



Assessment of Acid Sulfate Soil Materials (Phase 2) Schillers Lagoon (12259), South Australia

P. Shand, S. Grocke, A.K. Baker, L. Smith, C. Fiebiger, G. Cozens, J. Gouzos, M. Smart, J. Smith & C. Wright

Report to the Murray-Darling Basin Authority

Australia is founding its future on science and innovation. Its national science agency, CSIRO, is a powerhouse of ideas, technologies and skills.

CSIRO initiated the National Research Flagships to address Australia's major research challenges and opportunities. They apply large scale, long term, multidisciplinary science and aim for widespread adoption of solutions. The Flagship Collaboration Fund supports the best and brightest researchers to address these complex challenges through partnerships between CSIRO, universities, research agencies and industry.

The Water for a Healthy Country Flagship aims to provide Australia with solutions for water resource management, creating economic gains of \$3 billion per annum by 2030, while protecting or restoring our major water ecosystems.

For more information about Water for a Healthy Country Flagship or the National Research Flagship Initiative visit www.csiro.au/org/HealthyCountry.html

Citation: Shand P, Grocke S, Baker AK, Smith L, Fiebiger C, Cozens G, Smart M, Gouzos J, Smith J & Wright C 2011. Assessment of Acid Sulfate Soil Materials (Phase 2) Schillers Lagoon (12259). CSIRO: Water for a Healthy Country National Research Flagship

#### **Copyright and Disclaimer**

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

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

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

#### **Cover Photograph:**

Schillers Lagoon (12259) Photographer: Gerard Grealish © 2011 CSIRO

# CONTENTS

Ackr	Acknowledgmentsiv							
Exec	utive	Summai	y	v				
1.	Intro	duction		1				
2.	Labo	Laboratory methods						
	2.1.	-	ry analysis methods					
		2.1.1.	Summary of laboratory methods					
		2.1.2.	Reactive metals method					
		2.1.3.	Contaminant and metalloid dynamics method	.5				
		2.1.4.	Monosulfide formation potential method	.6				
		2.1.5.	Mineral identification by x-ray diffraction	.6				
	2.2.	Quality a	ssurance and quality control	6				
3.	Resu	lts and o	discussion	8				
	3.1.	Summary	/ of soil laboratory results	8				
		3.1.1.	Reactive metals data	.8				
		3.1.2.	Contaminant and metalloid dynamics data					
		3.1.3.	Monosulfide formation potential data					
		3.1.4.	Mineral identification by x-ray diffraction					
	3.2.	Interpreta	ation and discussion of results1	6				
4.	Risk	assessn	nent1	9				
	4.1.	Risk asse	essment framework1	9				
	4.2.	Assessm	ent of risks	21				
		4.2.1.	Risks associated with acidification	21				
		4.2.2.	Risks associated with contaminant mobilisation	22				
		4.2.3.	Risks associated with de-oxygenation	23				
5.	Broa	d acid si	ulfate soil management options2	24				
Refe	rence	s	2	26				
Appe	endice	es		28				
			ve metals data2					
••			ninant and metalloid dynamics data3					
Appe	endix	3 Monos	ulfide formation potential data3	61				

## LIST OF FIGURES

 Figure 1-1 Schillers Lagoon (12259) aerial photograph with Phase 1 sampling sites identified.
 3

 Figure 3-1 Contaminant and metalloid dynamics results for Schillers Lagoon (12259) soil materials for pH, SEC, Eh, silver (Ag), aluminium (Al) and arsenic (As).
 11

 Figure 3-2 Contaminant and metalloid dynamics results for Schillers Lagoon (12259) soil materials for cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe) and manganese (Mn).
 12

 Figure 3-3 Contaminant and metalloid dynamics results for Schillers Lagoon (12259) soil materials for nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), vanadium (V) and zinc (Zn).
 13

 Figure 3-4 Selected trace elements plotted against pH.
 14

 Figure 3-5 pH and Eh dynamics during monosulfide formation potential tests in surface soil sample 12259\_7.1 from Schillers Lagoon.
 15

## LIST OF TABLES

Table 1-1 Priority ranking criteria adopted by the Scientific Reference Panel of the Murray- Darling Basin Acid Sulfate Soils Risk Assessment Project, from MDBA (2010)
Table 1-2 Rationale for Phase 2 sample selection, from MDBA (2010).       3
Table 1-3 Summary of Schillers Lagoon (12259) samples analysed for Phase 2 assessment.         4
Table 2-1 Phase 2 data requirements - list of parameters and objective for conducting the test, from MDBA (2010).         5
Table 3-1 Schillers Lagoon (12259) reactive metals data.         8
Table 3-2 Summary of contaminant and metalloid dynamics data         9
Table 3-3 Summary of monosulfide formation potential data for the Schillers Lagoon surface         soil material 12259_7.1 after 7 weeks (3.6 g/L sucrose).
Table 3-4 Summary of the degree of hazard associated with the measured contaminant andmetalloid concentrations in Schillers Lagoon (12259).17
Table 3-5 Guideline thresholds for the degree of hazard associated with acid volatile sulfide $(S_{AV})$ concentrations
Table 4-1 Standardised table used to determine the consequences of a hazard occurring,from MDBA (2011)
Table 4-2 Likelihood ratings for the disturbance scenario, from MDBA (2011)
Table 4-3 Risk assessment matrix, adapted from Standards Australia & Standards New         Zealand (2004).       20
Table 4-4 Summary of risks associated with acid sulfate soil materials in Schillers Lagoon (12259).         23
Table 5-1 Summary of management options and possible activities, from EPHC & NRMMC (2011).         25

## ACKNOWLEDGMENTS

This work was funded by the Murray-Darling Basin Authority. We are particularly grateful to Rob Kingham and his team from the Murray-Darling Basin Authority for support throughout this project. We would like to thank the many landholders who allowed access through their properties and contributed their local knowledge about the wetland and history of the areas.

The following CSIRO staff members are thanked for their outstanding turnaround of analytical data: Julie Smith, Claire Wright, John Gouzos and Michelle Smart. We are grateful to Rob Kingham, Lucy Paterson and Lea Weekes-Randall from the Murray-Darling Basin Authority and internal peer reviewers from CSIRO for constructively reviewing the report.

## **EXECUTIVE SUMMARY**

An initial Phase 1 acid sulfate soil investigation of Schillers Lagoon (12259) during March 2010 showed acid sulfate soils to be a priority concern within this wetland complex. Based on Phase 1 recommendations, a Phase 2 investigation was undertaken for Schillers Lagoon (12259) to determine the nature, severity and the specific risks associated with acid sulfate soil materials. The wetland contained surface water at the time of sampling, and has had a managed wetting and drying regime in place over a number of years.

The 24 hour **reactive metals** tests were undertaken to determine those metals and metalloids extractable with a moderately strong acid i.e. potentially available from binding sites on soil minerals such as iron (Fe), manganese (Mn) and aluminium (Al) oxides. Although comparisons can be made with soil and sediment quality guidelines, these are defined for total concentrations and not partial extractions. The results showed that concentrations were below the sediment quality guidelines (SQG) and soil ecological investigation levels (EIL) for those elements where guidelines are available. Although the metals and metalloids did not breach sediment quality guidelines and soil ecological investigation level trigger values, the concentrations of some elements were high enough that they may impact water quality if mobilised, particularly for iron (Fe) and manganese (Mn).

The **contaminant and metalloid dynamics** tests were undertaken to assess the release of metals during a water extraction, and to assess dynamics in response to saturation over time by incubating soil materials for periods of 1, 7, 14 and 35 days. The degree to which metal and metalloid concentrations exceed ANZECC/ARMCANZ environmental protection guideline values was used to characterise the degree of hazard. For Schillers Lagoon (12259), aluminium (AI), copper (Cu) and vanadium (V) were assigned a moderate hazard with concentrations exceeding ANZECC/ARMCANZ environmental protection guidelines by more than 10 times. Arsenic (As), cobalt (Co), chromium (Cr), iron (Fe), lead (Pb) and zinc (Zn) were above the guideline values.

Schillers Lagoon (12259) has been classified as medium conservation status by the SA Murray-Darling Basin Natural Resources Management Board (Miles et al. 2010). The wetland was largely full at the time of sampling with both subaerial and subagueous soils studied. The tests undertaken for the subaqueous soils in this wetland are difficult to extrapolate to a case where the soils have dried and oxidised, as the generated acidity depends on a number of complex factors. In addition, it is not possible to predict the potential impacts of metal and metalloid release, as these may be present in reduced minerals such as pyrite and thus not easily released until oxidation occurs. The main hazards considered in this study that may impact on wetland values are acidification, contaminant mobilisation and deoxygenation. The wetland has been allocated a low risk rating due to acidification and a medium contaminant risk rating for soils. For surface waters, the risk is largely dependent on surface and sub-surface hydrology and is thus scenario dependent. Taking into account the range of likely scenarios, from very low flows (highest risk) to very high flows (lowest risk), the risk to surface waters in the wetland has been allocated a low risk rating for acidification and a medium risk rating for contaminant mobilisation. The risk associated with *deoxygenation* was determined to be **low** as there was no identified hazard associated with monosulfide formation and no evidence of monosulfides either in the wetland at the time of the Phase 1 field survey or forming during laboratory experiments.

In designing a management strategy for dealing with acid sulfate soils in Schillers Lagoon (12259), other values and uses of the wetland need to be taken into account to ensure that any intervention is compatible with other management plans and objectives for the wetland.

The data suggest that management options for acidification are less important for this wetland. However, the identification of hazards and risks related to contaminant mobilisation should be considered in managing the wetland. The data from the reactive metals and contaminant and metalloid dynamics tests show that metal and metalloid mobility are a risk, particularly during wetting and drying periods where contaminants may be cycled between oxidised (oxide/oxyhydroxide) and reduced (sulfide) minerals. This data helps to provide information on impacts related to contaminant mobilisation. Due to the medium risks to the wetland values associated with contaminant mobilisation in Schillers Lagoon (12259), a monitoring program is recommended during any disturbance to the soils.

