



# Assessment of Acid Sulfate Soil Materials (Phase 2) Coolcha Lagoon, South Australia

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Report to the Murray-Darling Basin Authority

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## EXECUTIVE SUMMARY

An initial Phase 1 acid sulfate soil investigation of Coolcha Lagoon during March 2008 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 Coolcha Lagoon to determine the nature, severity and the specific risks associated with acid sulfate soil materials.

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 (AI) 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 and soil ecological investigation levels for those elements where guidelines are available. The concentrations for this reactive metals partial extraction are considered to be moderately high for aluminium (AI), 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 Coolcha Lagoon, cobalt (Co) and iron (Fe) were assigned a moderate hazard with concentrations exceeding ANZECC/ARMCANZ environmental protection guidelines by more than 10 times. Arsenic (As), nickel (Ni) and zinc (Zn) were also significantly above ANZECC/ARMCANZ environmental protection guideline values (3-4 times) and represent significant hazards. The dominant control on metal solubility is the pH of the extractions. All samples showed a decrease in Eh, but only one sample decreased sufficiently for iron to become soluble. The Eh was not low enough for sulfate reduction. The increase in iron (Fe) was associated with the release of arsenic (As), probably due to the reductive dissolution of iron oxides/oxyhydroxides. Although pH is an initial control on most metals, longer term release of metals and particularly metalloids pose a risk to the soil materials studied.

Coolcha Lagoon has been classified as medium conservation status by the SA Murray-Darling Basin Natural Resources Management Board (Miles *et al.* 2010). 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 **medium** risk rating for *acidification* and a **high** *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 to medium** risk rating for *acidification* and a **medium to high** risk rating for *contaminant* **mobilisation**. The risk associated with *deoxygenation* from monosulfides is considered to be **low** as there was no evidence of monosulfides forming either in the wetland or during laboratory experiments.

In designing a management strategy for dealing with acid sulfate soils in Coolcha Lagoon, 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 wetland soils studied were largely dry at the time of sampling, therefore management options considered should relate to controlling or treating acidification and the protection of connected or adjacent wetlands. Due to the medium to high risks to the wetland values associated with acidification and contaminant mobilisation in Coolcha Lagoon, a monitoring program is strongly 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 Soil 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 Coolcha Lagoon 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), Coolcha Lagoon was selected for Phase 2 detailed assessment.

The Phase 1 assessment sampled 6 sites (Figure 1-1) from the wetland which comprised cracking clay soils. The wetland was dry at the time of sampling. Sites CLG 1-3 were sampled from a transect in the western part of the wetland and sites CLG 4-6 from a transect towards the eastern part of the wetland. The Phase 1 assessment identified 3 high priority sites based on the presence of sulfuric materials, no high priority sites based on the presence of hypersulfidic materials, 2 high priority sites based on hyposulfidic materials with SCR  $\geq$  0.10% and 4 moderate priority sites based on the presence of hypersulfidic materials were carried out on selected surface soil samples from two sites (CLG 1 and CLG 3) identified in the Phase 1 assessment (Grealish *et al.* 2010).

Table 1-1 Priority ranking criteria adopted by the Scientific Reference Panel of the	he 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.



#### Figure 1-1 Coolcha Lagoon aerial photograph with Phase 1 sampling sites identified.

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 Coolcha Lagoon is presented in Table 1-3.

#### Table 1-2 Rationale for Phase 2 sample selection, from MDBA (2010)

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 a 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	Coolcha Lagoon samples	Sample depth (cm)	Number of samples analysed
Reactive metals	CLG1.1	0-10	4
	CLG1.2	10-20	
	CLG3.1	0-5	
	CLG3.2	5-10	
Contaminant and	CLG1.1	0-10	4
metalloid dynamics	CLG1.2	10-20	
	CLG3.1	0-5	
	CLG3.2	5-10	
Monosulfide formation potential	CLG3.1	0-5	1
Mineral identification by X-ray diffraction (XRD)	-		0

#### Table 1-3 Summary of Coolcha Lagoon 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 is 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 and 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 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 values and soil ecological investigation levels for those elements for which guidelines exist. The concentrations for most reactive metals and metalloids are relatively low, but relatively high for aluminium (AI), iron (Fe) and manganese (Mn) (Table 3-1).

51	2.4	335	61	4.5					
			01	4.5	1.8	< 1.8	20	7.8	3.4
63	1.8	413	45	4.3	1.3	< 2.1	38	9.3	3.9
111	4.4	920	169	6.6	3.3	< 1.7	45	12	6.9
50	2.2	680	76	6.0	4.8	< 2.1	34	9.7	4.3
80000	65	-	-	21	50	2000	-	-	200
-	100	-	500	60	600	-	-	50	200
8	63 111 50 00000 -	63     1.8       111     4.4       50     2.2       30000     65       -     100	63     1.8     413       111     4.4     920       50     2.2     680       00000     65     -       -     100     -	63         1.8         413         45           111         4.4         920         169           50         2.2         680         76           00000         65         -         -           -         100         -         500	63       1.8       413       45       4.3         111       4.4       920       169       6.6         50       2.2       680       76       6.0         00000       65       -       -       21         -       100       -       500       60	63         1.8         413         45         4.3         1.3           111         4.4         920         169         6.6         3.3           50         2.2         680         76         6.0         4.8           00000         65         -         -         21         50           -         100         -         500         60         600	63         1.8         413         45         4.3         1.3         < 2.1           111         4.4         920         169         6.6         3.3         < 1.7	63       1.8       413       45       4.3       1.3       < 2.1	63       1.8       413       45       4.3       1.3       <2.1

**Table 3-1 Coolcha Lagoon 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 Coolcha Lagoon 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).

