uniquely identifies site
Site location – co-ordinates	Zone, Easting and Northing co-ordinates	Global positioning system (GPS), locate to the Geocentric Datum of Australia 1994	Not applicable	Accurately place the sample site within the study area
Site location – map	Map	Locate site on an appropriately scaled map, preferably a photo image	Not applicable	Shows relationship of the sample site to other sites and features of the study area
Site description (includes general location, position in the wetland, surface condition, and vegetation)		Text description for the measured parameters, including a sketch map and cross-section	Refer for guidance to National Committee on Soil and Terrain 2009	Places the sample site within the landscape and surrounding environment, to enable extrapolation of the profile information and to estimate the proportion that it represents in the study area
Depth to free water	cm	Tape measure	National Committee on Soil and Terrain 2009	Current status of water level relative to the soil surface
Type of soil observation	Categories	Text description	National Committee on Soil and Terrain 2009	Provides detail on how the sample was obtained
Upper and lower depth of sampled/described layer	cm	Tape measure	National Committee on Soil and Terrain 2009	Estimating the layer thickness and position in the profile of the soil sample

Parameter	Units	Method or Method Code	Method Reference	Objective
Soil morphology description (colour, field texture, consistence, structure, moisture status, and other unique features if they occur, such as mottling [redoximorphic features], odour, organic material, shell fragments, minerals such as jarosite, crystals, coarse fragments)	Categories	As per the categories listed for the soil morphology description parameters	National Committee on Soil and Terrain 2009; Schoeneberger <i>et al.</i> (2002) – for redoximorphic features	For characterisation and classification of the soil. To facilitate understanding of soil variability and transfer of quantitative data between profiles and layers that appear similar through this qualitative description
Field soil pH	pH unit	Field pH meter	Not applicable	Measures the current status of the soil acidity or alkalinity
Photographs – soil profile, soil (or water) surface, surrounding landscape (at a minimum on the 4 opposite points of the compass), and any other features of interest, including chip-tray samples	Digital	See Appendix 2. Sufficient quality for reports. Soil profile photographs must have a scale marker on left side	Photographs saved as JPG format. See Appendix 2 for photographs required and file naming convention	Provides a visual record of the sampled site and location
Water sample (if present) – Temperature pH Specific Electrical Conductance (SEC) Redox potential (Eh) Dissolved Oxygen (DO) Turbidity	Temperature (°C) pH (pH unit) SEC ($\mu\text{S cm}^{-1}$) Eh (mV) relative to standard hydrogen electrode DO (% and mg l^{-1}) Turbidity (NTU)	Calibrated electrode		Measures the current status of the water quality
Water sample (if present) – Alkalinity	Alkalinity and/or acidity (mg l^{-1} as HCO_3)	2320 B Field alkalinity kit using appropriate strength acid	APHA 21st ed.	Measures the current status of the water quality

Parameter	Units	Method or Method Code	Method Reference	Objective
Sample Collection				
Soil sample 500 g in one plastic bag		Stored refrigerated at 4 °C		For storage and used if Phase 2 laboratory analysis is required
Soil sample in 2 separate 70 ml plastic jars with screw top lid		Stored refrigerated at 4 °C		Jar 1: Phase 1 laboratory analysis for acid base accounting parameters Jar 2: Phase 1 pH _w , pH _{peroxide} , water extractable sulfate (surface soil sample only) and specific electrical conductance, and then dried for storage and used if Phase 2 XRD and XRF analysis is required
Soil sample in 2 separate chip-trays				Tray 1: Long term archive storage Tray 2: Ageing test to determine pH _{incubation}
Water sample (if present) in two 125 mL polyethylene bottles, sample filtered through 0.45 µm membrane filters		Stored refrigerated at 4 °C		Bottle 1: For laboratory analysis of Phase 1 major and trace cation analyses Bottle 2: For laboratory analysis of major and minor anion analyses
Monosulfide sample (if present) 70 ml plastic jar with screw top lid		Frozen immediately for storage		For Phase 1 analysis. Please note that the residual sample must be retained frozen for Phase 2 analysis of elemental sulfur
Monosulfide sample (if present) 500 ml plastic jar with screw top lid		Frozen immediately for longer term storage		For Phase 2 analysis
Laboratory Analysis				
Soil pH _w	pH unit	pH meter; 1:1 soil:water	Rayment and Higginson 1992	Measures the current sampled status of the soil acidity or alkalinity

Parameter	Units	Method or Method Code	Method Reference	Objective
Soil pH _{peroxide}	pH unit	pH meter; Method 4E1 (modified)	Rayment and Higginson 1992	Measures the potential end oxidized status of the soil pH
Soil pH _{incubation}	pH unit	See Appendix 4	Sullivan 2009 Fitzpatrick <i>et al.</i> 2008	Represents a scenario for soil sample on exposure to air (oxygen) for a specified period of time
Moisture content (of soil sample)	Weight%	80 °C drying	Ahern <i>et al.</i> 2004	Provides moisture status of the soil sample
Chromium reducible sulfur	sulfide %S	Method 22B	Ahern <i>et al.</i> 2004	Identifies presence of sulfides. For acid base accounting
pH _{KCl}	pH unit	Method 23A	Ahern <i>et al.</i> 2004	pH value. Provides trigger value (pH _{KCL} >6.5) for deciding to test for acid neutralising capacity
Titrateable actual acidity	mole H ⁺ /tonne	Method 23F	Ahern <i>et al.</i> 2004	Identifies soil acidity. For acid base accounting
Retained acidity	mole H ⁺ /tonne	Method 20J	Ahern <i>et al.</i> 2004	Identifies stored soil acidity. For acid base accounting
Acid neutralising capacity (where pH _{KCl} >6.5)	%CaCO ₃	Method 19A2	Ahern <i>et al.</i> 2004	Identifies neutralising capacity of soil. For acid base accounting
Water extractable sulfate (1:5 soil:water extract)	mg SO ₄ /kg	Method 14F Conducted on surface soil sample only	Rayment and Higginson 1992	Indicates potential for monosulfide formation
Water (if present)				
Major cations (Na, K, Ca, Mg) and Si	mg/L	APHA3120 ICPOES	APHA 21 st ed., USEPA SW846 – 6010	Determines the concentration of major cations in water or acid extracts
Dissolved bromide and chloride (Cl, Br)	mg/L Cl-, Br-	APHA 4500 Cl- APHA 4500 Br-	APHA 21st ed.	Determines the concentration of bromide and chloride in water or acid extracts

Parameter	Units	Method or Method Code	Method Reference	Objective
Dissolved nitrate (NO ₃ ⁻)	mg/L NO ₃ ⁻	APHA 4500 NO ₃ ⁻	APHA 21st ed.	Determines the concentration of nitrate in water
Dissolved ammonia (NH ₄)	mg/L NH ₄	APHA 4500 NH ₃ -H	APHA 21st ed.	Determines the concentration of ammonia in water
Dissolved phosphate (PO ₄)	mg/L PO ₄ ³⁻	APHA 4500 P-E	APHA 21st ed.	Determines the concentration of reactive phosphate in water
Dissolved sulfate (SO ₄)	mg/L SO ₄ ²⁻	APHA 3120 ICPOES	APHA 21st ed.	Determines the concentration of sulfate in water
Trace metals or metalloids including Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Zn			APHA 21st ed.	Determines the concentration of metals and metalloids in water
Dissolved organic carbon			APHA 21st ed.	Determines the concentration of organic carbon in water
Acid volatile sulfur	sulfide %S _{AV}	See Appendix 5 Conducted on surface samples where monosulfides are identified	Hsieh <i>et al.</i> (2002)	Quantify S in form of FeS minerals

Table 1–2. Phase 2 data requirements – list of parameters, units of measurement, methods, method references, and objectives for conducting the test. These tests are only conducted on samples that meet the Phase 2 priority selection criteria at wetlands that have been agreed for Phase 2 analysis.

Parameter	Units	Method or Method Code	Method Reference	Objective
Elemental sulphur		See Appendix 5 Conducted on surface samples where monosulfides are identified	Burton <i>et al.</i> 2006	Quantify S
Rapid metal release	mg/L µg/L	See Appendix 6 Conducted on selected upper two surface samples	Simpson <i>et al.</i> (2008)	Assists with determining impacts on water quality by simulation of rewetting for a 24 hour time frame. Identifies metal release concentrations that may occur in a short time frame
Contaminant and metalloid dynamics	mg/L µg/L	See Appendix 7 Anaerobic – reductive batch incubation Conducted on selected surface samples	Simpson <i>et al.</i> (2008)	Assists with determining impacts on water quality by simulating longer time frames that create anaerobic conditions. Identifies metal release concentrations that may occur over a 6 to 10 week time frame
Monosulfidic formation potential		See Appendix 8 Conducted on surface samples of dry sites that meet the water extractable sulfate criteria for monosulfides		Determine relative propensity for monosulfides to form following inundation
Mineral identification by X-ray diffraction		See Appendix 9 Conducted on limited number of selected crystals and minerals (if present). Most likely to be associated with sulfuric layers to confirm acid mineral presences		Characterisation and confirmation of minerals present
Trace elements by X-ray fluorescence spectroscopy		See Appendix 10 Conducted on a limited number of selected samples at a ratio of about 2 samples for every 15 collected. Usually one surface and one deeper sample for a profile along a transect		Characterisation and confirmation of geochemistry

1.3 Background

Acid sulfate soils are those soils containing iron sulfide minerals (e.g. Pons 1973; Fanning 2002). These soils may either contain sulfuric acid (sulfuric material), or have the potential to form sulfuric acid (sulfidic material), or cause de-oxygenation (monosulfidic material often known as monosulfidic black ooze), or release contaminants when the sulfide minerals are exposed to air (oxygen). Acid sulfate soils form naturally when sulfate in the water is converted to sulfide by bacteria. These sulfides react with metals, especially iron (Fe), to form sulfidic materials (typically pyrite: FeS_2) in subaqueous acid sulfate soil or sediments in rivers and wetlands.

Changes to the hydrology in regulated sections of the Murray–Darling Basin (MDB) system, and the chemistry of rivers and wetlands have caused significant accumulation of sulfidic material in subaqueous and margin soils. If left undisturbed and covered with water, sulfidic material poses little or no threat to human health or the environment. However, when sulfidic material is exposed to the air, the sulfides react with air (oxygen) to form sulfuric materials with $\text{pH} < 4$. When these sulfuric materials subsequently come into contact with water, significant amounts of sulfuric acid can be released into the water.

Other risks associated with acid sulfate soils include: (i) mobilisation of metals, metalloids and non-metals, (ii) decrease in oxygen in the water column when monosulfidic materials are mobilised into the water column, (iii) production of noxious gases, (iv) direct exposure to acidic minerals, (v) mobilisation of acidic minerals by wind, and (vi) damage to infrastructure. In severe cases, these risks can potentially lead to damage to the environment, and have impacts on water supplies, and human and livestock health.

Record low inflows and river levels in recent years have led to the drying of the Murray River system and many wetlands in the Murray–Darling Basin. The anaerobic sulfidic materials that were once covered by water are now exposed to air, resulting in the exposure of sulfidic material and soil acidification in many areas. With continued lowering of water levels, the hypersulfidic material can become progressively oxidised to greater depths of the soil profile.

Despite decades of scientific investigation of the ecological (e.g. Living Murray Icon Site Environmental Management Plan: MDBC, 2006a,b,c), hydrological (salinity), water quality and geological features of wetlands in the Murray–Darling Basin, we have only recently begun to appreciate the wide spectrum of acid sulfate soil subtypes and processes that are operating in these contemporary environmental settings – especially from continued lowering of water levels (e.g. Lamontagne *et al.* 2004; Fitzpatrick *et al.* 2008a,b,d,e,f; 2009a,b; Shand *et al.* 2008a,b; Simpson *et al.* 2008; 2010). Hence, the Murray–Darling Basin Ministerial Council at its meeting in March 2008 directed the then Murray–Darling Basin Commission (MDBC) to undertake an assessment of acid sulfate soil risk at key wetlands in the Murray–Darling Basin. The Murray–Darling Basin Commission (now the Murray–Darling Basin Authority), in partnership with its Partner Governments and scientists, designed the Murray–Darling Basin Acid Sulfate Soil Risk Assessment Project, which aims to assess the spatial extent of, and risks posed by, acid sulfate soils in the Murray–Darling Basin. The project also aims to identify and assess broad management options.