## 1. INTRODUCTION

At its March 2008 meeting, the Murray–Darling Basin Ministerial Council discussed the emerging issue of inland acid sulfate soils and the associated risks to Murray–Darling Basin waterways and agreed that the extent of the threat posed by this issue required assessment. The purpose of the Murray–Darling Basin Acid Sulfate Soils Risk Assessment Project was to determine the spatial occurrence of, and risk posed by, acid sulfate soils at priority wetlands in the River Murray system, wetlands listed under the Ramsar Convention on Wetlands of International Importance and other key environmental sites in the Murray–Darling Basin. The project involved the selection of wetlands of environmental significance, as well as those that may pose a risk to surrounding waters. These wetlands were then subjected to a tiered assessment program, whereby wetlands were screened through a desktop assessment stage, followed by a rapid on-ground appraisal, and then detailed on-ground assessment if results of previous stages indicated an increased likelihood of occurrence of acid sulfate soils.

Detailed assessments of acid sulfate soils within the Murray-Darling Basin (MDB) are conducted as a two-phase process under the MDB Acid Sulfate Soils Risk Assessment Project (ASSRAP). Phase 1 investigations are initially undertaken to determine whether or not acid sulfate soil materials are present in the study area, and provide characterisation of the properties and types of acid sulfate soils. Phase 2 investigations are only 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, selected samples undergo further investigations to determine the nature, severity and the specific risks associated with the acid sulfate soil materials. Phase 2 activities include: (i) soil laboratory analysis to confirm and refine the hazards associated with contaminant mobilisation and/or deoxygenation, (ii) a risk assessment, and (iii) interpretation and reporting, including discussion on broad acid sulfate soil management options.

Detailed Phase 1 acid sulfate soil assessments were undertaken at almost 200 wetlands and river channels throughout the Murray-Darling Basin. In South Australia, 56 wetlands along the River Murray between Lock 1 and Lock 5 were investigated by CSIRO Land and Water (Grealish *et al.* 2010). From these Phase 1 investigations, 13 wetlands were selected for further investigation. Nearly all of the wetlands along the River Murray between Wellington and Blanchetown (Lock 1) in South Australia also received detailed Phase 1 acid sulfate soil assessments (Grealish *et al.* 2011) and of these 23 wetlands were selected for further investigation in Phase 2. This included some wetlands below Lock 1 from earlier studies (Fitzpatrick *et al.* 2008; Fitzpatrick *et al.* 2010).

Following the Schillers Lagoon (12259) Phase 1 assessment (Grealish *et al.* 2010) and the priority ranking criteria adopted by the Scientific Reference Panel of the MDB ASSRAP (see Table 1-1), Schillers Lagoon (12259) was selected for Phase 2 detailed assessment. The Phase 1 assessment sampled from 8 sites along three transects (Figure 1-1). The Phase 1 assessment identified no high priority sites based on the presence of sulfuric materials, 1 high priority site based on the presence of hypersulfidic materials, no high priority sites based on the presence of hyposulfidic materials with SCR  $\geq$  0.10% and 5 moderate priority sites based on the presence of hyposulfidic materials with SCR < 0.10%. Phase 2 investigations were carried out on selected surface soil samples from 2 sites (12259\_5 and 12259\_7) identified in the Phase 1 assessment (Grealish *et al.* 2010).

The soils were very varied and those sampled comprised sands, clays and loams. Net acidities were also very variable, ranging overall from -895 to 21 mol  $H^+$ /tonne. However, only the upper two soil layers from profile 12259\_1 (not studied in Phase 2) had positive net acidities above 17 mol  $H^+$ /tonne (20 and 21 mol  $H^+$ /tonne). The wetland was well buffered, with ANC varying from 0 to 6.7 % ANC.

Table 1-1 Priority ranking criteria adopted by the Scientific Reference Panel of the Murray-Darling Basin Acid Sulfate Soils Risk Assessment Project, from MDBA (2010).

Priority	Soil material
High Priority	All sulfuric materials.
	All hypersulfidic materials (as recognised by either 1) incubation of sulfidic materials or 2) a positive net acidity result with a Fineness Factor of 1.5 being used).
	All hyposulfidic materials with $S_{CR}$ contents $\ge 0.10\%$ S.
	All surface soil materials (i.e. within 0-20 cm) with water soluble sulfate (1:5 soil:water) contents $\geq$ 100 mg kg <sup>-1</sup> SO <sub>4</sub> .
	All monosulfidic materials.
Moderate Priority	All hyposulfidic materials with $S_{CR}$ contents < 0.10% S.
No Further Assessment	Other acidic soil materials.
	All other soil materials.

A summary of the soil laboratory analyses undertaken as part of the Phase 2 assessment and the sample selection criteria for each analysis is given in Table 1-2. Soil samples identified to undergo Phase 2 laboratory analysis are primarily from the surface and nearsurface layers, as these are the soils most likely to have initial contact with water. A list of the samples selected for Phase 2 analysis for Schillers Lagoon (12259) is presented in Table 1-3.

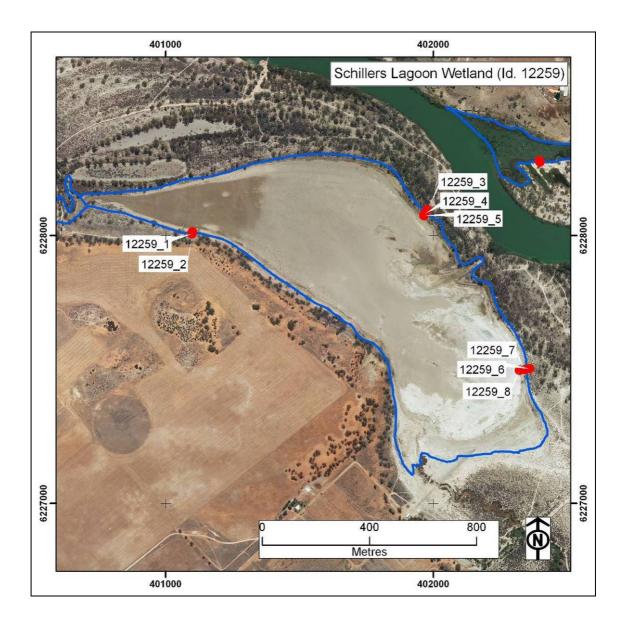


Figure 1-1 Schillers Lagoon (12259) aerial photograph with Phase 1 sampling sites identified.

Parameter	Samples selected
Reactive metals	Conducted on selected upper two surface samples.
Contaminant and metalloid dynamics	Conducted on selected upper two surface samples.
Monosulfide formation potential	Conducted on surface samples of dry sites that meet the water extractable sulfate criteria for monosulfides.
Mineral identification by X-ray diffraction (XRD)	Conducted on limited number of selected crystals and minerals (if present). Most likely to be associated with sulfuric layers to confirm acid mineral presences.
Acid base accounting data	Conducted only on samples from wetlands below Lock 1 and Burnt Creek/Loddon River if not previously analysed and $pH_{KCI}$ <4.5.

Soil Laboratory Test	Schillers Lagoon (12259) samples	Depth of sample (cm)	Number of samples analysed
Reactive metals	12259_5.1	0-2	4
	12259_5.2	2-10	
	12259_7.1	0-2	
	12259_7.2	2-10	
Contaminant and	12259_5.1	0-2	4
metalloid dynamics	12259_5.2	2-10	
	12259_7.1	0-2	
	12259_7.2	2-10	
Monosulfide formation potential	12259_7.1	0-2	1
Mineral identification by X-ray diffraction (XRD)	-	-	0

#### Table 1-3 Summary of Schillers Lagoon (12259) samples analysed for Phase 2 assessment.

## 2. LABORATORY METHODS

## 2.1. Laboratory analysis methods

#### 2.1.1. Summary of laboratory methods

A list of the method objectives for the Phase 2 assessment are summarised below in Table 2-1. All soil samples analysed in this Phase 2 assessment were collected and subsequently stored as part of the Phase 1 field assessment.

# Table 2-1 Phase 2 data requirements - list of parameters and objective for conducting the test, from MDBA (2010).

Parameter	Objective					
Reactive metals	Assists with determining impacts on water quality by determining weakly to moderately strongly bound metals.					
Contaminant and metalloid dynamics	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 5 week time frame.					
Monosulfide formation potential	Determine relative propensity for monosulfides to form following inundation.					
Mineral identification by X-ray diffraction (XRD)	Characterisation and confirmation of minerals present.					

Guidelines on the approaches that were followed as part of this Phase 2 assessment are presented in full in the detailed assessment protocols (MDBA 2010).

#### 2.1.2. Reactive metals method

The guidelines for the reactive metals method are outlined as an addendum to the detailed assessment protocols (MDBA 2010). In this method, samples were prepared by disaggregation (not grinding) using a jaw crusher, and then sieved to include only the <2 mm fine earth fraction. A total of 2.5 g soil was added to 40 ml of 0.1 M HCl, gently mixed for 1 hour and filtered through a pre-acid washed 0.45  $\mu$ m nitro-cellulose filter. The metals examined comprised silver (Ag), aluminium (Al), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), vanadium (V) and zinc (Zn).

#### 2.1.3. Contaminant and metalloid dynamics method

The guidelines for the contaminant and metalloid dynamics method are outlined in Appendix 7 of the detailed assessment protocols (MDBA 2010). The contaminant and metalloid dynamics method was designed to determine the release of metals and metalloids in soils after 24 hours. The data represent the availability of metals and metalloids from a weak extraction (water, and thus easily bioavailable) of saturated soils, and for dry wetland soils, those easily mobilised from mineral surfaces and readily soluble mineral phases (such as salts). The exercise was repeated in a batch process for longer time periods (7 days, 14 days, 35 days). The latter approach was aimed at understanding changes in concentrations over time. This is particularly important for dried soils which have been in contact with the

atmosphere. The soil materials and the release/uptake of metals/metalloids are expected to change as the chemical environment changes from oxidising to reducing. The data can be compared to existing water quality guidelines, although care should be taken when extrapolating to surface waters without knowledge of hydrological conditions and natural chemical barriers. The impact on surface waters will be governed by the upward chemical flux which is a function of soil type, water flow, diffusion and the chemistry of the soils near the sediment-water interface.