The project established a list of more than 19,000 wetlands that were then assessed against a number of criteria aimed at identifying those that had potential for acid sulfate soil occurrence. This process identified a large number of wetlands in the Murray–Darling Basin requiring further assessment.

A prioritisation process then determined the level of assessment required at each wetland. A desktop investigation showed that some wetlands did not require further consideration as these had a low probability of containing acid sulfate soil material. However, those considered likely to contain acid sulfate soil material required rapid assessment using the Murray–Darling Basin Authority’s ‘Acid Sulfate Soils Field Guide’ (MDBA 2009), which comprises field measurements of water quality and wetland sediments. The data collected through the rapid assessments were screened using agreed criteria (Appendix 1) to identify wetlands which have an increased likelihood of developing acid sulfate soil materials that require detailed assessment. The aim of this protocol document is to provide a standardised method for these detailed assessments.

1.4 Definitions of Acid Sulfate Soil Material

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

The criteria to define the soil materials are as follows:

Acid Sulfate Soil Materials

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

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

3. **Hypersulfidic material** – Hypersulfidic material is a sulfidic material that 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.*

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

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

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

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

Non-Acid Sulfate Soil materials

In addition the Scientific Reference Panel of the Murray–Darling Basin Acid Sulfate Soil Risk Assessment Project agreed to identify the other acidic soil materials arising from the detailed assessment of wetland soils in the Murray–Darling Basin, even though these materials may not be the result of acid sulfate soil processes (e.g. the acidity developed during ageing may be the result of Fe^{2+} hydrolysis, which may or may not be associated with acid sulfate soil processes). Also the acidity present in field soils may be due to the accumulation of acidic organic matter and/or the leaching of bases. Of course, these acidic soil materials may also pose a risk to the environment and would be identified during the present course of the Phase 1 detailed assessment. The definition of these *other acidic soil materials* for the detailed assessment of acid sulfate soils in the Murray–Darling Basin is as follows:

- 1. Other acidic soil materials** – either:
 - c. non-sulfidic soil materials that acidify by at least a 0.5 pH_w unit to a pH_w of < 5.5 during moist aerobic incubation
 - d. soil materials with a $\text{pH}_w \geq 4$ but < 5.5 in the field.
- 2. Other soil materials** – soils that do not have acid sulfate soil characteristics.

1.5 Framework for Defining and Assessing Hazard and Risk

The following framework is provided to ensure the consistent and objective assessment and reporting of risk of acid sulfate soil materials to priority wetlands under the MDB Acid Sulfate Soils Risk Assessment Project ('the Project'). While this framework is based on accepted standards in risk assessment, it has been developed to suit the unique needs and design of the Project and thus some deviation from standard practices can be expected.

The framework defines hazards and risk in the context of the Project, and describes the reporting requirements of both Phase 1 and Phase 2 of the detailed assessment.

Defining and Assessing Acid Sulfate Soil Materials

1. Acid sulfate soil materials have been defined by Sullivan *et al.* (2008) to include:
 - a. Hypersulfidic materials
 - b. Hyposulfidic materials
 - c. Sulfuric materials
 - d. Monosulfidic materials.
2. Phase 1 of the detailed assessment will characterise and report on the presence or absence of acid sulfate soil materials at each identified wetland, and where present the nature and extent of the materials observed.

Defining and Assessing Hazards

3. Acid sulfate soil materials when disturbed can lead to the following hazards:
 - a. Acidification
 - b. Contaminant mobilisation
 - c. Deoxygenation.
4. It is acknowledged there are other hazards associated with acid sulfate soil materials such as production of odours, noxious gases and dust. These hazards may be acknowledged in reports emanating from the detailed assessment of acid sulfate soil materials but associated risks will not be assessed due to their limited relevance to the Project's emphasis on risks to environmental values and water quality.
5. The field and laboratory analyses carried out in Phase 1 will determine whether the acid sulfate soil materials present a potential hazard to the wetland which requires further investigation through Phase 2 analyses to elucidate risk.
6. Reports emanating from Phase 1 will therefore:

- a. Report on the presence, nature and extent of observed acid sulfate soil materials;
- b. Advise on potential hazards posed by those acid sulfate soil materials where possible;
- c. Make recommendations on the requirement for further analyses through Phase 2, including the number of samples to be analysed.

Defining and Assessing Risk

- 7. Phase 2 will assess the risk of acid sulfate soil materials to the wetland/s.
- 8. Risk is a measure of both the consequences of a hazard occurring, and the likelihood of its occurrence.
- 9. Consequence is the impact of the acid sulfate soil materials being expressed and primarily takes into account environmental and water quality impacts, both to the wetland and to adjacent waters. Level of consequence will be determined in consultation with wetland managers for each identified hazard at a wetland using a standardised table (Table 1–3).

Table 1–3. Standardised table used to determine the consequence of a hazard occurring.

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

- 10. Likelihood is the probability of disturbance of the acid sulfate soil material and requires understanding of both the nature and severity of the acid sulfate soil materials (e.g. extent, net acid generating potential, etc.) as well as contributing factors influencing the risk (e.g. disturbance of acid sulfate soil materials, wetland management regime).

- 11. Level of likelihood will be determined separately for each hazard type. This is due to the variability of contributing factors for each hazard.
- 12. Likelihood will be determined by assessing the probability of disturbance of the acid sulfate soil materials (Table 1–4). Examples of disturbance include:
 - re-wetting of acid sulfate soil materials after they have oxidised
 - acid sulfate soil materials that are currently inundated and that may be oxidised
 - acid sulfate soil materials that are currently inundated and that may be dispersed by flushing (e.g. scouring flows).

Table 1–4. Likelihood ratings for the disturbance scenario.

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.

- 13. Risks are ranked using a standardised risk assessment matrix (Table 1–5) as the product of the likelihood of disturbance of the acid sulfate soil materials and the consequences to wetland values and/or adjacent waters. This must also take into account the scientific assessment of the nature and extent of the acid sulfate soil materials present at the site as confirmed through the field and laboratory analyses through Phases 1 and 2.
- 14. Acid sulfate soil scientists conducting detailed assessments cannot alone determine the level of consequence or likelihood at a given wetland – input of relevant wetland managers will be critical. As such, assessment of risk through Phase 2 must be made in consultation with wetland managers. This is to ensure that acid sulfate soil scientists have an understanding of the wetland values and context of wetland management for the site.

Table 1–5. Risk assessment matrix (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.

Reporting on Risk

15. Reports of Phase 2 assessments will establish the level of risk associated with each identified hazard at a wetland using the framework outlined here and in consultation with relevant wetland managers.
16. In order to assist wetland managers in decision-making, the level of risk outlined in final reports should be accompanied by an explanation of the major contributing factors to the risk level (e.g. water management regimes, water chemistry, wetland values etc.).

1.6 Reporting of Findings

Reporting of findings will be a two stage process consistent with the Phase 1 and 2 investigations. Note that only one Final Report will be prepared for the entire acid sulfate soil investigation (both Phase 1 and 2) that is conducted for the study area. This is required so that all relevant information, even though conducted in two phases, is consolidated into one study area report.

The Phase 1 investigation report will undergo internal and client review and be prepared as an Interim Final Report for the study area.

Subject to the recommendation for Phase 2 investigations and the authorisation by the client to conduct this work, the Phase 2 report will be appended to the Phase 1 report as Part 2. After internal and client review the entire report will be prepared as the Final Report for the study area. Should a study area not require Phase 2 investigations, and the client confirms this, then

the Interim Final Report will be upgraded to be the Final Report for the study area and a note included that Phase 2 investigations were not conducted.

The report requirements are outlined for Phase 1 in Section 3.7 and for Phase 2 in Section 4.3.

2 Quality Assurance and Quality Control

Strict adherence to Quality Assurance and Quality Control (QA/QC) procedures shall occur at all stages of the work to ensure scientific integrity of the data results.

Quality Assurance and Quality Control procedures should be documented for:

- site selection and sample collection
- laboratory analysis
- data interpretation and reporting of findings.

2.1 Site Selection and Sample Collection

Proper site selection and sample collection from the correct soil layers is critical. Collected samples that are not representative will waste valuable resources on subsequent laboratory analysis and data interpretation, and produce invalid information for acid sulfate soil assessment of the study area.

All site locations and the layers within a soil profile or water body to be sampled shall be identified and selected by a senior soil surveyor or a person equivalently skilled, using best practice principles.

In the report section for Quality Assurance and Quality Control, a statement will be included that identifies the senior soil surveyor, when they were at the study area, what they did to select the site locations and the layers to be sampled, and any issues of concern.

At the discretion of the client, an independent observer may be used to review the field procedures being carried out, provide feedback to the surveyors on their approach and report directly back to the client, including a letter report on the review findings.

2.2 Laboratory Analysis

Laboratory analyses will be conducted at recognised laboratories that are National Association of Testing Authorities (NATA) accredited for the particular parameters and methods required. At the client's discretion, and for analyses that are not NATA accredited, tests can also be conducted at recognised laboratories that maintain appropriate standards that satisfy the client. For all tests and analyses, the Quality Assurance and Quality Control procedures will be equivalent to those endorsed by NATA.

All data prior to being released will undergo checks and be signed off by the laboratory Quality Assurance/Quality Control manager. The laboratory report should be a NATA endorsed report or equivalent standard.

In the report section for Quality Assurance and Quality Control a statement will be included that provides a summary of quality control results and any issues arising and details where the QA/QC data is held should a review be necessary.

At the discretion of the client, the laboratory may be requested to provide all QA/QC data. This would include the raw data and calculations made to obtain the delivered results.

Prior to the laboratory data being used for interpretations it should be reviewed by the organisation against field data and observations to identify any inconsistencies. If inconsistencies are identified appropriate action is to be taken that could require re-sampling, re-analysis, the use of data with caution or no further action.

2.3 Data Interpretation and Reporting of Findings

Internal review of the Interim Final Report or Final Report is to be conducted according to the organisation's publication and contractual requirements prior to submitting to the client.

At the discretion of the client, the Interim Final Report or Final Report may be submitted to a third party for external review. The authors of the report will then address all comments and edits requested by the client and their reviewers prior to submitting the Interim Final Report or Final Report.

3 Detailed Assessment – Phase 1

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

Phase 1 activities include:

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

3.1 Site Selection

Site selection is critical to ensure that the samples obtained are representative of the study area for acid sulfate soil assessment. There are two possible rationales for site selection:

1. To characterise the study area as a whole – sites selected to be representative of the soil variation throughout the entire study area.
2. To characterise acid sulfate soil occurrence – sites selected to target where acid sulfate soils are expected to occur within the study area.

To date there are no definitive linkages between observable landscape features (e.g. geology, landform, remote sensed imagery, distance from water, surface condition, vegetation) that can be used to target where acid sulfate soil materials may occur. However, experienced soil surveyors should have some understanding to assist with predicting likely areas by visually observing landscape variability and associated soil variability, and if available, information from the rapid assessment sample event data or landholder knowledge.

The general rationale to site selection is a clear focus on characterising the study area as a whole, and not just focused on potential hazard areas that would introduce a bias to the wetland assessment. Sites should be placed to understand the variation in the study area and to draw linkages with observable features that would allow the point source information from the site to be extrapolated spatially across the study area. This would then allow the distribution to be understood, the hazard extent to be mapped, and the soil proportions to be used as part of the risk assessment.

A transect approach is to be used to place sites logically within different zones of the wetland. As shown in Figure 3–1, sites are to be placed along the transect at different landscape positions. This provides the opportunity to identify the range of soil materials that occur. The transect approach allows a conceptual hydro-toposequence cross-section to be developed that

relates the soil information with landscape position and features. It can then be extrapolated spatially across the study area to generate a map of areas or proportions of the wetland that may contain different soil material types.

The study aims to characterise acid sulfate soil materials, however the general transect approach to site selection may occasionally miss a potential hazard area. Therefore it is appropriate to locate an ad hoc site in the area of interest if it is determined that the acid sulfate soil materials will impact significantly on the wetland, for example a probable acid sulfate soil location that may be small in area, but is of concern because it is low lying and would be one of the first areas to be inundated with water.

Careful planning and expert judgement is required to meet objectives with the limited number of profiles to be sampled and analysed.