Redox potential (Eh) and pH were determined using calibrated electrodes linked to a TPS WP-80 meter; Eh measurements were undertaken in an anaerobic chamber to minimise the rapid changes encountered due to contact with the atmosphere, and are presented relative to the standard hydrogen electrode (SHE). Specific electrical conductance (SEC) was determined using a calibrated electrode linked to a TPS WP-81 meter. All parameters were measured on filtered (0.45  $\mu$ m) water samples.

#### 2.1.4. Monosulfide formation potential method

The guidelines for the monosulfide formation potential method are outlined in Appendix 8 of the detailed assessment protocols (MDBA 2010). In this study 3.6 g/L sucrose was used as an organic substrate instead of the 7.2 g/L outlined in the protocols. In addition to sampling after seven weeks, water samples were collected and analysed immediately after inundating the soils (i.e. Day 0). The pore-water pH and Eh were determined at Day 0.

The reactive iron (Fe) fraction in field moist sediments was extracted using 1.0 M HCl (Claff *et al.* 2010). The ferrous iron (Fe<sup>2+</sup>) and total iron (Fe<sup>2+</sup> + Fe<sup>3+</sup>) fractions were immediately fixed following extraction. The ferrous iron trap was made up from a phenanthroline solution with an ammonium acetate buffer (APHA 2005), and the total iron trap also included a hydroxylamine solution (APHA 2005). The iron species were quantified colorimetrically using a Hach DR 2800 spectrophotometer.

Redox potential and pH were determined using calibrated electrodes linked to a TPS WP-80 meter; Eh measurements are presented versus the standard hydrogen electrode. In this study the solid phase elemental sulfur fraction was extracted using toluene as a solvent and quantified by high-performance liquid chromatography (HPLC) (McGuire and Hamers 2000). Pore-water sulfide was preserved in zinc acetate prior to determination by the spectrophotometric method of Cline (1969).

#### 2.1.5. Mineral identification by x-ray diffraction

The guidelines for mineral identification by x-ray diffraction are outlined in the detailed assessment protocols (MDBA 2010).

### 2.2. Quality assurance and quality control

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

Reagent blanks and method blanks were prepared and analysed for each method. All blanks examined here were either at, or very close to, the limits of detection. On average, the frequencies of quality control samples processed were: 10% blanks, 10% laboratory duplicates, and 10% laboratory controls. The analytical precision was  $\pm 10\%$  for all analyses. In addition, for all samples, reactive metals and contaminant and metalloid dynamics tests were duplicated. For the reactive metals, two International Standards (Reference Stream Sediment STSD-2 and STSD-3 Canadian Certified Reference Materials) were processed in

an identical manner to the samples. Precision was excellent with the coefficient of variation (standard deviation/mean\*100) typically being in the range < 1 to 2 %.

## 3. RESULTS AND DISCUSSION

## 3.1. Summary of soil laboratory results

#### 3.1.1. Reactive metals data

The data are presented on a dry weight basis (mg kg<sup>-1</sup>) and shown in Table 3-1. The 24 hour reactive metals studies provide an indication of those metals and metalloids which are more strongly bound to minerals (or weakly soluble with an acid extraction) than would be soluble with a water extraction, and thus have the potential to be released. The use of a moderately strong acid (0.1 M HCl) should provide an indication of "stored metals" and metalloids associated with iron (Fe) and manganese (Mn) oxides and organic materials as well as acid soluble minerals. It is commonly found that the concentrations of metals and metalloids released using extractions are much higher than those found in solution (Gooddy *et al.* 1995). Although guideline values exist for soils and sediments, these are generally for total soil concentrations, and therefore, are not directly appropriate for the data from metal mobilisation studies. Nevertheless, they provide a basis for comparison; and concentrations close to or above guideline values indicate an elevated hazard.

The concentrations of metals and metalloids were below sediment quality guideline (SQG) values and soil ecological investigation levels (EIL) for those elements for which guidelines exist (Table 3-1). However, manganese (Mn) and especially iron (Fe) are considered high for these partial extractions.

Sample	Ag*	AI	As	Cd*	Co	Cr*	Cu	Fe	Mn	Ni	Pb	Sb*	Se*	v	Zn
12259_5.1	0.49	193	1.1	7.4	0.90	79	0.15	907	96	1.8	1.3	< 20	7.4	3.4	1.7
12259_5.2	1.8	117	2.3	13	0.51	26	1.7	96	88	0.89	1.2	< 16	6.9	1.8	0.79
12259_7.1	0.52	381	0.84	11	2.9	52	3.4	1761	357	2.0	3.8	< 21	20	6.5	2.3
12259_7.2	3.2	166	0.13	13	0.31	23	1.9	27	29	1.1	0.12	< 18	10	1.8	0.44
<sup>1</sup> SQG	1000	-	20	1500	-	80000	65	-	-	21	50	2000	-	-	200
<sup>2</sup> Soil EIL	-	-	20	3000	-	-	100	-	500	60	600	-	-	50	200

**Table 3-1 Schillers Lagoon (12259) reactive metals data.** Concentrations in mg kg<sup>-1</sup> and  $\mu$ g kg<sup>-1</sup> as indicated by asterisk.

\* Units are in µg kg<sup>-1</sup>

< value is below detection limit

<sup>1</sup>SQG: Sediment Quality Guideline Value (Australian and New Zealand Guidelines for Fresh and Marine Water Quality 2000) <sup>2</sup>Soil EIL: Soil – Ecological Investigation Level (NEPC 1999)

### 3.1.2. Contaminant and metalloid dynamics data

The contaminant and metalloid dynamics data for the four Schillers Lagoon (12259) soil materials examined are presented in Appendix 2, summarised in Table 3-2 and plotted against time in Figure 3-1 to Figure 3-3. Table 3-2 also compares the pore-water metal contents to the relevant national water quality guideline for environmental protection (ANZECC/ARMCANZ 2000). For cadmium (Cd) and antimony (Sb) the detection limits (due to sample dilution) were higher than ANZECC/ARMCANZ environmental protection guideline values.

Parameter	units	ANZECC Guidelines	Schillers Lagoon					
			Min.	Median	Max.			
pН		6.5-8.0	6.6	7.0	8.5			
SEC*	µS cm⁻¹	2200	77	121	168			
Eh	mV	-	-81	232	312			
Ag	µg l⁻¹	0.05	<0.01	<0.01	<0.04			
Al <sup>A</sup>	mg l⁻¹	0.055	0.16	0.44	6.03			
As <sup>B</sup>	µg l⁻¹	13	2.2	11	90			
Cd	µg l⁻¹	0.2	<0.01	<0.04	<0.3			
Со	µg l⁻¹	2.8	0.16	0.44	5.4			
Cr <sup>C</sup>	µg l⁻¹	1	<0.2	0.33	2.5			
Cu <sup>H</sup>	µg l⁻¹	1.4	1.4	2.4	15			
Fe <sup>l</sup>	mg l⁻¹	0.3	0.11	0.34	2.39			
Mn	µg l⁻¹	1700	2.7	48	738			
Ni <sup>H</sup>	µg l⁻¹	11	<0.50	1.2	7.7			
Pb <sup>H</sup>	µg l⁻¹	3.4	<0.06	0.75	6.0			
Sb	µg l⁻¹	9	<0.50	<1	<20			
Se	µg l⁻¹	11	<0.03	0.13	0.50			
V	µg l⁻¹	6	3.6	14	75			
Zn <sup>H</sup>	µg l⁻¹	8	<0.40	2.1	14			

Table 3-2 Summary of contaminant and metalloid dynamics data

Exceeded	Exceeded	Exceeded
ANZECC	ANZECC	ANZECC
Guideline (x1)	Guideline (x10)	Guideline (x100)

#### Notes.

The ANZECC guideline values for toxicants refer to the Ecosystem Protection – Freshwater Guideline for protection of 95% of biota in 'slightly-moderately disturbed' systems, as outlined in the Australian Water Quality Guidelines for Fresh and Marine Water Quality (ANZECC/ARMCANZ 2000).

\* ANZECC water quality upper guideline (125-2200  $\mu$ S cm<sup>-1</sup>) for freshwater lowland rivers in South-east Australia is provided for salinity (there are currently no trigger values defined for 'Wetlands'.)

<sup>A</sup> Guideline is for Aluminium in freshwater where pH > 6.5.

<sup>B</sup> Guideline assumes As in solution as Arsenic (AsV).

<sup>c</sup> Guideline is for Chromium is applicable to Chromium (CrVI) only.

<sup>*H*</sup> Hardness affected (refer to Guidelines).

<sup>1</sup> Fe Guideline for recreational purposes

The pH of the soil materials were generally within the range of ANZECC/ARMCANZ environmental protection guidelines, although one sample had a high pH (Figure 3-1). Most samples had a slightly higher pH on day 35 than on day 1, but there was no significant increase in pH.

The Eh showed a decrease over the day 35 period in all samples, from relatively oxidising initially on day one (Figure 3-1). By day 35, the Eh varied from slightly reducing to quite strongly reducing. The most reducing samples were the two surface soils samples. Salinities, as indicated by the SEC, were low (Figure 3-1). There was a trend of decreasing SEC in sample 12259\_5 and an increasing trend in samples from profile 12259\_7, but differences were relatively small.

Iron (Fe) concentrations increased in all samples, with a more dramatic increase in samples from profile 12259\_7 (Figure 3-2). All 4 samples, by day 35, were above the ANZECC/ARMCANZ environmental protection guideline for iron (Fe). The data are consistent with pH-Eh relationships for the stability fields of iron (Fe). Manganese (Mn) also increased with time in 3 of the 4 samples, but concentrations were well below the ANZECC/ARMCANZ environmental protection guideline value (Figure 3-2).