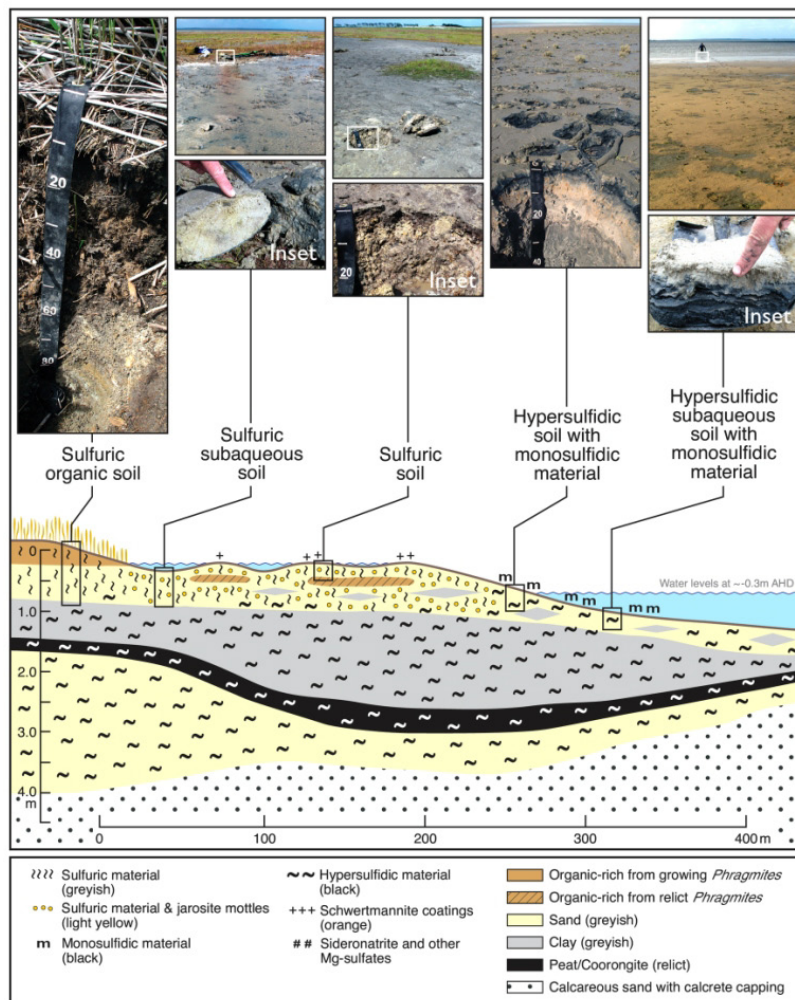


Figure 3-1. Example of a transect approach to placement of sites in the different zones and the type of soil information that is captured that then allows a conceptual hydro-toposequence to be developed, providing information to then extrapolate the results spatially (figure provided by RW Fitzpatrick, CSIRO).

3.1.1 Guidelines for Site Selection

The following points should be considered as guidelines for site selection:

- The number of sites placed in a study area will depend on the size of the study area, as indicated in Table 3–1.
- A transect approach is to be used to locate sites within a wetland. An example of a transect and placement of sites is presented in Figure 3–1.
- Prior to the transects being placed, the wetland as a whole should be observed to determine the likely landscape or geomorphic zones that occur. Currently the wetlands are in a drying phase and therefore the water level decreases and contracts to the lower parts of the wetland. This happens over a period of time and the retreating water level leaves behind a drying soil environment across a range of geomorphic landscapes within the wetland. In a hypothetical wetland this forms a concentric pattern like 'onion rings' around the centre or lowest part. There is a somewhat gradational change in soils, from the dried soils on the periphery to transitional moist to wet soils, and then those that are covered with water at the centre. This pattern identifies a sequence related to the hydrology and topography.
- The study areas are generally lower than the surrounding landscape, either as a wetland, river, stream, lake, estuary, or receding shoreline. The transects and sample sites should be topographically related in short traverses that extend from the step-up high edge of the shore/bank (where generally reeds are growing and marks the old high water-level shoreline) to the lowest point (in dry wetlands) or to the deepest water depth (where water is present) at which it is practical to sample.
- Other wetland features may identify zones that should be taken into consideration when selecting different landscapes within the wetland that require sampling. These include:
 - soil surface condition (for example, cracks, in-filled cracks, no cracks, sandy, firm, sealed)
 - vegetation pattern (no-vegetation, reeds, weeds, trees)
 - location and number of water entry and exit points and the distribution of the inlet/outlet channel features throughout the wetland
 - soil surface topography
 - presence of surface gels, algae or organic matter on the soil surface underwater
 - water depth (as an extension of the toposequence).
- Once potential zones of interest have been identified, one or more transects may be located depending on the study area size and variability.
- Sites for sampling are then placed along the transect and located within each of the zones that the transect crosses. In this way the site sample data can be associated with the topographic position in the wetland and other associated wetland features that determined the zone. This will assist with providing an understanding of where acid sulfate soils occur in the landscape and extrapolating from the site to similar areas.

- The site locations and the number of sites placed along the transect traverses will be determined by the senior soil surveyor or person equivalently skilled. If necessary other ad hoc sites can be placed in the study area to capture particular sites of interest.
- Soil surveyor (or equivalent) experience should be used to guide the selection of site locations and should take into account the following:
 - Safe access and working area, and ease of access to a sampling site location (farm tracks, gates, proximity to public roads and permission from landholders).
 - Visually observed variability (vegetation habitat changes, soil surface condition changes, water on the surface, topography changes) and observed variability on remotely sensed image maps and other mapped information.
 - Information about the area supplied by the landholder and relevant State/Territory staff.
 - Data from the earlier Rapid Assessment sample event, if conducted.
- All sites are to be accurately geo-referenced and notes made as to the rationale behind the transect position and site locations, including a cross-section sketch showing the transect and features.

Table 3–1. Study area size and suggested number of sites.

Study area size (ha)	Number of sampled sites
<5	2
5 – 20	4
20 –100	8
100 – 500	12
>500	20

3.2 Site and Profile Description

Site and soil descriptions are made to accurately locate the sample site within the study area, place the site within the landscape and surrounding environment, to characterise the soil for classification and to facilitate the understanding of soil variability between sites and soil layers. To do this a list of parameters are provided in Table 1–1; this is the required dataset of field information that is to be collected at each site.

3.2.1 Occupational Health and Safety

Your employer has obligations to you under relevant Occupational Health and Safety legislation. If you are self-employed, you also have duties under this legislation. While this protocol

document is provided to assist you and your employer to assess the risks and implement controls whilst conducting the on-site acid sulfate soil testing, you must follow your employer's policies and procedures as they apply to the tasks that you are involved in throughout the testing and collection of wetland soil and water.

If acid sulfate soils are present they can pose a number of risks and control measures should be implemented. In particular, if sulfidic sediments are oxidised they produce acid. Skin contact with the water or sediment should be prevented through the use of gloves, safety glasses or goggles, waders or gumboots, and appropriate clothing at all times.

Other occupational health and safety issues to consider are with regard to working around and digging soil inspection pits and hydrogen sulfide gas poisoning. Any risks to the public and landowners should be identified and action taken to minimise the risk, for example all pits once finished with should be filled in and returned as near as possible to original ground surface level.

3.2.2 Guidelines for Site and Profile Description

The following points should be considered as guidelines for site and profile description:

- This survey is targeting the identification of acid sulfate soils, therefore appropriate (as determined by the organisation conducting the work) occupational health and safety should be observed, including the use of personal protective equipment.
- Parameters to be measured, method of measurement and the categories to use are listed in Table 1–1. They are based on the 'Australian soil and land survey field handbook, 3rd edition' (National Committee on Soil and Terrain 2009).
- Photograph requirements at each site and the file name convention that is to be used is provided in Appendix 2.
- At dry site locations (no surface water) soil pits are to be dug to approximately 0.6 m deep for obtaining good photographs and soil samples, and then with a gouge auger (or similar tool) obtain soil samples below the base of the pit down to 1 m or to auger refusal.
- Where soils are below water (i.e. subaqueous soils), soil samples are to be obtained by wading and using a shovel to grab the upper 20 cm, and then a gouge auger (or similar tool) to approximately 90 cm depth or to auger refusal.
- Where deep water occurs (either beyond wading depth or unsafe to walk on) a grab sample of the subaqueous soil surface (about 10–20 cm of soil) should be collected if possible, by using a boat to get to the site location.
- Irrespective of the sampling method to extract soil material, soils are to be routinely sampled in defined depth intervals of 0–5 cm, 5–10 cm, 10–20 cm, 20–40 cm, and 40–90 cm. However, where there exists within these sample depth ranges an obvious and visually distinct or textually distinct layer change, or an identifiable redox boundary, then the layer should not be mixed across the change but be sampled separately.

- Descriptive layer depth range and sampling depth range for each layer are to be the same so that the description matches the soil sample collected.
- Where water occurs, either as a surface water body, in surface cracks or as pore water collecting in the bottom of a pit, if there is sufficient water depth a measurement of the water quality using a calibrated electrode probe is to be made.

3.3 Sample Collection and Storage

Soil and water samples are required for laboratory analysis that will provide quantitative data on the sample characteristics. The samples are being collected for a range of analyses related to testing of acid sulfate soil materials, and therefore a number of samples from each layer are required. A list of parameters describing the types and number of samples to be collected from each layer is provided in Table 1–1.

3.3.1 Guidelines for Soil Sample Collection

The following points should be considered as guidelines for soil sample collection:

- This survey is targeting the identification of acid sulfate soils, therefore appropriate (as determined by the organisation conducting the work) occupational health and safety should be observed, including the use of personal protective equipment.
- All samples shall be collected in such a way to avoid cross-contamination of the sample – requiring careful extraction of the sample, clean sampling tools and clean sample containers.
- Soil sample collection at each site is by layer identified covering the entire depth increment that corresponds with the described layer.
- Soil samples should be labelled according to the convention outlined in Figure 3–3 to ensure clear identification of the wetland, site and layer from which the sample was collected.
- Soil samples are placed in plastic chip-trays (Figure 3–2; Fitzpatrick *et al.* 2010), and in a plastic bag that is then sub-sampled into plastic jars. Multiple soil samples are required to be taken from each layer and are to include:
 - One bulk soil sample (typically about 500 g), is placed in a pre-labelled, thick, sealable plastic bag and mixed up. To be kept and used if Phase 2 laboratory analysis is required.
 - Two sub-samples from the bag are placed in two 70 ml screw-top plastic jars, with care taken to exclude air by filling the jars to the maximum level to limit sulfur oxidation during transit and storage.
 - One jar for acid base accounting parameters.
 - The second jar for pH_w, pH_{peroxide}, water extractable sulfate (surface soil sample only) and specific electrical conductance measurements. The

remainder for drying at 80 °C to be kept and used if Phase 2 XRD (powder X-ray diffraction) and XRF (X-ray fluorescence spectrometry) analysis are required.

- Two sub-samples from the layers are placed in two separate chip-trays.
 - One is used to display morphologically representative aggregates for each of the sampled layers (compartments filled to $\frac{3}{4}$ full with preferably undisturbed clods/samples) for later visual reference (e.g. during report writing and then placed in the CSIRO Land and Water soil archive).
 - The second chip-tray is used for the acid sulfate soil incubation test ($\text{pH}_{\text{incubation}}$) in the laboratory (compartments filled to $\frac{1}{3}$ full with disturbed crushed samples and moistened with distilled or deionised water).
 - Each compartment is to be adjacently labelled (on the inside of the lid) with the layer sample ID, and on the outside of the chip-tray labelled with survey locations and collection date (Figure 3–2).
- If monosulfidic material is present:
 - fill one 70 ml screw-top plastic jar and freeze immediately for Phase 1 AVS analysis
 - collect an additional minimum volume of 500 ml into airtight jars to be kept frozen for Phase 2 analyses.
- Occasionally, samples of salt efflorescences and coatings are observed in the field and they should be carefully collected into the chip-tray for mineralogical analysis.
- Visible shell and fragments greater than 2 mm should be removed from the sample.
- Air should be excluded as far as possible from all the jarred and bagged samples to minimise oxidation before laboratory analysis. Double bagging of samples is recommended.
- Jarred and bagged samples should be kept cold, at least below ambient temperature, in insulated containers (i.e. stored in a cool-box or Esky) when in the field and transferred to a fridge at 4 °C as soon as possible after sampling.
- All sample bags and containers are to be clearly marked with wetland, site and layer identification, sample depth and the date of sample collection. They should be marked with permanent marker (or stick-on labels) and preferably in two places. The markings should be waterproof and capable of withstanding oven drying at 85 °C.



Figure 3–2. Example of a chip-tray sample showing the inside lid marked up adjacent to the soil sample collected to show soil morphology (photograph provided by G Grealish).