Aluminium (AI) concentrations were relatively high in most samples, and in one sample increased significantly with time up to 6 mg  $I^{-1}$  (Figure 3-1). Aluminium solubility should be very low at these pH values, and it is probable that the aluminium (AI) exists in colloidal form, possibly dispersed due to the effective dilution in the tests.

Arsenic (As) increased in all samples, but only breached the ANZECC/ARMCANZ environmental protection guideline value in the two samples from profile 12259\_5 (Figure 3-1). For one of these (12259\_5.2), the increase was very significant reaching 90  $\mu$ g l-1, reaching nearly 7 times the guideline value.

The two profiles displayed different concentrations of trace metals, with those from profile 12259\_7 generally having higher concentrations of cobalt (Co), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn). Most of these increased up to day 14, subsequently levelling out or decreasing in concentration (Figure 3-1 to Figure 3-3). Vanadium increased over time, being higher in the sub-surface soils (Figure 3-3).

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 lability 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; and 11) porosity (MDBA 2010). The relationship with pH for metals and metalloids is shown on Figure 3-4. There is little correlation with pH, although the pH variation was small. The correlation is slightly better with Eh, but a number of metals and metalloids show a better correlation with iron (Fe) in individual samples, suggesting a genetic control.

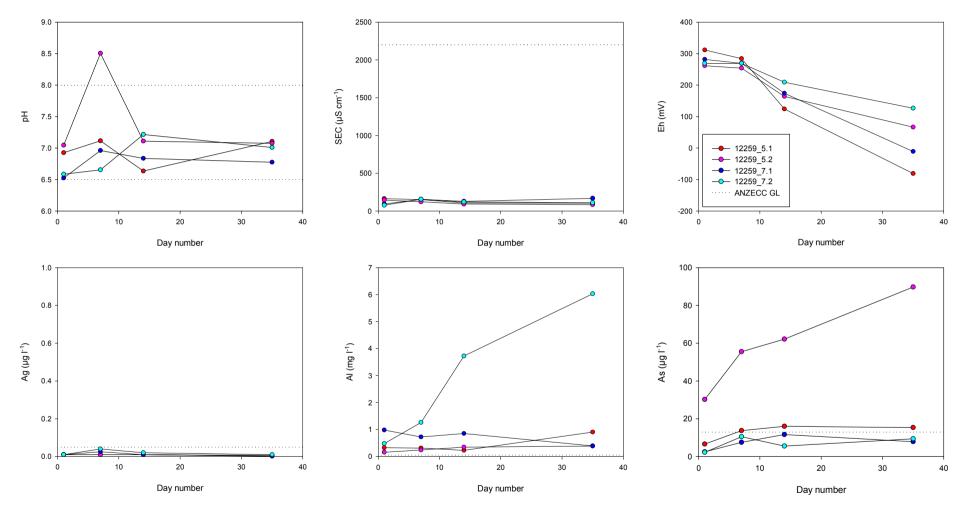


Figure 3-1 Contaminant and metalloid dynamics results for Schillers Lagoon (12259) soil materials for pH, SEC, Eh, silver (Ag), aluminium (AI) and arsenic (As).

Note: silver (Ag) in all samples was < detection limit, data represent detection limits which vary according to required dilutions.

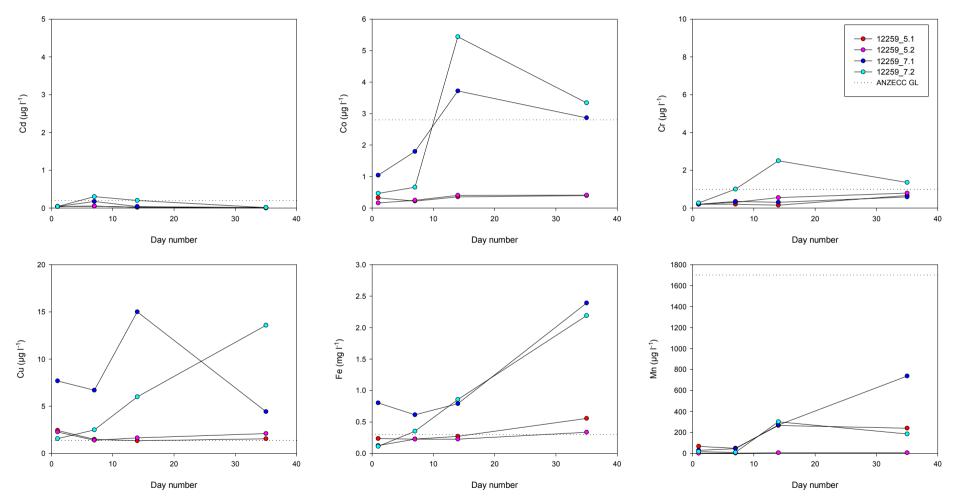


Figure 3-2 Contaminant and metalloid dynamics results for Schillers Lagoon (12259) soil materials for cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe) and manganese (Mn).

Note: cadmium (Cd) in all samples was < detection limit, data represent detection limits which vary according to required dilutions.

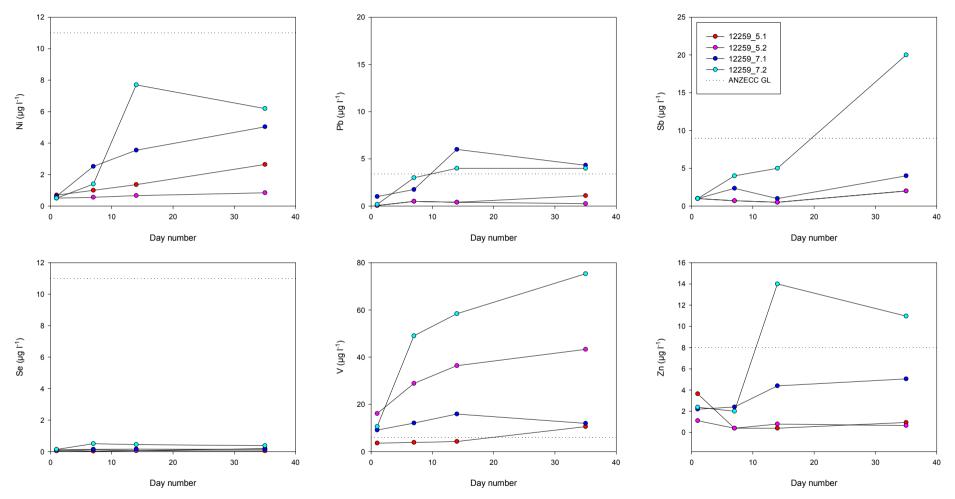


Figure 3-3 Contaminant and metalloid dynamics results for Schillers Lagoon (12259) soil materials for nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), vanadium (V) and zinc (Zn).

Note: antimony (Sb) was all < detection limit, data represent detection limits which vary according to required dilutions.

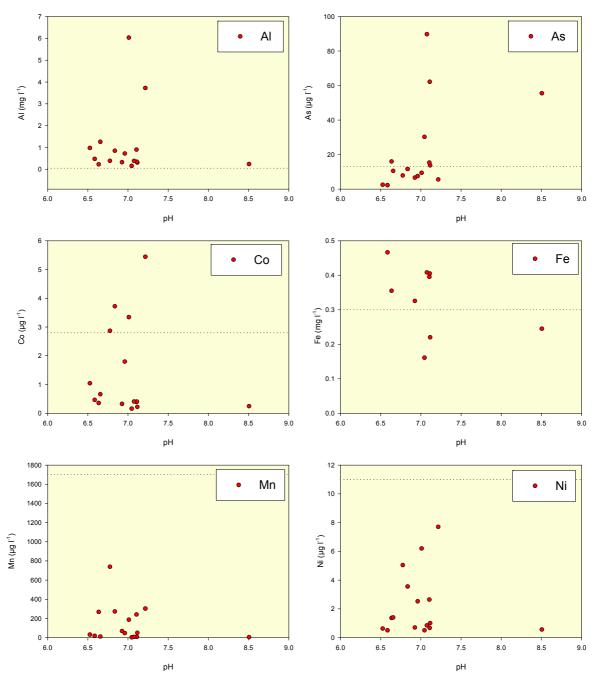


Figure 3-4 Selected trace elements plotted against pH.

#### 3.1.3. Monosulfide formation potential data

The monosulfide formation potential data for sample 12259\_7.1 are shown in Table 3-3. The pH of the soil water changed from 8.77 to 4.56 over the seven week incubation period (Figure 3-5). The decrease in pH is different from the contaminant and metalloid dynamics tests, where pH increased from 6.53 to 6.78 (Figure 3-1). This may be due to fermentation of organic substrate added (sucrose) which caused acidification of the pore-waters.

The Eh decreased significantly from 391 to 121 mV indicating a significant change to more reducing conditions. The Eh data are generally consistent with the Eh trend in the contaminant and metalloid dynamics experiments, where Eh decreased from 282 to -11 mV.

Inundation Time	Parameter	Units	12259_7.1
Day 0	Total Fe	mg/kg	2891
	Fe(II) <sup>-</sup>	mg/kg	2167
	Sulfate*	mg/kg	286
	рН		8.77
	Eh	mV	391
Week 7	рН		4.56
	Eh	mV	121
	S <sub>AV</sub>	Wt. %S	<0.01
	S°	Wt. %S	<0.01
	Pyrite-S	Wt. %S	0.01
	Dissolved S <sup>2-</sup>	µg/L	3614

Table 3-3 Summary of monosulfide formation potential data for the Schillers Lagoon surface soil material 12259\_7.1 after 7 weeks (3.6 g/L sucrose).