3.3.2 Guidelines for Water Sample Collection

The following points should be considered as guidelines for water sample collection:

- This survey is targeting the identification of acid sulfate soils; therefore appropriate (as determined by the organisation conducting the work) occupational health and safety should be observed, including the use of personal protective equipment.
- In wetlands that contain surface water, water samples are to be collected from two sites along a hydro-toposequence (see Figure 3–3) when there is:
 - surface water or water pooling in surface cracks
 - soil pore water that enters the base of the excavated soil pit. Clearly there has to be sufficient depth and volume of water to allow sufficient liquid to be extracted in a practical way.
- Surface water samples should be collected from 30 cm below the water surface or as deep as possible if there is an insufficient depth of water. In saline wetlands, an assessment of stratification should be made prior to sampling by first measuring the specific electrical conductance down the water profile, and if significant, the stratified water layers should be sampled separately.
- Surface cracks and pit water should be sampled once sediment has settled.

- In wetlands that do not contain any surface water, a water sample is to be collected from one site along a toposequence when soil pore water enters the base of the excavated soil pit. This will preferably be the site sampled at the lowest elevation in the wetland. Clearly there has to be sufficient depth and volume of water to allow sufficient liquid to be extracted in a practical way.
- All water samples should be filtered through a 0.45 µm membrane. Coarser pre-filters can be used for surface waters which contain high contents of particulate matter to minimise filtering time. A pressure device, such as a garden sprayer or spray bottle is ideal for sampling, as most wetlands contain high contents of particulate matter, making them difficult to filter with a hand syringe.
- All sampling devices should be clean and rinsed prior to sample collection. The first few millilitres of sample should be discarded following filtration and all sample bottles rinsed three times prior to collection.
- Water samples should be kept cold, at least below ambient temperature, in insulated containers (i.e. stored in a cool-box or Esky) when in the field and transferred to a fridge at 4 °C as soon as possible after sampling.
- The samples for cation analysis should be acidified, in order to minimise adsorption onto container walls, using a high grade acid as specified by the laboratory.
- All sample bags and containers must be clearly marked with wetland, site and layer identification, sample depth and date of sample collection. They must be marked with permanent marker (or stick-on labels) and preferably in two places. The markings should be waterproof and capable of withstanding oven drying at 85 °C.
- Water samples should be labelled according to the convention outlined in Figure 3–3 to ensure clear identification of the wetland, site and layer from which the sample was collected.

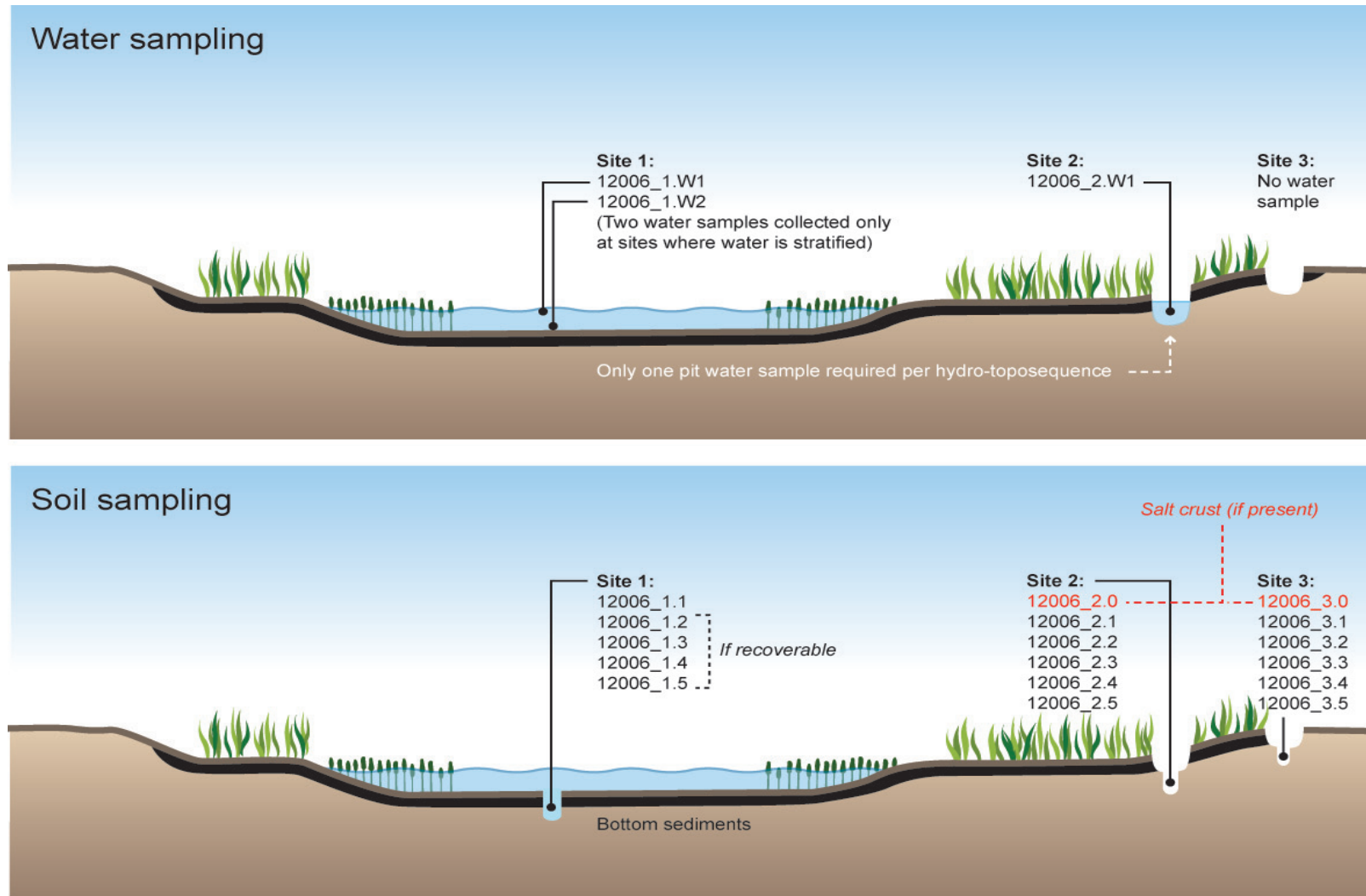


Figure 3–3. Cross section diagram of a hydro-toposequence showing the sample labelling convention for an example wetland (12006).

3.3.3 Guidelines for Sample Handling and Storage

The following points should be considered as guidelines for sample handling and storage:

- This survey is targeting the identification of acid sulfate soils; therefore appropriate (as determined by the organisation conducting the work) occupational health and safety should be observed, including the use of personal protective equipment.
- All sample bags and containers must be clearly marked with the wetland ID, site and layer identification, sample depth and date of sample collection. They must be marked with permanent marker (or stick-on labels) and preferably in two places. The markings should be waterproof and capable of withstanding oven drying at 85 °C.
- Soil and water samples to be placed into clean containers or plastic bags.
- Exclude as much air as possible from jarred and bagged samples.
- Samples transported to the laboratory should be kept cold in insulated containers (i.e. stored in a cool-box or Esky).
- All sample bags and containers will be clean on the outside to minimise contamination during transportation and on receipt at the laboratory.
- Transfer of samples to the laboratory should be conducted as quickly as practical, and before a maximum of 10 days has elapsed.
- A sample delivery list (chain of custody form) should be emailed to the laboratory and also provided in hardcopy with the sample shipment.
- The maximum time available between sample collection and laboratory analysis is considered the holding time. If the analysis is not conducted within this holding time frame there is a risk that the results will not be a true reflection of the material when collected. Note that the length of holding time varies depending on the parameter to be analysed and the method of storage prior to analysis. The allowable holding time will be specified by the laboratory and these timeframes should be followed.

3.4 Laboratory Analysis

Laboratory analysis for Phase 1 provides quantitative data that can be used to assess the type of acid sulfate soil material present (sulfuric, hypersulfidic, hyposulfidic, monosulfidic or other as defined in Section 1.4) and the acid base accounting measurements to determine net acidity level. Phase 1 laboratory analysis also provides water quality for the current conditions if water was present at the time of sampling.

3.4.1 Soil

Three sets of laboratory analysis have been identified to be conducted on soil samples collected for Phase 1 laboratory testing (Table 1–1). These measures and the objective for conducting them are listed here:

- Soil pH_w , $\text{pH}_{\text{incubation}}$, and $\text{pH}_{\text{peroxide}}$ analysis. These measures are used to determine the current status of the soil acidity (pH_w), the type of acid sulfate soil material present as defined in Section 1.4 that are based on the soil pH_w value (to identify sulfuric materials) or change in pH on ageing ($\text{pH}_{\text{incubation}}$ to identify hypersulfidic or hyposulfidic materials). $\text{pH}_{\text{peroxide}}$ identifies a potential end pH after oxidation and if it declines to 2.5 or less then it can be assumed that soil acidity problems will emerge when the soil or sediment is exposed to air.
- Chromium reducible sulfur, titratable actual acidity, retained acidity, pH_{KCl} and acid neutralising capacity analyses are used in acid base accounting. These measures are 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.
- Water extractable sulfate analysis is used to identify surface soil samples that may potentially form monosulfidic soil materials when inundated.

Soil pH_w , $\text{pH}_{\text{incubation}}$ and $\text{pH}_{\text{peroxide}}$

Measuring soil pH_w is a standard test

Measuring $\text{pH}_{\text{incubation}}$ is the standard method used in the Australian Soil Classification (Isbell 1996). The method has been described in more detail by Sullivan *et al.* (2009) and Fitzpatrick *et al.* (2008b,c,d,e,f; 2009a; 2010) where the method has been used and refined. A description of the method is provided in Appendix 4.

Measuring $\text{pH}_{\text{peroxide}}$ is a standard test.

Acid Base Accounting

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

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

Where:

- Potential Sulfidic Acidity (PSA) also known as the ‘acid generation potential’ (AGP) is most easily and accurately determined by assessing the Chromium reducible sulfur (S_{CR} or CRS) and then converting this to PSA (AGP) as described in Ahern *et al.* 2004.
- Titratable Actual Acidity (TAA) is a measure of the actual acidity in acid sulfate soil materials that have already oxidised. It measures the sum of both soluble and exchangeable acidity.
- Retained Acidity (RA) is the acidity ‘stored’ in minerals such as jarosite, schwertmannite and other hydroxy sulfate minerals. Although these minerals may be stable under acidic conditions, they can release acidity to the environment when these conditions change.

- Acid Neutralising Capacity (ANC) is measured in soils with pH_{KCl} values > 6.5 . These soils may potentially have ANC in the form of (usually) carbonate minerals, principally of calcium, magnesium and sodium. The carbonate minerals present are estimated by titration and alkalinity present expressed in CaCO_3 equivalents. By accepted definition (Ahern *et al.* 2004), any acid sulfate soil material with a $\text{pH}_{\text{KCl}} < 6.5$ has a zero ANC.
- Fineness Factor (FF) is defined by Ahern *et al.* (2004) as 'A factor applied to the acid neutralising capacity result in the acid base account to allow for the poor reactivity of coarser carbonate or other acid neutralising material. The minimum factor is 1.5 for finely divided pure agricultural lime, but may be as high as 3.0 for coarser shell material'. Fine grinding of soil materials may lead to an over-estimate of ANC when carbonates are present in the form of hard nodules or shells. In the soil environment, they may provide little effective ANC as exposure to acid may result in the formation of surface crusts (iron oxides or gypsum), preventing or slowing further neutralisation reactions. For reasons including those above, the use of the Fineness Factor also applies to those naturally occurring alkalinity sources in soil materials as measured by the ANC methods.

Water Extractable Sulfate

Water extractable sulfate measurement is conducted on a 1:5 soil:water extract for the surface soil sample only.

Sulfate contents >10 mg/L in water of inland water bodies such as wetlands and rivers give a strong indication that the soil materials underlying those water bodies are able to sulfidise (Sullivan and Bush 2002; Hall *et al.* 2006; Baldwin *et al.* 2007; Sullivan *et al.* 2008a) forming monosulfidic material or sulfidic sediments.

In dry soils where there are no overlying water bodies it is considered that water extractable sulfate contents of greater than or equal to 100 mg/L in 1:5 soil:water extracts of surface soil layers (i.e. soil layers in the top 20 cm of the soil profile) would be able to create similar sulfate contents in overlying water bodies as a result of inundation.

3.4.2 Water

A number of laboratory analyses have been identified to be conducted on water samples for Phase 1 laboratory testing, and they are listed in Table 1–1.

The water data is not required to identify an acid sulfate soil material nor is it used to determine if a sample should be recommended for Phase 2 analysis. However, this list of tests was identified by the Scientific Reference Panel of the Murray–Darling Basin Acid Sulfate Soil Risk Assessment Project as providing useful information on the current impact of the soils on the water quality.

Surface water and pore water samples should be collected for laboratory chemical analysis where possible, for the following reasons:

- In wetlands where drying has not occurred, surface waters provide a guide to the baseline water quality of the wetland. Note, however, that the baseline water quality of any water body is variable, varying spatially and with time, and should be described by a range of concentrations (Shand and Edmunds, 2008). Taking this into account, the data can then help to provide criteria to monitor changes induced by drying and oxidation of sulfidic materials.

- Groundwater samples collected from soil pits adjacent to wetlands provide a guide to solute inputs and interactions with the surface waters of the wetlands. The data can then be used to monitor changes induced by drying and oxidation of sulfidic materials.
- Groundwater samples from dried wetlands may provide a guide to the potential impacts of oxidation of acid sulfate soil materials, as well as an indicator of potential alkalinity buffering by the groundwater.
- Sulfate concentrations of surface water and groundwater are required to assess the potential risks of monosulfide or sulfide reformation potential.

3.5 Identification of Acid Sulfate Soil Materials

Classifying soil materials and soil profiles provides a means to communicate and integrate data that describes the key features of the soil.

Field and laboratory data results are to be used to allocate soil samples to an acid sulfate soil material class according to the criteria specified in Section 1.4.

Each sampled soil profile may have one or more classified acid sulfate soil materials that occur at different depths down the profile. To provide an overall description for the sampled soil profile, an assessment of these classified soil layers is made by using the Australian Acid Sulfate Soil Identification Key that is presented in Appendix 3.

3.6 Determining Priorities for Phase 2 Laboratory Analysis and Assessment

Phase 2 detailed laboratory analyses will be conducted on a subset of samples collected from the Phase 1 investigations. Selection of samples will generally depend on identifying those wetlands where the Phase 1 results are of concern so that an improved understanding of their characteristics can be determined to assist with making planning and management decisions. To assist with making the selection, a set of criteria have been established to rank the soil materials.

The Scientific Reference Panel of the Murray–Darling Basin Acid Sulfate Soil Risk Assessment Project agreed to recommend that soil materials be assigned based on the set of criteria for the following priorities for Phase 2 detailed assessment:

High Priority

- 1) All sulfuric materials.
- 2) All hypersulfidic materials, as recognised by either
 - a. incubation of sulfidic materials or
 - b. a positive net acidity result (with a Fineness Factor of 1.5 being used).
- 3) All hyposulfidic materials with S_{CR} contents $\geq 0.10\%S$.

- 4) All surface soil materials (i.e. within 0–20 cm) with water extractable sulfate (1:5 soil:water) contents $>100 \text{ mgSO}_4/\text{L}$.
- 5) All monosulfidic materials.

Moderate Priority

- 1) All hyposulfidic materials with S_{CR} contents $< 0.10\% \text{ S}$.

No further assessment

- 1) Other acidic soil materials.
- 2) All other soil materials.

Priority samples exceeding thresholds for Phase 2 analysis will likely occur throughout the depth of the soil profile. Samples that are recommended to undergo Phase 2 laboratory analysis will firstly be those that occur on the surface layer, as this is the soil most likely to have initial contact with water. Recommendations for other samples (not necessarily all samples) within the soil profile for Phase 2 analysis should also be made and justified to assist the client in authorisation for Phase 2 analysis to be conducted. Examples of justification could include deep cracks exposing the deeper soil layers to oxidisation and then water, representative of a large proportion of the study area, or provide continuity to understand behaviour of a key soil profile.

Following Phase 1 analyses, a table listing all samples analysed for the study area, their priority for Phase 2 analysis based on the above criteria, selection and justification for Phase 2 analysis will be provided to the client.

3.7 Interpretation and Reporting

Phase 1 of the detailed assessment will not report on the risks associated with acid sulfate soil materials, and will only determine the presence, extent, nature (chemistry) and frequency of observed hazards (e.g. '*Hypersulfidic materials were observed in 32 of 38 (84%) sites*').

The report requirements for Phase 1 should include the following report sections and information where relevant as listed in Table 3–2.

Table 3–2. Phase 1 report structure and information requirements.

Report section	Information to be included
Executive Summary	<ul style="list-style-type: none"> • Project background and purpose of study • Objectives of the study • Summary of field and laboratory results, including presence/absence and type of acid sulfate soils, their extent and assessment of hazard • Summary of conclusions and recommendations
Introduction	<ul style="list-style-type: none"> • Project background and purpose of study • Objectives of the study • Background information and summary of previous work • Wetland overview including general description of study area: location, topography, shape, hydrology, soil, vegetation, infrastructure, surroundings • Definitions of acid sulfate soil materials
Field and Laboratory Methods	<ul style="list-style-type: none"> • Field sampling of soils and water (referencing this protocol document and describing any variations) • Rationale for site location selection and density of sites • Rationale for number of samples selected and distribution • Description of the equipment and the method used to obtain samples • Laboratory soil analysis methods (referencing this protocol document and describing any variations) • Laboratory water analysis methods (referencing this protocol document and describing any variations)
Quality Assurance and Quality Control (QA/QC)	<ul style="list-style-type: none"> • Field QA/QC report • Laboratory QA/QC report • Evaluation of all QA/QC information
Results and Discussion	<ul style="list-style-type: none"> • Study area location and setting description • Map showing sample site locations (preferably image map with grid) • Summary and assessment of soil field and laboratory results including: <ul style="list-style-type: none"> ○ Soil pH ○ CRS

Report section	Information to be included
	<ul style="list-style-type: none"> ○ ANC ○ Net Acidity ○ Water extractable sulfate ● Soil field and laboratory data presented in tables and as summary graphs for pH (pH_w, $pH_{incubation}$, $pH_{peroxide}$) and Net Acidity ● Summary and assessment of water field and laboratory results ● Soil identification according to Soil Identification Key (Appendix 3) ● Interpretation and discussion on distribution, extent and proportion of acid sulfate soil materials in the study area (including cross-sections like that presented in Figure 3–1, and maps where appropriate)
Hazard Assessment	<ul style="list-style-type: none"> ● Basis for hazard assessment ● Criteria used in the hazard assessment (from Section 3.6) ● Assessment of soil and water data ● Discussion of assessment and impact ● Discussion of assumptions
Selection of Phase 2 Samples	<ul style="list-style-type: none"> ● Basis for selection ● Recommendations and justification for selection/non-selection of samples for Phase 2 analysis (tabled)
Conclusions and Recommendations	<ul style="list-style-type: none"> ● Summary of key findings and outcomes ● Assumptions used and uncertainties ● Recommendations for Phase 2 analysis ● Recommendations for monitoring and further work
References	<ul style="list-style-type: none"> ● List of all references included throughout the report
Appendices	<ul style="list-style-type: none"> ● Site and sample descriptions ● Field and laboratory soil analytical data ● Field and laboratory water analytical data ● Classification of soil materials according to the Soil Identification Key (Appendix 3)
Database	<ul style="list-style-type: none"> ● Electronic database, in Microsoft Excel[®] format, of all field and laboratory data including quality control and quality assurance measurements using the supplied standard data collection template
Photographic library	<ul style="list-style-type: none"> ● Digital, in JPEG format, of all field site and soil photographs, labelled according to the guidelines in Appendix 2.

4 Detailed Assessment – Phase 2

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

Phase 2 activities include:

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

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

4.1 Laboratory Analysis

The list of potential Phase 2 analyses is presented in Table 1–2. These tests are only conducted on samples that meet the Phase 2 priority criteria as defined in Section 3.6.

Samples that meet the criteria are then screened further as follows:

- Elemental sulfur and acid volatile sulfur tests will be conducted on the two uppermost samples that meet the criteria.
- Rapid metal release and contaminant and metalloid dynamics tests will be conducted on the two uppermost samples that meet the criteria (note that the inclusion of these tests is under review and may change).
- Monosulfidic formation potential tests will be conducted on the uppermost sample that meets the criteria and where the water extractable sulfate exceeds 100 mg/L at sites that were dry at the time of sampling (note that the inclusion of this test is under review and may change).
- X-ray diffraction analysis tests will be conducted on a very limited number of samples to determine the nature of the mineral or crystals identified in the sample. Usually these samples are associated with sulfuric layers to determine the presence and type of acid mineral presence.
- X-ray fluorescence analysis tests will be conducted at a ratio of about 2 samples for every 15 collected. Samples selected will be from the same profile and include the surface and one other sample from deeper in the profile.

A number of the Phase 2 analyses are not formally documented in laboratory chemical procedure books but have been described elsewhere in the literature. References to the literature and a description of the methods are identified in Table 1–2 and guidelines to the approach given in Appendices 5 to 8.

4.2 Risk Assessment

A risk assessment framework will be applied as part of the Phase 2 detailed assessment to determine the specific risks associated with acidification, metal mobilisation and de-oxygenation. The risk assessment framework is presented in Section 1.5.

4.3 Interpretation and Reporting

Subject to the recommendation for Phase 2 investigations and the conducting of this work, the Phase 2 report will be appended to the Phase 1 report as Part 2. After internal and client review the entire report will be prepared as the Final Report for the study area. Should a study area not require Phase 2 investigations, and the client confirms this, then the Interim Final Report will be upgraded to be the Final Report for the study area and a note explaining that Phase 2 investigations were not conducted and why.

The report requirements for Phase 2 (this will be appended to the Phase 1 report as Part 2) should include the following report sections and provide the following information where relevant as listed in Table 4–1.

Table 4–1. Phase 2 report structure and information requirements.

Report section	Information to be included
Executive Summary	<ul style="list-style-type: none"> Objectives of the Phase 2 investigations Summary of laboratory results Summary of risk assessment, including specific risks associated with acidification, metal mobilisation, and de-oxygenation Summary of conclusions and recommendations
Introduction	<ul style="list-style-type: none"> Provide linkage and history with Phase 1 work Samples to be analysed Rationale for the samples selected for Phase 2 analysis
Laboratory Methods	<ul style="list-style-type: none"> Laboratory soil analysis methods (referencing this protocol document and describe any variations)
Quality Assurance and Quality Control (QA/QC)	<ul style="list-style-type: none"> Laboratory QA/QC report Evaluation of all QA/QC information
Results and Discussion	<ul style="list-style-type: none"> Summary and assessment of soil laboratory results Summary soil field and laboratory data presented in tables Interpretation and discussion of results and relating to soil

Report section	Information to be included
	materials and distribution in the study area
Risk Assessment	<ul style="list-style-type: none"> • Basis for risk assessment including framework and criteria used • Assessment of risks associated with each identified hazard (acidification, contaminant mobilisation, and de-oxygenation) • Level of risk and explanation of the major contributing factors • Discussion of assumptions
Broad Acid Sulfate Soil Management Options	<ul style="list-style-type: none"> • Identify areas of concern relating to the specific risks • Describe broad management options and their advantages and disadvantages • Discuss assumptions, limitations, and further information required
Conclusions and Recommendations	<ul style="list-style-type: none"> • Summary of key findings and outcomes • Assumptions used and uncertainties • Recommendations for monitoring and further work • Recommendations for management
Appendix	<ul style="list-style-type: none"> • Tables of laboratory soil analytical data
Database	<ul style="list-style-type: none"> • Electronic database, in Microsoft Excel[®] format, of all laboratory data including quality control and quality assurance measurements using the supplied standard data collection template.