\* completed during Phase 1

The sample originally contained 0.02%  $S_{CR}$  (pyrite-S +  $S_{AV}$ ) and 0.26% ANC (Fitzpatrick *et al.* 2010). After 7 weeks, acid volatile sulfide ( $S_{AV}$ ) and elemental sulfur (S°) were both <0.01 %, and pyrite-S was 0.01 % (Table 3-3). It appears, therefore, that monosulfide formation (or pyrite formation as SCR was initially 0.02 wt. %) has not occurred in this sample during the tests. Dissolved sulfide concentrations were relatively high at 3614 µg l<sup>-1</sup> (Table 3-3), suggesting that redox conditions are sufficiently low for reduced sulfur to be stable as sulfide. Iron does not appear to be limiting in these soils as indicated by high acid soluble and dissolved iron in the contaminant and metalloid dynamics tests.

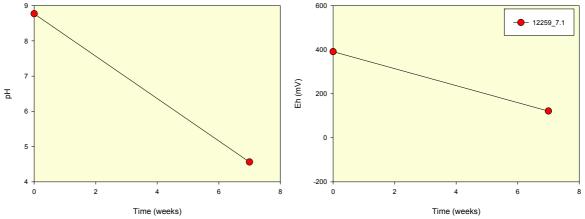


Figure 3-5 pH and Eh dynamics during monosulfide formation potential tests in surface soil sample 12259\_7.1 from Schillers Lagoon.

#### 3.1.4. Mineral identification by x-ray diffraction

No surface mineral efflorescences were identified or sampled at this wetland during the Phase 1 field survey.

### 3.2. Interpretation and discussion of results

The reactive metals and contaminant and metalloid dynamics tests undertaken as part of this Phase 2 assessment assist in determining the impacts on water quality by simulating the release of metal and metalloid concentrations that may occur under saturated conditions.

The 24 hour **reactive metals** studies provide an indication of those metals and metalloids which are more strongly bound to minerals (or weakly soluble with an acid extraction), and thus have the potential to be released. The use of a moderately strong acid (HCI) should provide an indication of "stored metals" and metalloids associated with iron (Fe) and manganese (Mn) oxides and organic materials as well as acid soluble minerals. It is commonly found that the concentrations of metals and metalloids released using extractions are much higher than those found in solution (Gooddy *et al.* 1995). Although guideline values exist for soils and sediments, these are generally for total soil concentrations, and therefore, are not directly appropriate for the data from metal mobilisation studies. Nevertheless, they provide a basis for comparison; and concentrations close to or above guideline values indicate an elevated hazard.

The metal and metalloid concentrations were generally below sediment quality guidelines and soil ecological investigation level values for those elements for which guideline values are available (Table 3-1). However, iron (Fe) was very high, although there are no guideline values for total soils. Nevertheless, the concentrations of many metals are sufficiently high (mg kg<sup>-1</sup>) compared to water quality guidelines (generally  $\mu$ g kg<sup>-1</sup>) that significant release could pose a hazard to soil and surface water quality.

The contaminant and metalloid dynamics test was designed to determine the release of metals and metalloids in soils. The data represent the availability of metals and metalloids from a weak extraction (water, and thus easily bioavailable) of saturated soils, and for dry wetland soils (especially below Lock 1), those easily mobilised from mineral surfaces and readily soluble mineral phases (such as salts). The exercise was undertaken in a batch process for time periods of 1 day, 7 days, 14 days and 35 days. This approach was aimed at understanding changes in concentrations over time. This is particularly important for dried soils which have been in contact with the atmosphere. The soil materials and the release/uptake of metals/metalloids are expected to change as the chemical environment changes from oxidising to reducing. Typical changes would be a reduction in redox potential (Eh), providing sufficient organic matter or other reducing agents are present, and an increase in pH (providing the soils contain or have the capacity to generate acid neutralising agents). The data can be compared to existing water quality guidelines, although care should be taken when extrapolating to surface waters without knowledge of hydrological conditions and natural chemical barriers. The impact on surface waters will be governed by the upward chemical flux which is a function of soil type, water flow, diffusion and the chemistry of the soils near the sediment-water interface. The mobility of most metals is commonly related to the stability of iron (Fe) and manganese (Mn) minerals. Under oxidising conditions iron (Fe) and manganese (Mn) oxide minerals are important sorbents for trace metals, whilst under very reducing conditions they may be incorporated into sulfide minerals. However, under moderately reducing conditions i.e. during the transition (suboxic) from oxidising to reducing conditions, iron (Fe) and manganese (Mn) are soluble and this is the period where metals may be released into solution and pose the greatest hazard.

The soils had slightly acidic to circumneutral pH on day one of the contaminant and metalloid dynamics tests, and the pH generally remained within the pH range for ANZECC/ARMCANZ environmental protection guideline values (Figure 3-1). The pH in these soils appears well buffered in agreement with the generally high buffering capacity of the soil materials (Grealish *et al.* 2010). The Eh on day 1 was slightly oxidising but decreased over time, in some cases becoming quite strongly reducing.

Although aluminium (AI) breached the ANZECC/ARMCANZ environmental protection guideline values by more than ten times, it is likely that the aluminium does not exist in its most toxic form (Al<sup>3+</sup>) at the pH measured, but as colloidal material smaller than the 0.45 µm filters used. The main control on a number of metals and metalloids is likely to be the Eh of the pore-waters. There is often a relationship between iron (Fe) and manganese (Mn) and a range of metals and metalloids, as oxidised minerals (oxides and oxyhydroxides) of iron and manganese, and reduced minerals of iron (monosulfides and pyrite) scavenge metals and metalloids and release them to solution under moderately reducing conditions. There is good relationship between these metals and metalloids, and for those elements which breached the ANZECC/ARMCANZ environmental protection guideline values. Eh is therefore considered the dominant control. There is a close correlation between metals and metalloids and iron concentration e.g. for arsenic in sample 12259\_ 5.2 (the sample with the highest arsenic), the correlation coefficient is 0.99 (n=4). For some elements *i.e.* iron (Fe), manganese (Mn), arsenic (As), copper (Cu), nickel (Ni) and vanadium (V), concentrations were increasing at the end of the tests, and this should be considered in any risk assessment.

The degree to which samples exceed guideline concentrations has been used to assign a degree of hazard (Table 3-4). The data are consistent with the generally low (and often negative) net acidities noted by Grealish *et al.* (2010) which suggest that these shallow soils will take little time to recover in terms of any acidification. This appears to be largely confirmed in the contaminant and metalloid dynamics experiments where most samples reached circumneutral to slightly alkaline pH during the experiments (Figure 3-1). The higher pH may limit the solubilities of most trace cation metals, but this will depend to a degree on redox conditions. At higher pH, some of the metalloids identified as a hazard in this study (arsenic and vanadium) may be stable due to limited adsorption of oxyanions at high pH. These metalloids may dissolve over longer timescales, at least until very reducing conditions in the field of iron sulfide stability, in which case they may be scavenged by precipitating iron (Fe) sulfides.

Degree of Hazard	Guideline Threshold	Metal/Metalloid		
No Hazard	Value below ANZECC/ARMCANZ guideline threshold	Ag, Mn, Ni, Se		
Low Hazard	Value exceeds ANZECC/ARMCANZ guideline threshold, but is less than 10x exceedance	As, Co, Cr, Fe, Pb, Zn		
Moderate Hazard	Value exceeds ANZECC/ARMCANZ guideline threshold by 10x or more, but is less than 100x exceedance	Al, Cu, V		
High Hazard	Value exceeds ANZECC/ARMCANZ guideline threshold by 100x or more			

Table 3-4 Summary of the degree of hazard associated with the measured contaminant and metalloid concentrations in Schillers Lagoon (12259).

Note: Cd and Sb were below detection limits in some samples due to dilutions, and therefore are likely to be in low or no hazard classification.

The monosulfide formation potential test assists in determining the propensity for monosulfides to form during future inundation. Water soluble sulfate concentrations were generally very high in most samples, with a range from 130-6917 mg kg<sup>-1</sup>. The sample used for this test contained no acid volatile sulfide ( $S_{AV}$ ) and low elemental sulfur ( $S^0$ ). The lack of acid volatile sulfide ( $S_{AV}$ ) ranks the monosulfide formation potential hazard as 'No hazard' (Table 3-5).

Table 3-5 Guideline thresholds for the degree of hazard associated with acid volatile sulfide ( $S_{AV}$ ) concentrations.

Degree of Hazard	Guideline Threshold
No Hazard	< 0.01 % S <sub>AV</sub>
Low Hazard	0.01 % S <sub>AV</sub>
Moderate Hazard	>0.01 – 0.05 % S <sub>AV</sub>
High Hazard	> 0.05 % S <sub>AV</sub>

## 4. RISK ASSESSMENT

#### 4.1. Risk assessment framework

Risk is a measure of both the consequences of a hazard occurring, and the likelihood of its occurrence (MDBA 2011). According to the National Environment Protection Measures (NEPM), risk is defined as "the probability in a certain timeframe that an adverse outcome will occur in a person, a group of people, plants, animals and/or the ecology of a specified area that is exposed to a particular dose or concentration of a hazardous agent, i.e. it depends on both the level of toxicity of hazardous agent and the level of exposure" (NEPC 1999).

The MDB Acid Sulfate Soils Risk Assessment Project developed a framework for determining risks to wetland values from acid sulfate soil hazards (MDBA 2011). The risk assessment framework has been applied in this study to determine the specific risks associated with acidification, contaminant mobilisation and de-oxygenation. In this risk assessment framework, a series of standardised tables are used to define and assess risk (MDBA 2011). The tables determine the consequence of a hazard occurring (Table 4-1), and a likelihood rating for the disturbance scenario for each hazard (Table 4-2). These two factors are then combined in a risk assessment matrix to determine the level of risk (Table 4-3).

Table 4-1 determines the level of consequence of a hazard occurring, ranging from insignificant to extreme, and primarily takes account of the environmental and water quality impacts, to the wetland values and/or adjacent waters.

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

Table 4-1 Standardised table used to determine the consequences of a hazard occurring, from	
MDBA (2011).	

Table 4-2 determines the likelihood (i.e. probability) of disturbance for each hazard, ranging from rare to almost certain. This requires an understanding of the nature and severity of the materials (including the extent of acid sulfate soil materials, the acid generating potential and the buffering capacity of wetland soil materials) as well as contributing factors influencing the risk (MDBA 2011). Examples of disturbance include: (i) rewetting of acid sulfate soil materials

after oxidation, (ii) acid sulfate soil materials that are currently inundated and may be oxidised, or (iii) acid sulfate soil materials that are currently inundated and may be dispersed by flushing (e.g. scouring flows) (MDBA 2011). As mentioned previously, the consequence of a hazard occurring and the likelihood rating for the disturbance scenario for each hazard are then ranked using a standardised risk assessment matrix (Table 4-3).

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

#### Table 4-2 Likelihood ratings for the disturbance scenario, from MDBA (2011).

# Table 4-3 Risk assessment matrix, adapted from Standards Australia & Standards New Zealand (2004).

Likelihood		Co	onsequences ca	tegory	
category	Extreme	Major	Moderate	Minor	Insignificant
Almost certain	Very High	Very High	High	Medium	Low
Likely	Very High	High	Medium	Medium	Low
Possible	High	High	Medium	Low	Low
Unlikely	High	Medium	Medium	Low	Very low
Rare	High	Medium	Low	Very low	Very low

It is suggested that:

- For very high risk immediate action is recommended.
- For high risk senior management attention is probably needed.
- Where a medium risk is identified management action may be recommended.
- Where the risk is low or very low, routine condition monitoring is suggested.

These categories of management responses have been kept quite broad to acknowledge that jurisdictional authorities and wetland managers may choose to adopt different approaches in dealing with acid sulfate soils. The imprecise nature of these management responses is intended to provide flexibility in jurisdictional and wetland manager responses to the risk ratings associated with the acid sulfate soil hazards (MDBA 2011).

### 4.2. Assessment of risks

Realisation of the main risks associated with acid sulfate soil hazards (acidification, contaminant mobilisation and deoxygenation) is highly dependent on transport and therefore on the surface and sub-surface hydrology. The risks are thus scenario dependent, and difficult to quantify without predicted changes of water flows and inputs and hydrogeological controls.

The consequences of a hazard, as outlined in Table 4-1, relate to reversible or irreversible damage to wetland values. Few studies have documented in sufficient detail the short or long term damage to inland wetland ecosystems and values caused by acid sulfate soil hazards, but short term consequences have been clearly illustrated e.g. for water quality and ecosystem impacts (McCarthy et al. 2006; Shand et al. 2010). Irreversible damage is difficult to assess due to lack of sufficient data over longer timescales and lack of knowledge, for example, on sub-surface soil recovery and metal mobilisation impacts on benthic organisms. Nevertheless, the following sections detail the hazards and likelihood of a number of scenarios and discuss consequences based on limited previous work (e.g. McCarthy et al. 2006; Shand et al. 2010). The risks to soil water quality and surface water quality are necessarily different. The risks to soil water quality in terms of acidification and contaminant release are easier to assess from the tests carried out in this study than the risks posed to surface water quality. The impacts on surface water quality will be largely controlled by upward flux of acidity and metals from the soils and sediments into the water column. This will be controlled by *inter alia* surface water volume and groundwater connectivity and level, soil type, hydraulic conductivity and degree and depth of soil cracking.

Schillers Lagoon (12259) has been classified as medium conservation status by the SA Murray-Darling Basin Natural Resources Management Board (Miles *et al.* 2010).

#### 4.2.1. Risks associated with acidification

The generally low net acidities in the soils of Schillers Lagoon (12259) suggest that the overall acidification hazard is likely to be minimal. The ageing of soils during Phase 1 agreed with contaminant and metalloid dynamics tests in suggesting that acidification is unlikely to be an issue. The acidification hazard is therefore considered to be low.

The wetland contained surface water when the samples were collected, however, it is a managed wetland and had been closed in October 2006, opened in March 2009, closed in September 2009, and opened again in February 2010. The soils are, therefore, likely to have had a complex evolution in terms of wetting and drying, and oxidation and reduction. Some soils contained yellow/brown mottles which suggests that a return to fully reducing conditions had not occurred. The wetland is close to the river, and separated from the river by a raised floodplain. It is connected to the river by a small creek, and is managed by a regulating structure on the creek. The likelihood of disturbance is therefore selected as *likely*, as water levels are known to vary significantly in the wetland. The consequences for soil ecology from acidification are likely to be small in the surface and sub-soils as they are generally well buffered with high ANC. The results from the contaminant and metalloid dynamics experiments suggest that an overall rating for consequence would be *insignificant* if further oxidation of the soils occurred. This provides a risk rating for soil acidification of low if the soils are dried. A rating for surface water acidification will most likely also be minimal. The smallest risk to surface water acidification would be where high flows were available to both dilute any locally derived acidity and will induce transport acidity downwards in the soil profile where ANC is more abundant. In the case of Schillers Lagoon (12259), acidification of surface water would potentially be *insignificant*, and therefore the risk to surface water acidification is therefore classed as low.

#### 4.2.2. Risks associated with contaminant mobilisation

The risks of metal and metalloid mobilisation are controlled primarily by metal abundance and availability, geochemical controls on speciation and transport mechanisms. The master variables pH and Eh exert a direct major influence on the solubility of individual metals and metalloids and minerals such as iron (Fe), iron (Fe) and manganese (Mn) oxides and hydroxides which are important sorbents of metal and metalloids species. The low acidification hazard due to the oxidation of sulfide minerals means that metals and metalloids are not likely to be present at high concentrations. Reduction processes may lead to reincorporation of metals and metalloids into sulfide minerals (following sulfate reduction). but at intermediate redox potentials mobility may be high where iron (Fe) and manganese (Mn) are soluble. The reactive metals results attest to the limited availability and mobility of a number of metals, the exceptions being manganese (Mn), aluminium (Al) and iron (Fe). The concentrations of most metals and metalloids were generally low and below ANZECC/ARMCANZ environmental protection guidelines. The exceptions were aluminium (AI), copper (Cu) and vanadium (V). Aluminium (AI) is likely to be present as colloidal material at the circumneutral pH observed. The dissolved toxic trivalent form of aluminium  $(Al^{3+})$  is not likely to be present, except under acidic conditions (pH < 5.5), and aluminium is unlikely to be impacted by a return to reducing conditions since it is not redox-sensitive. The oxyanion vanadium (V) increased throughout the 35 day experiments and should be considered a future hazard. Arsenic (As) and copper (Cu) also increased with time and should be considered for risks associated with longer timescales. It is not known how long the Eh would continue to decrease, but further decreases would allow the reductive dissolution of iron (Fe) and manganese (Mn) oxyhydroxides and any associated adsorbed metals and metalloids.

Although the timescales cannot be assessed with existing information, the data suggest that metal availability is significant for a number of metals and metalloids. Comparisons with other studies (e.g. Nelwart Lagoon, Shand *et al.* 2010), suggest that at the pH levels of the surface layers after 35 days of the contaminant and metalloid dynamics tests, reductive processes may occur rapidly once initiated if there is sufficient organic matter available, and soil recovery may be rapid. The risks of metal and metalloid mobilisation are dependent on the degree of oxidation of soils and the depth to which oxidation occurs, hence related to the time of drying. For the soils of Schillers Lagoon (12259), the risks due to rewetting cannot be fully assessed as the soils were largely un-oxidised, although the wetland had dried previously (Grealish *et al.* 2010) and the availability may relate to previous oxidation events. The results should be seen in this context, which may represent a best case scenario, as with future drying and oxidation of the soils the concentrations of metals may be higher due to release from pyrite.

The main solutes likely to present a longer term hazard are copper (Cu) and vanadium (V) which exceeded ANZECC/ARMCANZ environmental protection guidelines more than ten times, and also arsenic (As), cobalt (Co), chromium (Cr), iron (Fe), lead (Pb) and zinc (Zn). The connection to the river means that impacts on the river are possible, especially at high flow, but under this scenario dilution effects will also be significant. Taking into account the metal and metalloid mobility assessed and limitations discussed above, a *moderate* rating is applied for consequence. This provides a risk rating for contaminant mobilisation in soils of **medium** (Table 4-4).

A rating for surface water impacts from metals and metalloids will also depend on the degree of drying and oxidation, and also on surface and sub-surface hydrology. The circumneutral pH values by day 35 in the contaminant and metalloid dynamics tests undertaken in this study, however, mean that longer term impacts for many metals are unlikely. The risks for surface waters will relate to those metals and metalloids discussed above, and decrease as the soils become more reducing if the Eh falls to within the stability field for sulfide minerals (due to scavenging by the sulfide minerals). Chemical reactions with soils and interactions at the soil/water interface are likely to diminish hazards from upward soil metal flux. The highest risk is likely to be following drying and during low flows where the soil to water ratio is high: metals will be most concentrated. The risk to surface metal and metalloid flux is considered lowest where high flows are available to both dilute metal and metalloid concentrations and transport these downwards in the soil profile. Due to enhanced mobility of metalloids at higher pH, the hazard cannot be assumed to be insignificant with the limited time series data available in this study, hence a *minor* rating for consequence is applied. The risk to surface waters from metal mobilisation is therefore considered to be **medium** (Table 4-4). The phase 1 study sampled three surface waters and noted high concentrations above ANZECC/ARMCANZ environmental protection guidelines for some contaminants. This included the nutrients ammonium (NH<sub>4</sub>) and phosphate (PO<sub>4</sub>) as well as zinc (Zn). These results support the medium risks suggested above.