5 References

- Ahern C.R., Ahern M.R., and Powell B. (1998). Guidelines for Sampling and Analysis of Lowland Acid Sulfate Soils (ASS) in Queensland 1998. QASSIT, Department of Natural Resources, Resource Sciences Centre, Indooroopilly.
- Ahern C.R., McElnea A.E., and Sullivan L.A. (2004). Acid sulfate soils laboratory methods guidelines. In 'Queensland Acid Sulfate Soils Manual 2004'. Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia.
<http://www.nrw.qld.gov.au/land/ass/pdfs/lmg.pdf> (Accessed 2 October 2007).
- APHA (1998). Standard methods for the examination of water and wastewater. (20th Ed.) American Public Health Association – American Water Works Association. Baltimore, USA.
- Baldwin D.S., Hall K.C., Rees G.N., and Richardson A.J. (2007). Development of a protocol for recognising sulfidic sediments (potential acid sulfate soils) in freshwater wetlands. *Ecological Management Restoration* 8:56–60.
- Bartlett, J.K. and Skoog, D.A. (1954). Colorimetric determination of elemental sulfur in hydrocarbons. *Anal. Chem.* 26:1008–1011.
- Burton E.D., Bush R.T., and Sullivan L.A. (2006a). Reduced inorganic sulfur speciation in drain sediments from acid-sulfate soil landscapes. *Environmental Science and Technology* 40:888–893.
- Burton E.D., Bush R.T., and Sullivan L.A. (2006b). Acid-volatile sulfide oxidation in coastal floodplain drains: iron-sulfur cycling and effects on water quality. *Environmental Science & Technology* 40:1217–1222.
- DEC (2009). Identification and Investigation of acid sulfate soils and acidic landscapes. Department of Environment and Conservation, Government of Western Australia, Acid Sulfate Soils Guideline Series, May 2009.
- Fanning D.S. (2002). Acid sulfate soils. Pages 11–13. In R Lal (ed.). *Encyclopedia of Soil Science*. Marcel Dekker, New York.
- Fitzpatrick R.W., Grealish G., Shand P., Simpson S.L., Merry R.H., and Raven M.D. (2009a). Acid Sulfate Soil Assessment in Finniss River, Currency Creek, Black Swamp and Goolwa Channel, South Australia. CSIRO Land and Water Science Report 26/09. CSIRO, Adelaide, 213 pp. <http://clw.csiro.au/publications/science/2009/sr26-09.pdf>
- Fitzpatrick Rob, Gerard Grealish, Paul Shand, Richard Merry, Nathan Creeper, Mark Thomas, Andrew Baker, Brett Thomas, Warren Hicks and Nilmini Jayalath (2010). Chip-tray incubation – a new field and laboratory method to support Acid Sulfate Soil Hazard Assessment, Classification and Communication. 19th World Congress of Soil Science, Soil Solutions for a Changing World 1 – 6 August 2010, Brisbane, Australia. Published on CDROM (In press).
- Fitzpatrick R.W., Marvanek S.P., Shand P., Merry R.H., Thomas M., and Raven M.D. (2008a). Acid Sulfate Soil Maps of the River Murray below Blanchetown (Lock 1) and Lakes Alexandrina and Albert when water levels were at pre- drought and current drought conditions. CSIRO Land and Water Science Report 12/08. CSIRO, Adelaide, 10 pp. There are 2 versions of the report – one without maps as appendix and one with maps:

http://www.clw.csiro.au/publications/science/2008/sr12-08_withmaps.pdf

http://www.clw.csiro.au/publications/science/2008/sr12-08_nomaps.pdf

Fitzpatrick R.W., Powell B., and Marvanek S. (2008b). Atlas of Australian Acid Sulfate Soils. In *Inland Acid Sulfate Soil Systems Across Australia* (Eds Rob Fitzpatrick and Paul Shand). pp 63–77. CRC LEME Open File Report No. 249. (Thematic Volume) CRC LEME, Perth, Australia.

Fitzpatrick R.W., Shand P., Marvanek S., Merry R.H., Thomas M., Simpson S.L., Raven M.D., and McClure S. (2008c). Acid sulfate soils in subaqueous, waterlogged and drained soil environments in Lake Albert, Lake Alexandrina and River Murray below Blanchetown (Lock 1): properties, distribution, genesis, risks and management. Prepared for Department of Environment and Heritage, SA. CSIRO Land and Water Science Report 46/08. CSIRO, Adelaide, 167. pp. <http://www.clw.csiro.au/publications/science/2008/sr46-08.pdf>

Fitzpatrick R.W., Shand P., and Merry, R.H. (2009b). Acid Sulfate Soils. In: J.T Jennings (Ed.). 'Natural History of the Riverland and Murraylands'. Royal Society of South Australia (Inc.) Adelaide, South Australia, pp. 65–111

Fitzpatrick R.W., Shand P., Raven M.D., and Merry R.H., (2008e). Acid sulfate soil materials and salt efflorescences in subaqueous and wetland soil environments at Lake Bonney, SA: Properties, risks and management. CSIRO Land and Water Science Report 21/08.

Fitzpatrick R.W., Shand P., Thomas B., Marvanek S., Merry R.H., Creeper N., Thomas M., Raven M.D., Simpson S.L., McClure S., and Jayalath N. (2008f). Acid sulfate soils in subaqueous, waterlogged and drained soil environments in the Coorong, Lake Alexandrina and Lake Albert: properties, distribution, genesis, risks and management. Prepared for Department of Water, Environment, Heritage and Arts. CSIRO Land and Water Science Report 52/08. CSIRO, Adelaide, 167. pp. <http://www.clw.csiro.au/publications/science/2008/sr52-08.pdf>

Hall K.C., Baldwin D.S., Rees G.N., and Richardson A.J. (2006). Distribution of inland wetlands with sulfidic sediments in the Murray–Darling Basin, Australia. *Science of the Total Environment* 370:235–244.

Hsieh Y.P., Chung S.W., Tsau Y.J., and Sue C.T. (2002). Analysis of sulfides in the presence of ferric minerals by diffusion methods. *Chem. Geol.* 182:195–201.

Isbell R.F. (1996). *The Australian Soil Classification*. CSIRO Australia.

Lamontagne S., Hicks W.S., Fitzpatrick R.W., and Rogers S. (2004). 'Survey and description of sulfidic materials in wetlands of the Lower River Murray floodplains: Implications for floodplain salinity management.' CSIRO Land and Water, Technical Report 28/04. CRC LEME Open File Report 165. August 2004. 65pp.

MDBA (2009). *Acid Sulfate Soils Field Guide – A field guide for the identification of wetlands at risk of acid sulfate soils in the Murray–Darling Basin*.

MDBC (2006a). *The Barmah-Millewa Forest Icon Site Environmental Management Plan 2006–2007*. MDBC Publication No. 30/06. http://thelivingmurray.mdbc.gov.au/_data/page/195/B-M_EMP_2006-07.pdf (last accessed 15/04/2009)

MDBC (2006b). *The Hattah Lakes Icon Site Environmental Management Plan 2006–2007*. MDBC Publication No. 31/06.

http://thelivingmurray.mdbc.gov.au/data/page/1327/HL_EMP_2006-07.pdf (last accessed 15/04/2009)

MDBC (2006c). The Gunbower-Koondrook-Perricoota Forest Icon Site Environmental Management Plan 2006–2007. MDBC Publication No. 32/06.

http://thelivingmurray.mdbc.gov.au/data/page/195/GKP_EMP_2006-07.pdf (last accessed 15/04/2009)

National Committee on Soil and Terrain (2009). 'Australian soil and land survey field handbook (3rd edn).' CSIRO Publishing: Melbourne.

Pons L.J. (1973). Outline of the genesis, characteristics, classification and improvement of acid sulphate soils. In: Dost, H. (Ed.) 'Proceedings of the 1972 (Wageningen, Netherlands) International Acid Sulfate Soils Symposium', Volume 1. International Land Reclamation Institute Publication 18. (Wageningen, Netherlands), pp3–27.

Rayment G.E. and Higginson F.R. (1992). 'Australian laboratory handbook of soil and water chemical methods'. Inkata Press, Melbourne.

Schoeneberger P.J., Wysocki D.A., Benham E.C., and Broderson W.D. (editors) (2002). Field book for describing and sampling soils, Version 2.0. Natural Resources Conservation Service, National Soil Survey Center, Lincoln, NE.

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

Shand P., Fitzpatrick R.W., and Merry R.H. (2008b). Development of a methodology and protocol for sampling and rapid risk assessment of acid sulfate soils in subaqueous and sub-aerial environments of the Murray Darling Basin. In, 6th International Conference on ASS and AMD. China. pp301–302.

Shand P. and Edmunds W.M. (2008). The baseline inorganic chemistry of European groundwaters. In, WM Edmunds & P Shand (eds.), Natural Groundwater Quality, 21–58. Blackwell Publishing, Oxford.

Simpson S., Angel B., Spadara D., Fitzpatrick R.W., Shand P., Merry R.H., and Thomas M. (2008). Acid, Metal and Nutrient Mobilisation Following Rewetting of Acid Sulfate Soils in the Lower Murray. Prepared for the South Australian Environmental Protection Agency. CSIRO Land and Water Science Report 27/08. CSIRO, Adelaide, 150. pp.
<http://www.clw.csiro.au/publications/science/2008/sr27-08.pdf>

Simpson Stuart L, Rob W. Fitzpatrick, Paul Shand, Brad M. Angel, David A. Spadaro and Luke Mosley (2010). Climate-driven mobilisation of acid and metals from acid sulfate soils Seasonal trends in soil electrical conductivity to better distinguish salinity types in the Mount Lofty Ranges, South Australia. Marine and Freshwater Research Volume: 61, Issue: 1, 2010, pp. 129 – 138.

Soil Survey Staff, (2003). 'Keys to Soil Taxonomy.' 9th edn. (United States Department of Agriculture, Soil Conservation Service, Blacksburg).
http://soils.usda.gov/technical/classification/tax_keys

Standards Australia / Standards New Zealand (2004).

Sullivan L.A., Bush R.T. and McConchie D.M. (2000). A modified chromium-reducible sulfur method for reduced inorganic sulfur: optimum reaction. *Aust. J Soil Res.*, 38:729–34.

Sullivan L.A., Bush R.T., and Fyfe D. (2002). Acid sulfate soil drain ooze: Distribution, behaviour and implications for acidification and deoxygenation of waterways. In: Lin C. Melville M.D. and Sullivan L.A. (Eds.). 'Acid sulfate soils in Australia and China.' (Science Press, Beijing), pp 91–99.

Sullivan L.A., Fitzpatrick R.W., Bush R.T., Burton E.D., Shand P., and Ward N.J. (2009). Modifications to the classification of acid sulfate soil materials. Southern Cross GeoScience Technical Report No. 309. April, 2009. pp. 11.

Sullivan L.A., Fitzpatrick R.W., Burton E.D., Bush R.T., and Shand P. (2008). Assessing environmental hazards posed by acid sulfate soil materials and other inorganic sulfide-containing soil materials: classification issues. Plenary session, Joint Conference of the 6th International Symposium in Acid Sulfate Soils and the Acid Rock Drainage Symposium. Guangzhou, China, 16–20 September 2008.

Sullivan L.A., Ward N.J., Bush R.T., and Burton E.D. (2009 in press). Improved identification of sulfidic soil materials by a modified incubation method. *Geoderma*.

Yao W. and Millero, F.J. (1996). Oxidation of hydrogen sulfide by hydrous Fe(III) oxides in seawater. *Mar. Chem.* 52:1–16.

APPENDIX 1: Screening Criteria for Selecting Detailed Assessment Study Areas

The following criteria were developed by the Scientific Reference Panel of the Acid Sulfate Soils Risk Assessment Project for the identification and prioritisation of wetlands requiring detailed assessment. These screening criteria are applied to the results from rapid assessments to determine those wetlands requiring detailed assessment, and their relative priority.

Only one threshold needs to be exceeded for a wetland to be recommended for detailed assessment.

These trigger values will be reviewed as detailed assessments progress.

Parameter	Trigger value	Action required	Priority [†]
pH soil*	< 4 [#]	Detailed assessment	Extreme
	4 – 5.5	Detailed assessment	Moderate
	> 5.5	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
EC soil (1:5)	> 1000 EC	Detailed assessment	High
	400 – 1000 EC	Detailed assessment	Moderate
	< 400 EC	No further assessment	N/A
EC water	> 5000 EC	Detailed assessment	High
	1750 – 5000 EC	Detailed assessment	Moderate
	< 1750 EC	No further assessment	N/A
Sulfate soil	> 500 mg/L	Detailed assessment	High
	100 – 500 mg/L	Detailed assessment	Moderate
	< 100 mg/L	No further assessment	N/A
Sulfate water	> 50 mg/L	Detailed assessment	High
	10 – 50 mg/L	Detailed assessment	Moderate
	< 10 mg/L	No further assessment	N/A

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

[#] MDBA will advise jurisdictions of any wetlands identified as an 'Extreme' priority as soon as practicable upon receipt of data.

[†]In the context of prevailing regional conditions, variations in these priorities are possible.