#### 4.2.3. Risks associated with de-oxygenation

Monosulfidic materials are considered the main cause of deoxygenation risk in acid sulfate soils. The water soluble sulfate concentrations in the sample were generally high and above the trigger value for monosulfidic black ooze formation (MDBA 2010). However, there was no evidence of monosulfides being present in the wetland during the Phase 1 field survey, and despite the high water soluble sulfate concentrations there was no monosulfide formation during the laboratory experiments. The consequence from monosulfide disturbance is therefore considered to be *insignificant* and as such the risk rating for deoxygenation is **low** (Table 4-4).

# Table 4-4 Summary of risks associated with acid sulfate soil materials in Schillers Lagoon (12259).

Acidifica	tion Risk	Contaminant	Deoxygenation	
Soil	Water	Soil	Water	
Low	Low	Medium	Medium	Low

## 5. BROAD ACID SULFATE SOIL MANAGEMENT OPTIONS

The options available for rehabilitation of inland waterways containing acid sulfate soils has recently been reviewed (Baldwin & Fraser 2009) and incorporated into the *National guidance on managing acid sulfate soils in inland aquatic ecosystems* (EPHC & NRMMC 2011; see Table 5-1). The national guidance document provides a hierarchy of management options for managing acid sulfate soils in inland aquatic ecosystems including:

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

In designing a management strategy for dealing with acid sulfate soils in affected inland wetlands, other values and uses of a wetland need to be taken into account to ensure that any intervention is compatible with other management plans and objectives for the wetland. The medium conservation status for this wetland suggests that the management responses required should align with those suggested following the risk assessment ratings (Table 4-3).

A number of options for treating acid sulfate soils in inland wetlands have been identified (see Table 5-1). By far the best option is not to allow acid sulfate soils to build up in the first instance. This requires removing the source of sulfate from the wetland, for example, by lowering saline water tables and/or introducing frequent wetting and drying cycles to the wetland so that the amount of sulfidic material that can build up in the sediments during wet phases is limited, hence reducing the likely environmental damage (acidification, metal release or deoxygenation) that would occur as a consequence of drying.

If acid sulfate soils have formed, prevention of oxidation, usually by keeping the sediments inundated to sufficient depth, is a potential strategy. If oxidation of acid sulfate soils occurs and the sediment and/or water column acidifies, neutralisation may be necessary.

Schillers Lagoon (12259) contained surface water at the time of sampling. The first two options in Table 5-1 provide the best options for minimising damage to ecosystem health and costs. Risks associated with soil and surface water acidification are low and likely to be very local in nature. The main risk is probably due to contaminant mobilisation within the confines of the wetland.

A number of metals and metalloids have been identified as posing some risk. Prevention options, including keeping the wetland fully saturated, will depend on connectivity with the river and the availability of water for this purpose. Although acidification is not seen as a serious risk, some of the metals and metalloids identified are mobile at higher pH, particularly under moderately reducing conditions where iron (Fe) and manganese (Mn) are soluble. At lower Eh, where sulfide minerals are stable, these metals and metalloids are likely to be scavenged by sulfides and be less of a risk. However, drying and oxidation may release these contaminants again, hence wetting-drying episodes will simply cycle these contaminants between different mineral phases and solution. The data from this study do not provide sufficient information on which to base best management options, but are valuable in showing what contaminants are available and their potential impact under different management scenarios.

Since the risks are so scenario dependent, it is recommended that surface water monitoring be undertaken at this wetland if any disturbance occurs, particularly because a number of contaminants were noted to increase in some samples over the 35 days of the contaminant and metalloid dynamics experiments. Based on the data from this study and elsewhere (Shand *et al.* 2010), it is likely that soil recovery from any future acidification or metal and metalloid release will be variable and depend on the actual pH and Eh of the soil materials prior to recovery. The impacts on surface and sub-surface ecosystems are not well understood and are worthy of further work, particularly long term impacts on ecosystem functionality and diversity.

Management Objective	Activities
1. Minimising the formation of acid sulfate soils in inland aquatic ecosystems	<ul> <li>Reduce secondary salinisation through:</li> <li>Lowering saline water tables</li> <li>Maintaining the freshwater lens between saline groundwater and the aquatic ecosystem</li> <li>Stopping the delivery of irrigation return water</li> <li>Incorporating a more natural flow regime.</li> </ul>
2. Preventing oxidation of acid sulfate soils or controlled oxidation to remove acid sulfate soils	<ul> <li>Preventing oxidation:</li> <li>Keep the sediments covered by water</li> <li>Avoid flow regimes that could re-suspend sediments.</li> <li>Controlled oxidation:</li> <li>Assess whether neutralising capacity of the sediments and water far exceeds the acidity produced by oxidation</li> </ul>
3. Controlling or treating acidification	<ul> <li>Assess the risk of deoxygenation and metal release. Monitor intervention and have a contingency plan to ensure avoidance of these risks.</li> <li>Neutralise water column and/or sediments by adding chemical ameliorants</li> <li>Add organic matter to promote bioremediation by micro-organisms</li> <li>Use stored alkalinity in the ecosystem.</li> </ul>
4. Protecting adjacent or downstream environments if treatment of the affected aquatic ecosystem is not feasible	<ul> <li>Isolate the site</li> <li>Neutralise and dilute surface water</li> <li>Treat discharge waters by neutralisation or biological treatment.</li> </ul>
5. Limited further intervention	<ul> <li>Assess risk</li> <li>Communicate with stakeholders</li> <li>Undertake monitoring</li> <li>Assess responsibilities and obligations and take action as required.</li> </ul>

 Table 5-1 Summary of management options and possible activities, from EPHC & NRMMC (2011).

## REFERENCES

ANZECC/ARMCANZ 2000 Australian and New Zealand Guidelines for Fresh and Marine Water Quality, Australian and New Zealand Environment and Conservation Council and agriculture and Resource Management Council of Australia and New Zealand, Canberra.

APHA 2005 Standard methods for the examination of water and wastewater (21st Ed.). (American Public Health Association - American Water Works Association: Baltimore, USA).

Baldwin D & Fraser M 2009 Rehabilitation options for inland waterways impacted by sulfidic sediments. *Journal of Environmental Management* 91:311–319.

Claff SR, Sullivan LA, Burton ED & Bush RT 2010 A sequential extraction procedure for acid sulfate soils: Partitioning of iron. *Geoderma* **155**, 224-230.

Cline ID 1969 Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnology and Oceanography* **14**, 454-458.

EPHC & NRMMC (Environment Protection and Heritage Council and Natural Resource Management Ministerial Council) 2011 National Guidance for the management of acid sulfate soils in inland aquatic ecosystems, Canberra, ACT.

Fitzpatrick RW, Shand P, Thomas M, Grealish G, McClure S, Merry RH & Baker A 2010 Acid Sulfate Soil investigations of vertical and lateral changes with time in five managed wetlands between Lock 1 and Wellington. CSIRO Land and Water Science Report 03/10.

Fitzpatrick RW, Shand P, Thomas M, Merry RH, Raven MD & Simpson S 2008 Acid sulfate soils in subaqueous, waterlogged and drained soil environments of nine wetlands below Blanchetown (Lock 1), South Australia: properties, genesis, risks and management. CSIRO Land and Water Science Report 42/08.

Gooddy DC, Shand P, Kinniburgh DG & Van Riemsdijk WH 1995 Field-based partition coefficients for trace elements in soil solutions. *Journal of Soil Science*, 46, 265-285.

Grealish G, Fitzpatrick RW & Shand P 2011 Assessment of Acid Sulfate Soil Materials in the Lock 1 to Wellington Region of the Murray-Darling Basin. CSIRO: Water for a Healthy Country National Research Flagship.

Grealish G, Shand P, Grocke S, Baker A, Fitzpatrick R & Hicks W 2010 Assessment of Acid Sulfate Soil Materials in Lock 1 to Lock 5 Region of the Murray-Darling Basin. CSIRO: Water for a Healthy Country National Research Flagship. 769 pp.

McCarthy B, Conalin A, D'Santos P & Baldwin DS 2006 Acidification, salinisation and fish kills at an inland wetland in south-eastern Australia following partial drying. Ecological Management and Restoration, vol. 7, pp. 218–23.

McGuire MM & Hamers RJ 2000 Extraction and quantitative analysis of elemental sulfur from sulfide mineral surfaces by high-performance liquid chromatography. *Environmental Science & Technology* **34**, 4651-4655.

MDBA 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.

MDBA 2011 *Acid sulfate soils in the Murray–Darling Basin*, Murray–Darling Basin Authority, Canberra. MDBA Publication No. 147/11.

Miles M, Wainwright P, Gonzalez D, Turner R, Frankiewicz D & Jones L 2010 Application of the South Australian River Murray wetland prioritisation methodology, Department for Environment and Heritage, Adelaide.

NEPC 1999 National environment protection (assessment of site contamination) measure 1999. National Environment Protection Council.

Shand P, Merry R, Grocke S, Thomas M, Fitzpatrick RW, Thomas B, Baker A & Creeper N 2010 Water and soil quality impacts during reflooding of Nelwart Lagoon, South Australia. CSIRO: Water for a Healthy Country National Research Flagship. 158 pp.

Standards Australia & Standards New Zealand 2004, HB 436: 2004, Risk Management, Sydney, NSW.

## APPENDICES

## **APPENDIX 1 REACTIVE METALS DATA**

Schillers Lagoon (12259)

Sample	Depth	Analysis	Ag*	AI	As	Cd*	Со	Cr*	Cu	Fe	Mn	Ni	Pb	Sb*	Se*	V	Zn
		а	< 0.49	171	1.3	7.4	0.87	69	0.20	915	90	2.0	1.3	< 20	7.4	3.5	1.6
12259_5.1	0-2	b	< 0.49	214	0.96	7.4	0.93	89	0.10	900	102	1.6	1.3	< 20	7.4	3.3	1.8
		а	2.0	131	2.6	17	0.56	32	1.8	109	141	1.1	1.3	< 16	7.9	1.9	1.0
12259_5.2	2-10	b	1.6	102	2.0	9.9	0.46	20	1.7	82	35	0.69	1.0	< 16	5.9	1.7	0.56
		а	< 0.52	381	0.75	10	2.8	57	2.9	1866	323	1.8	3.8	< 21	18	6.4	2.4
12259_7.1	0-2	b	< 0.52	380	0.92	12	3.0	47	4.0	1655	391	2.2	3.7	< 21	21	6.6	2.2
	0.40	а	3.7	173	0.15	13	0.30	23	1.9	28	29	1.3	0.14	< 18	12	1.9	0.44
12259_7.2	2-10	b	2.8	159	0.12	14	0.32	23	1.8	26	29	0.85	0.09	< 18	9.2	1.6	0.44

Units are mg kg<sup>-1</sup> unless indicated otherwise as below

\* Units are in µg kg<sup>-1</sup>

< value is below detection limit

## **APPENDIX 2 CONTAMINANT AND METALLOID DYNAMICS DATA**

Schillers Lagoon (12259)

Sample	Day	Depth cm	Analysis	Eh mV	<b>EC</b> μS/cm	рН	<b>Ag</b> μg/L	AI mg/L	<b>As</b> μg/L	Cd µg/L	<b>Co</b> μg/L	<b>Cr</b> μg/L	<b>Cu</b> μg/L	<b>Fe</b> mg/L	<b>Mn</b> μg/L	Ni µg/L	<b>Ρb</b> μg/L	Sb µg/L	Se µg/L	<b>ν</b> μg/L	<b>Zn</b> μg/L
			а	314	141	7.26	< 0.01	0.25	6.1	< 0.04	0.17	<0.2	1.5	0.16	31	< 0.5	< 0.06	<1	0.05	2.9	<0.8
	1		b a	309	185	6.59	<0.01	0.20	7.0	<0.04	0.17	<0.2	3.4	0.10	105	0.89	<0.06	<1	0.05	4.3	6.5
	-		a	284	133	7.32	<0.01	0.45	12	<0.04	0.40	0.20	1.8	0.31	41	1.0	<0.00	<0.7	< 0.03	3.3	<0.4
12259 5.1	7	0-2	a b	284	169	6.91	<0.01	0.43	15	<0.05	0.21	0.20	1.0	0.23	58	0.96	<0.5	<0.7	< 0.03	4.5	<0.4
12259_5.1		0-2	a	189	109	6.61	< 0.01	0.17	16	<0.03	0.23	0.20	2.1	0.17	116	1.2	<0.3	< 0.7	0.03	3.7	0.40
	14		b a	59	101	6.66	<0.01	0.33	16	<0.02	0.23	0.10	0.60	0.20	420	1.5	<0.4	< 0.5	0.04	4.9	0.40
		-	a	-81	112	7.03	0.01	0.76	10	<0.02	0.42	0.20	1.1	0.20	272	2.5	0.78	<2	0.08	4.9	0.40
	35		a b	-81	95	7.18	< 0.01	1.1	21	0.00	0.30	0.64	2.0	0.47	212	2.3	1.4	<2	0.00	11	0.90
			a	264	155	7.12	<0.01	0.14	27	< 0.00	0.43	<0.2	2.2	0.04	3.2	< 0.5	<0.06	<1	0.03	16	<0.8
	1		b	259	134	6.97	<0.01	0.14	33	<0.04	0.17	<0.2	2.2	0.11	2.2	<0.5	<0.06	<1	0.04	16	1.4
	_		a	254	116	8.90	< 0.01	0.17	46	<0.05	0.20	0.30	1.0	0.17	3.4	0.36	< 0.5	<0.7	0.09	26	<0.4
12259 5.2	7	2-10	b	254	128	8.11	< 0.01	0.31	65	< 0.05	0.29	0.30	1.8	0.29	4.8	0.76	< 0.5	< 0.7	0.15	31	0.40
			а	149	92	7.24	< 0.01	0.49	68	< 0.02	0.52	0.60	1.8	0.30	8.3	0.84	< 0.4	< 0.5	0.06	38	1.2
	14		b	179	92	6.98	<0.01	0.21	57	<0.02	0.29	0.50	1.5	0.15	4.5	0.49	<0.4	<0.5	0.07	35	0.40
	35		а	64	85	6.87	<0.01	0.38	89	<0.001	0.30	0.72	1.9	0.37	4.7	0.67	0.14	<2	0.16	45	0.42
	35		b	69	85	7.28	<0.001	0.39	91	<0.001	0.52	0.86	2.4	0.31	9.1	1.0	0.38	<2	0.22	42	0.88
	1		а	284	120	6.38	<0.01	0.60	2.9	<0.04	1.5	<0.2	11	0.62	49	0.75	1.4	<1	0.15	8.5	1.8
	I		b	279	64	6.67	<0.01	1.4	2.0	<0.04	0.53	<0.2	4.3	0.98	12	<0.5	0.61	<1	0.09	9.7	2.6
	7		а	264	164	7.06	<0.01	0.44	7.0	<0.05	1.2	0.20	4.4	0.43	45	2.0	<0.5	<0.7	0.09	8.7	0.80
12259_7.1		0-2	b	274	146	6.86	<0.04	1.0	8.0	<0.3	2.4	<0.5	9.0	0.80	48	3.0	<3	<4	<0.2	16	4.0
	14		а	169	126	6.76	<0.01	0.83	11	<0.04	3.5	<0.2	13	0.78	283	3.2	5.6	<1	0.16	14	4.8
		_	b	179	129	6.91	<0.01	0.88	12	< 0.04	3.9	0.40	17	0.80	261	3.9	6.4	<1	0.16	18	4.0
	35		а	-1.0	176	6.49	< 0.01	0.34	8.0	0.01	3.1	0.59	2.8	2.9	956	4.7	2.4	<4	0.11	7.9	3.9
			b	-21	160	7.06	< 0.01	0.44	7.7	0.01	2.6	0.59	6.1	1.9	521	5.4	6.2	<4	0.16	16	6.2
	1		а	269	77	6.55	< 0.01	0.45	2.5	< 0.04	0.48	0.33	1.9	0.11	17	<0.5	0.16	<1	0.13	11	2.2
		-	b	269	78	6.62	< 0.01	0.50	2.0	< 0.04	0.45	< 0.2	1.2	0.12	19	< 0.5	0.20	<1	0.15	10	2.6
40050 7.0	7	0.40	a	264	158	6.68	< 0.04	1.1	10.0	< 0.3	0.76	1.5	3.0	0.35	11	1.6	<3	<4	0.60	51	2.0
12259_7.2		2-10	b	274	154 120	6.63 7.58	< 0.04	1.4	11 5.0	<0.3 <0.2	0.56	< 0.5	2.0	0.36	10.0	1.2	<3	<4	0.40	48	<2
	14		a b	174 244	120	6.85	<0.02 <0.02	3.9 3.5	5.0 6.0	<0.2	5.2 5.6	2.0 3.0	6.0 6.0	0.96	255 349	7.0 8.4	<4 <4	<5 <5	0.60	66 51	16 12
		4	D a	124	120	6.91	<0.02	3.5 5.9	0.0 11	0.01	3.2	3.0 1.8	8.1	2.3	349 143	0.4 5.3	<4 <4	<20	0.30	96	12
	35		a b	124	109	7.11	< 0.01	5.9 6.2	7.7	<0.01	3.2	0.87	0.1 19	2.3	228	5.3 7.0	<4 <4	<20	0.42	96 55	9.8
			U	129	112	1.11	<u>~0.01</u>	0.2	1.1	NU.U I	3.0	0.07	19	Z. I	220	1.0	<u>\</u> 4	<u>~20</u>	0.34	- 55	9.0

< value is below detection limit

## **APPENDIX 3 MONOSULFIDE FORMATION POTENTIAL DATA**

#### Schillers Lagoon (12259)

MBO Format	ion Potent	ial (MBO FP) - DAY 0					IRON	DATA			DAY 0								
				т	otal Reactiv	/e Fe (mg/k	g)		Fe(II) (I	mg/kg)			Eh (	mV)		рН			
Sample No.	org	Site Name	Site ID	Replicate	Replicate	Mean	+/-	Replicate	Replicate	Mean	+/-	Replicate	Replicate	Mean	+/-	Replicate	Replicate	Mean	+/-
				1	2			1	2			1	2			1	2		
31	csiro	Schillers Lagoon	12259_7.1 (MD1232)	2950	2832	2891	59	2408	1926	2167	241	395	387	391	4	8.65	8.89	8.77	0.12
32	-	Blank	-	0.3	0.1	0.2	0.1	<0.1	<0.1	<0.1	<0.1	183	186	185	2	6.17	6.10	6.14	0.04

#### MBO Formation Potential (MBO FP) - Week 7

					AVS	(%S)		Pyrite (%S)				ES (%S)				pH					Eh (	mV)		Aqueous Sulfide (µg/L)			)
Sample No.	org	Site Name	Site ID	Replicate	Replicate	Mean	+/-	Replicate	Replicate	Mean	+/-	Replicate	Replicate	Mean	+/-	Replicate	Replicate	Mean	+/-	Replicate	Replicate	Mean	+/-	Replicate	Replicate	Mean	+/-
				1	2			1	2			1	2			1	2			1	2			1	2		
31	csiro	Schillers Lagoon	12259_7.1 (MD1232)	0.00	0.00	<0.01	<0.01	0.00	0.01	0.01	0.01	0.00	0.00	<0.01	<0.01	4.51	4.61	4.56	0.05	143	99	121	22	4720	2509	3614	1106
32	csiro	Blank														5.45	5.42	5.44	0.02	325	338	331	6	< 0.1	< 0.1	< 0.1	<0.1

Contact Us Phone: 1300 363 400 +61 3 9545 2176 Email: enquiries@csiro.au Web: www.csiro.au

#### Your CSIRO

Australia is founding its future on science and innovation. Its national science agency, CSIRO, is a powerhouse of ideas, technologies and skills for building prosperity, growth, health and sustainability. It serves governments, industries, business and communities across the nation.