APPENDIX 2: Guidelines for Photographs and File Name Convention

Photographs are to be taken at each site of:

- Surrounding landscape (at a minimum on the four points of the compass) – these photographs are to characterise the wetland, in particular the vegetation, slope position and extent of the wetland. At least one of the photographs should have the soil pit in the foreground.
- Soil (or water) surface – vertical photograph to characterise surface condition, particularly important if the surface has cracks. A scale should be included in the photograph.
- Soil profile – with a scale tape placed to one side of the soil profile, angle of photograph should be taken as horizontal as possible. If the soil sample is extracted from below water then include a photograph of the sample.
- Any other features of interest – as determined by the surveyor, may include close-up photographs of a soil feature, flora and fauna.
- Crystal minerals or salt crusts.
- Chip-tray samples – photograph should include all chip-tray samples for the soil profile, including the sample identification labels written on the adjacent inside lid of the chip-tray. It may be more appropriate to take these photographs at the end of the survey under good light conditions.

The photograph file name convention described here is to be followed. Example given for file name 10024_03G02.JPG

Component	Purpose	Example	Template and allowed values
Wetland identifier	Wetland code that uniquely identifies the wetland area. This identifier is associated with other database information.	10024	Five digits in the form 'nnnnn'.
Site number	Unique number that identifies the site within the study area. This number and the wetland code can be associated with coordinate information to locate the site position and where the photographs are taken from.	_03	An underscore to separate, followed by two digits in the form '_nn'.
Feature type identifier	An alphabet letter to identify the feature being photographed. G for general landscape; S for surface condition; P for soil profile; C for chip-tray; M for minerals or salt crusts; O for other features of interest.	G	A single alphabet letter. Can be G; S; P; C; M; O.
Photograph number for the feature type	Starting at one, a consecutive number sequence associated with each photograph taken for the feature type.	02	A two digit number, in the form of 'nn'.
File extension	Separates the name from the file type	.	A dot, in the form of

separator	extension.		'
File type	Identifies the file format type.	JPG	Three letters, in the form of 'JPG'.

APPENDIX 3: Australian Acid Sulfate Soil Identification Key

Australia's current national soil classification (Isbell 1996), and other internationally recognised classification systems such as Soil Taxonomy (Soil Survey Staff 2003), require considerable expertise and experience to be used effectively. More importantly, these classification systems do not yet incorporate new acid sulfate soil terminologies such as: (i) monosulfidic, hypersulfidic and hyposulfidic material (Sullivan *et al.* 2008) and (ii) subaqueous soils, which is used in the nationally consistent legend of "The Atlas of Australian Acid Sulfate Soils" (Fitzpatrick *et al.* 2008a; available on the Australian Soil Resource Information System: www.asris.gov.au). To assist users to identify types and sub-types of soils a user-friendly Soil Identification Key was developed to more readily define and identify the various types and sub-types of acid sulfate soil and non-acid sulfate soil (see Fitzpatrick *et al.* 2008b,c,d,e; 2009a). The key is designed for people who are not experts in soil classification systems such as the Australian Soil Classification (Isbell 1996). Hence it has been used to deliver soil-specific land development and soil management packages to advisors, planners and engineers working in the Murray–Darling Basin.

The Soil Identification Key uses non-technical terms to categorise acid sulfate soils and other soils in terms of attributes that can be assessed in the field by people with limited soil classification experience. Attributes include water inundation (subaqueous soils), soil cracks, structure, texture, colour, features indicating water logging and 'acid' status – already acidified (i.e. sulfuric material), or with the potential to acidify (i.e. sulfidic material) – and the depths at which they occur or change in the soil profile.

The key consists of a systematic arrangement of soils into five broad acid sulfate soil types, each of which can be divided into up to six soil sub-types. The key layout is bifurcating, being based on the presence or absence of particular soil profile features (i.e. using a series of questions set out in a key). A soil is allocated to the first type of diagnostic features it matches, even though it may also match diagnostic features further down the key. The key uses a collection of plain language names for types and sub-types of acid sulfate soil in accordance with the legend for the Atlas of Australian Acid Sulfate Soils (Fitzpatrick *et al.* 2008c). It recognises the following five acid sulfate soil types: (i) Subaqueous Soils, (ii) Organic Soils, (iii) Cracking Clay Soils, (iv) Sulfuric Soils and (v) Hypersulfidic Soils (Table A4–1). These are further sub-divided into 18 soil sub-types based on occurrence of sulfuric material, hypersulfidic material, clayey or sandy layers; monosulfidic material and firmness.

Table A3–1. Summary Soil Identification Key for acid sulfate soils. After finding the soil type, use Table A3–2 to find the soil sub-type.






Diagnostic features for Soil Type	Soil Type	
<p>Does the soil occur in shallow permanent flooded environments (typically not greater than 2.5 m)?</p> <p>No ↓ Yes →</p>	<p>Subaqueous soil</p> 	<p>1</p>
<p>Does the upper 80 cm of soil consist of more than 40 cm of organic material (peat)?</p> <p>No ↓ Yes →</p>	<p>Organic soil</p> 	<p>2</p>
<p>Does the soil develop cracks at the surface OR in a clay layer within 100 cm of the soil surface OR have slickensides (polished and grooved surfaces between soil aggregates), AND is the subsoil uniformly grey coloured (poorly drained or very poorly drained)?</p> <p>No ↓ Yes →</p>	<p>Cracking clay soil</p> 	<p>3</p>
<p>Does a sulfuric layer (pH<4) occur within 150 cm of the soil surface, AND is the subsoil uniformly grey coloured (poorly drained)?</p> <p>No ↓ Yes →</p>	<p>Sulfuric soil</p> 	<p>4</p>
<p>Does sulfidic material (pH>4 which changes on incubation to pH<4) occur within 100 cm of the soil surface, AND is the subsoil uniformly grey coloured (poorly drained)?</p> <p>No ↓ Yes →</p>	<p>Hypersulfidic soil</p> 	<p>5</p>
<p>Other soils</p>	<p>Other soils</p>	<p>6</p>

Table A3–2. Soil Identification Key for acid sulfate soil subtypes.

Soil Type	Diagnostic features for Soil Subtype		Soil Subtype	
Subaqueous soil No ↓ Yes →	Does hypersulfidic material (pH>4 which changes on incubation to pH<4) occur within 100 cm of the soil surface? AND Does a clayey layer with slickensides occur within 100 cm of the soil surface? No ↓ Yes →	Does a monosulfidic black ooze (MBO) material layer >10 cm thick occur within 50 cm of the soil surface? No ↓ Yes →	Hypersulfidic subaqueous clayey soil with MBO	1.1
	↓	→	Hypersulfidic subaqueous clayey soil	1.2
	↓	Does a sandy or loamy layer occur within 100 cm of the soil surface? No ↓ Yes →	Sulfidic subaqueous soil	1.3
	Does sulfuric material occur within 100 cm of the soil surface? No ↓ Yes →	→	Sulfuric subaqueous soil	1.4
	→	→	Subaqueous soil	1.5
Organic soil No ↓ Yes →	Does hypersulfidic material (pH>4 which changes on incubation to pH<4) occur within 100 cm of the soil surface? AND Does a clayey layer with slickensides occur within 100 cm of the soil surface? No ↓ Yes →	Does a monosulfidic black ooze (MBO) material layer >10 cm thick occur within 50 cm of the soil surface? No ↓ Yes →	Hypersulfidic organic clayey soil with MBO	2.1
	→	→	Hypersulfidic organic clayey soil	2.2
	→	Does a sandy or loamy layer occur within 100 cm of the soil surface? No ↓ Yes →	Hypersulfidic organic soil	2.3
	Does sulfuric material occur within 100 cm of the soil surface? AND Does a clayey layer with slickensides occur within 100 cm of the soil surface? No ↓ Yes →	→	Sulfuric organic clayey soil	2.4

Soil Type	Diagnostic features for Soil Subtype		Soil Subtype	
	→	Does a sandy or loamy layer occur within 100 cm of the soil surface? No ↓ Yes →	Sulfuric organic soil	2.5
¹ Cracking clay soil No ↓ Yes →	Does hypersulfidic material occur within 100 cm of the soil surface? AND Does a clayey layer with slickensides occur within 100 cm of the soil surface? No ↓ Yes →	Does a monosulfidic black ooze (MBO) material layer >10 cm thick occur within 50 cm of the soil surface? No ↓ Yes →	Hypersulfidic cracking clay soil with MBO	3.1
	→	→	Hypersulfidic cracking clay soil	3.2
	Does sulfuric material occur within 100 cm of the soil surface? AND Does a clayey layer with slickensides occur within 100 cm of the soil surface? No ↓ Yes →	→	Sulfuric cracking clay soil	3.3
	→	→	Cracking clay soils	3.4
Sulfuric soil No ↓ Yes →	Does sulfuric material occur within 100 cm of the soil surface? No ↓ Yes →	→	Sulfuric soil	4.1
Hypersulfidic soil No ↓ Yes →	Does hypersulfidic material and a sandy to loamy layer occur within 100 cm of the soil surface? No ↓ Yes →	Does a monosulfidic black ooze (MBO) material layer >10 cm thick occur within 50 cm of the soil surface? No ↓ Yes →	Hypersulfidic soil with MBO	5.1
		No ↓ Yes →	Hypersulfidic soil	5.2
Other soils	→	→	Hydrosol – sandy or loamy	6.1

¹“Cracking clay soil” is equivalent to “Vertosol” (Isbell 1996) e.g. Sulfuric cracking clay soil is similar to “Sulfuric Vertosol”. The latter terminology is used in the Legend of the “Atlas for Australian Acid Sulfate Soils” by Fitzpatrick, Powell and Marvanek (2008a)

APPENDIX 4: Guidelines for pH_{incubation} Method

The concept underlying the formal Australian Soil Classification (Isbell 1996) definition for identification of sulfidic material (as described here) will be used:

A subsoil, waterlogged, mineral or organic material that contains oxidisable sulfur compounds, usually iron disulfide (e.g. pyrite, FeS₂), that has a field pH of 4 or more but which will become extremely acid when drained. Sulfidic material is identified by a drop in pH by at least 0.5 unit to 4 or less (1:1 by weight in water, or in a minimum of water to permit measurement) when a 10mm thick layer is incubated at field capacity for 8 weeks.

This test used for these acid sulfate soil protocols is a modification of this incubation procedure which involves the following steps:

- Incubate mineral or organic soil materials, which have a natural pH (1:1 soil:water) value > 4, as a layer 1 cm thick under continued moist conditions, while maintaining contact with the air at room temperature.
- Measure the pH and observe whether there is a drop in pH of 0.5 units or more to a value of 4.0 or less.
- The duration of incubation shall continue for a minimum of 8 weeks until a stable pH is reached (differs from the fixed 8 weeks in the formal Australian Soil Classification definition) as described in Sullivan *et al.* (2009).
- Collection and storage of moist samples in plastic chip-trays (Figure A3–1) produces similar conditions, and thus chip-trays are suitable for incubation testing as described and used in Fitzpatrick *et al.* (2008b,c,d,e,f; 2009a; 2010).

Field testing	8 weeks	10 weeks
Ageing Coo 7.1 0-10	Ageing Coo 7.1 0-10	Ageing Coo 7.1 0-10
Coo 7.2 10-25	Coo 7.2 10-25	Coo 7.2 10-25
Coo 7.3 25-40	Coo 7.3 25-40	Coo 7.3 25-40
Coo 8.1 0-2	Coo 8.1 0-2	Coo 8.1 0-2
Coo 8.2 2-30	Coo 8.2 2-30	Coo 8.2 2-30
Coo 9.1 0-3	Coo 9.1 0-3	Coo 9.1 0-3
Coo 9.2 3-8	Coo 9.2 3-8	Coo 9.2 3-8
Coo 10.1 0-5	Coo 10.1 0-5	Coo 10.1 0-5
Coo 10.2 5-40	Coo 10.2 5-40	Coo 10.2 5-40
Coo 10.3 40-60	Coo 10.3 40-60	Coo 10.3 40-60

Figure A4-1. The same chip tray showing incubation of soil after (i) sampled in the field, (ii) ageing (incubation) for the minimum 8 weeks and (iii) ageing (incubation) at 10 weeks. Here pH indicator strips indicate that most samples remain alkaline or neutral (blue colour indicating pH >7) with only two becoming acid after incubation for 10 weeks (red or pink colour indicating pH 3.9 to 4). (from Fitzpatrick *et al.* 2008f)

APPENDIX 5: Guidelines for Sulfur Species Suite Method – Acid Volatile Sulfur and Elemental Sulfur

Solid-phase S fractionations are to be determined by sequentially extracting: (1) acid-volatile sulfur (AVS) and acid-extractable SO_4 , (2) elemental S and (3) pyrite-S (Burton *et al.* 2006b). Acid-volatile sulfur (AVS) is readily extracted by the diffusion method described by Hsieh *et al.* (2002) using a modified apparatus. Approximately 2 g of wet sample is equilibrated (orbital shaking at 150 rpm for 18 hrs) with 10 ml of 6M HCl/0.1M ascorbic acid in gas-tight 55 cm³ polypropylene reactors. The evolved $\text{H}_2\text{S}(\text{g})$ is trapped in 7 ml of 3% Zn acetate in 2 M NaOH, and subsequently quantified via iodometric titration. The quantitative recovery of acid volatile sulfur using this method is $96 \pm 4\%$. Pyrite-S is not extracted by the acid volatile sulfur analytical method employed here (Hsieh *et al.* 2002). The slurry remaining after acid volatile sulfur extraction is diluted to 50 ml with deionised water and centrifuged (4000 g, 10 minutes).

Elemental S ($\text{S}^0_{(\text{s})}$) is then extracted by shaking the residual sample with 10 ml of chloroform for 16 hours (Yao and Millero, 1996). An aliquot of the chloroform phase is analysed for S^0 using cold cyanolysis in acetone (Bartlett and Skoog, 1954). Residual $\text{S}^0_{(\text{s})}$ is removed from the sample by three rinses with 25 ml of acetone, and a final rinse with 20 ml ethanol. Each rinse involves 10 minutes of shaking, with the sediment and acetone/ethanol phases separated between rinses by centrifugation at 4000 g for 10 minutes. This rinsing protocol is to minimise $\text{S}^0_{(\text{s})}$ carried over into the subsequent step (pyrite extraction) of the fractionation procedure. The residual AVS- and $\text{S}^0_{(\text{s})}$ -extracted sediment is finally transferred into a 250 ml Pyrex™ Erlenmeyer flask. Pyrite-S is extracted from the residual sediment by Cr(II)-reduction by method of Sullivan *et al.* (2000).

APPENDIX 6: Guidelines for Rapid Metal Release Method

Sample handling and preparation

All soils, whether they are dry, moist or waterlogged when collected, will be dried before use in the rapid (acid, metal and nutrient) mobilisation tests. Slow drying of soils in slightly humid conditions best resembles what may occur naturally in the field, however, due to the relatively short timeframe of the project, the soils will be dried at 80 °C in a temperature-controlled cabinet for three days.

All samples will be handled using protocols to avoid sample contamination. This includes the wearing of clean powder-free vinyl gloves for the handling of all sample bottles and sampling equipment. All containers used for samples will be either new (in the case of plastic bags and containers), for storage of solid phases, or new and acid-washed (in the case of plastic bottles) for handling and storage of water samples. The bottles used for analysis of dissolved metals will be soaked for 24 hours in 10% nitric acid then rinsed with MilliQ™ or similar quality water and stored dust-free in polyethylene bags.

Rapid acid, metal and nutrient mobilisation assessment methodology

The re-wetting of the soils is expected to occur at different rates at each site and may involve slow or rapid wetting with large or small volumes of water. The fate of the water following re-wetting is unknown and is expected to be different at each site and to be greatly affected by the soil properties, including the degree of surface cracking and sub-surface fissures, and land topography. Consequently, a large number of different mechanisms can be envisaged for the mobilisation and transport of various substances from the soils. The substances considered in the current study were acid (pH, alkalinity and acidity changes), anions (chloride and sulfate), nutrients (N and P compounds), carbon, major cations and trace metals. In the different soil types, these substances will be present in different forms and will have differing mobility. Because of the large variety of possible re-wetting scenarios and the variety of soils being considered (surface *versus* sub-surface soils, desiccated/cracked *versus* uncracked), some real scenarios may, however, exist where greater substance mobilisation occurs in certain areas.

The acidity, metal and nutrient metal mobilisation experiments will be undertaken by shaking the dried soils in oxygenated deionised water to simulate the possible re-wetting of the soils.

The conceptual model for the mobilisation processes assumes:

1. Soils in the field will be re-wetted by water resulting in release of substances from soil to the associated waters.
2. Substance release from soils re-suspended in water will be greater than from soils in contact with near-stationery water (as occurs for saturated sub-surface soils).
3. The use of deionised water for all rapid-mobilisation tests is proposed as a means of standardising the method and improving site to site comparison of results. The concentrations of major cations and anions (alkalinity and hardness) rapidly released from the soils are expected to greatly outweigh the concentrations of these substances in river water.

4. A 24 hour mixing period of soils in oxygenated water should provide sufficient time for the dissolution of the majority (e.g. >80%) of substances from most soils (Simpson *et al.*, 2008; 2010).
5. Above a total suspended solids (TSS) concentration of 100 g/L, the substance release should become relatively independent of TSS concentration (Simpson *et al.*, 2008; 2010).

Method Summary

A soil (TSS) concentration of 100 g (dry weight)/L and mixing period of 24 hours will be used for all rapid mobilisation tests. The soils will be re-suspended (50 g dry weight in 500 ml Nalgene™ bottles – 50 ml headspace) by rolling the bottles containing soil and water at 100 rpm on a purpose-built bottle roller. The water quality parameters, pH, redox potential (Eh), specific electrical conductance (SEC) and dissolved oxygen will be measured at the start and finish of all tests, and after 6 hours for selected tests. After 24 hours, the waters will be centrifuged before sample collection. Alkalinity, nutrient (N and P) and major ion analysis will be performed on unfiltered samples (centrifuged and no visible suspended solids present) and dissolved metals analyses will be made on <0.45 µm filtered samples so that they can be accurately compared to the water quality guidelines. The full set of analyses on water samples at the end of the tests will comprise (i) alkalinity (ii) dissolved organic carbon, (iii) the major anions/nutrients (Cl, NO₂, NO₃, PO₄, SO₄ and total N), (iv) the major cations Na, K, Ca, Mg, and (v) the trace metals or metalloids Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, V, Zn.

Quality Assurance and Quality Control (QA/QC)

For all tests and analyses, the QA/QC procedures will be equivalent to those endorsed by NATA and will allow accurate interpretation of accuracy and quality. Replicate tests and analyses will be undertaken for approximately 10% of samples.

Data interpretation

The acid, metal and nutrient mobilisation results will be interpreted in terms of the sediment/soil properties. The kinetics of mobilisation processes will be quantified for selected soils. The potential mobilisation per unit sediment volume will be estimated from the results under a number of scenarios. The outputs from this semi-quantitative modelling will be suitable for input into water quality models.

The results will be tabulated in a form suitable for comparing concentrations to water quality guidelines. For trace metals, the re-wetting water dilution required to meet Australia's water quality guidelines will be calculated. The concentrations of nutrients (e.g. N-species, phosphate) will be examined and compared to thresholds that stimulate algal blooms.

The ability of rivers in the Murray–Darling Basin to buffer releases of acid, metals and nutrients will be assessed for unfiltered water samples and also waters containing varying amounts of suspended sediments from an appropriate river in the Murray–Darling Basin.

The potential for low dissolved oxygen levels arising from re-wetting processes will be determined and the possible environmental impacts assessed.

APPENDIX 7: Guidelines for Contaminant and Metalloid Dynamics Method

The methodology assesses the potential for metals and metalloids (e.g. As) to be mobilised to an aqueous phase from oxic sediments when anoxic-reductive geochemical conditions are triggered by inundation. It is well established that re-flooding oxic soils can dramatically alter the mobility of metals and metalloids and concentrations in pore waters can be dramatically affected by a regime shift from oxic to reductive geochemical conditions. Aqueous concentrations of metals and metalloids in pore water represent the greatest hazard to water quality. The magnitude of metal mobilisation is affected by many factors that include but are not exclusive to:

- 1) the abundance and form of metal and metalloid contaminants
- 2) the abundance and liability of organic matter
- 3) the abundance and reactivity of iron minerals
- 4) availability of sulfate
- 5) acid/alkalinity buffering capacity
- 6) pH
- 7) EC
- 8) clay content
- 9) microbial activity
- 10) temperature
- 11) porosity.

Dynamics of metal and metalloid release is assessed by use of reductive batch incubations. The basic principle is to subject soil to anaerobic-reductive conditions for 7 weeks and assess the mobilisation of metals and metalloids. This test involves subjecting 5 g of field moist soil to reductive conditions by placing it into 100 ml Wheaton serum vial filled with deionised water for a period of 7 weeks. The vials need to be incubated in a controlled incubator at 23 °C. A sample of the supernatant needs to be collected and assessed at three key intervals based on reductive dynamics (initial oxic conditions (i.e. 24 hours), preliminary anoxic (14 days), and prolonged anoxic (56 days). pH, EC, Eh and metal contents are determined on filtered supernatant at each stage and determined by ICP-MS at the NATA registered laboratory. The concentrations of pore water metal contents are assessed with reference to relevant national water quality guidelines for environmental protection (ANZECC/ARMCANZ, 2000).

APPENDIX 8: Guidelines for Monosulfidic Formation Potential Method

Monosulfidic material formation potential will be assessed using a soil mesocosm approach. Each mesocosm will comprise of 9 g of soil. The soil is inundated with 90 ml of Type 1 reagent grade water (MilliQ™, Millipore Corp), (APHA, 1998), deionised water and a readily available organic substrate (7.2 g/L sucrose) is added to simulate the supply of organics associated with floodplain inundation. The experiment duration is 7 weeks (which is generally a sufficient period to quantify the magnitude of monosulfidic formation), after which the surface water and surface soil material is characterised.

Surface water samples will be filtered to $<0.45 \mu\text{m}$ using enclosed syringe-driven filter units (to minimize atmospheric exposure). Pore water pH and redox potential will be determined using probes calibrated against pH 4 and 7 buffers and Zoebell's solution, respectively. Pore water sulfide will be preserved with ZnOAc prior to determination by the methylene blue method (APHA, 1998). Aliquots of filtrate will be added directly to 1,10-phenanthroline solutions for total aqueous Fe and Fe(II) determination (APHA, 1998). Aqueous Fe(III) will be determined by the difference between total Fe and Fe(II). Sulfate will be determined by turbidimetric analysis (APHA, 1998).

For solid phase analysis, sediment moisture content will be determined by weight loss due to drying at 105 °C. The acid volatile sulfur, elemental sulfur and pyrite sulfur will be determined by sequential extraction (Burton *et al.* 2006a) on fresh samples (as per Appendix 5).

APPENDIX 9: Guidelines for Mineral Identification by X-Ray Diffraction

An example of an appropriate method for mineral identification by X-ray diffraction follows:

The soil samples will be ground in an agate mortar and pestle and either back pressed into steel holders or deposited onto Si low background holders (depending on how much sample is available).

XRD patterns will be recorded using Co K-alpha radiation, variable divergence slit, post diffraction graphite monochromator and fast X'Cellerator Si strip detector. The diffraction patterns will be recorded in steps of 0.05° 2 theta, with a total counting time of 30 minutes, and logged to data files for analysis using HighScore Plus.

APPENDIX 10: Guidelines for Geochemical Analysis by X-Ray Fluorescence Spectrometry

Examples of appropriate methods for geochemical analysis by X-ray fluorescence spectrometry follows:

1. Trace elements on pressed powder pellets.

Approximately 4 g of each oven dried sample (105 °C) will be accurately weighed with 1 g of Licowax binder and mixed using a test tube shaker. The mixtures will be pressed in a 32 mm die at 12 tons pressure and the resulting pellets were analysed on a PANalytical Axios Advanced, wavelength dispersive XRF system using an appropriate calibration.

Currently only trace elements analysis is conducted on samples for Phase 2 work. Information for major elements is included here should it be necessary in the future to include.

2. Major elements on fused borate glass discs.

Approximately 1 g of each oven dried sample (105 °C) will be accurately weighed with 4 g of 12-22 lithium borate flux. The mixtures are heated to 1050 °C in a Pt/Au crucible for 20 minutes to completely dissolve the sample then poured into a 32 mm Pt/Au mould heated to a similar temperature. The melt is cooled rapidly over a compressed air stream and the resulting glass discs are analysed on a PANalytical Axios Advanced wavelength dispersive XRF system using an appropriate Silicates calibration program.

BACK COVER PAGE

PAGE LEFT BLANK