Parameter	units	ANZECC Guidelines	Coolcha Lagoon				
			Min.	Median	Max.		
рН		6.5-8.0	4.4	5.8	6.5		
EC*	µS cm⁻¹	2200	84	84 274			
Eh	mV	-	77	458	504		
Ag	µg l⁻¹	0.05	<0.01	<0.01	<0.05		
Al <sup>A</sup>	mg l⁻¹	0.055	<0.05	0.10	0.49		
As <sup>B</sup>	µg l⁻¹	13	<1	1.1	54		
Cd	µg l⁻¹	0.2	<0.01	<0.05	0.2		
Co	µg l⁻¹	2.8	0.04	1.1	39		
Cr <sup>C</sup>	µg l⁻¹	1	<0.07	<0.5	<2		
Cu <sup>H</sup>	µg l⁻¹	1.4	<0.3	<2	<5		
Fe <sup>l</sup>	mg l⁻¹	0.3	<0.10	0.15	19		
Mn	µg l⁻¹	1700	2.9	152	2548		
Ni <sup>H</sup>	µg l⁻¹	11	<1	2.6	34		
Pb <sup>H</sup>	µg l⁻¹	3.4	<0.20	<3	<3		
Sb	µg l⁻¹	9	<0.60	<5	<10		
Se	µg l⁻¹	11	0.08	0.44	1.2		
V	µg l⁻¹	6	<0.60	3.0	8.3		
Zn <sup>H</sup>	µg ľ <sup>1</sup>	8	<0.30	2.2	27		

#### 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 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 two profiles varied from moderately acidic (CLG 1) to slightly acidic (CLG 3). All samples displayed an increase in pH over the 35 days (Figure 3-1). Three samples increased to pH above pH 6, whilst one remained moderately acidic with a pH of 5.35. The SEC was variable. The soil materials in profile CLG 1 showed little trend with time and were very fresh (Figure 3-1). For profile CLG 3, the SEC was higher and increased with time (Figure 3-1). The highest SEC was in the more acidic sample.

The Eh of the soils decreased with time for all samples. It changed from oxidising to moderately reducing in surface sample CLG 3.1. For the other soils, Eh remained moderately oxidising.

Iron (Fe) concentrations were initially low after day 1, and for most samples remained low consistent with the relatively high Eh and slightly acidic pH. The exception was the more reducing sample CLG 3.1, where iron (Fe) reached very high concentrations (19.25 mg  $I^{-1}$ ) in days 7 to 35, increasing consistently with time (Figure 3-2). The two profiles also had very different manganese concentrations, with the more acidic profile CLG 3 being much higher (Figure 3-2), and with the surface sample being above the ANZECC/ARMCANZ environmental protection guideline value.

Aluminium concentrations were high in samples from profile CLG 1, with a peak at day 7 (Figure 3-1). The observed concentrations are too high to be at equilibrium, and it is likely that the aluminium (AI) exists as colloidal particles in these samples. Arsenic (As) concentrations increased significantly in sample CLG 3.1 (sample with high iron) over time (Figure 3-1), with a maximum on day 14, breaching the ANZECC/ARMCANZ environmental protection guideline value significantly. Vanadium (V) increased above the ANZECC/ARMCANZ environmental protection guideline value significantly. Concentrations (Figure 3-3).

For the metals, the highest concentrations were typically present in the soil sample from profile CLG 3, with elevated cobalt (Co), nickel (Ni) and zinc (Zn), and to a lesser degree cadmium (Cd) (Figure 3-1 to Figure 3-3). The high iron (Fe) sample, CLG 3.1, which had the highest concentration, displayed a maximum after 14 days, subsequently decreased by day 35.

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) SEC; 8) clay content; 9) microbial activity; 10) temperature; and 11) porosity (MDBA 2010).

Most metals did not display a clear trend with pH (Figure 3-4), but there was a tendency for higher manganese (Mn), cobalt (Co) and zinc (Zn) at low pH and higher arsenic (As), vanadium (V) and aluminium (Al) at higher pH. For aluminium, it is likely that it is in a colloidal form.



Figure 3-1 Contaminant and metalloid dynamics results for Coolcha Lagoon soil materials for pH, SEC, Eh, silver (Ag), aluminium (AI) and arsenic (As). Note: silver (Ag) was all < detection limit, data represent detection limits which vary according to required dilutions.



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

Note: chromium (Cr) and copper (Cu) were all < detection limit, data represent detection limits which vary according to required dilutions.



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

Note: lead (Pb) and antimony (Sb) were 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 the single sample analysed for Coolcha Lagoon (CLG 3.1) are shown in Table 3-3. The pH of the soil water changed from 4.66 to 4.34 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 4.55 to 6.34 (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 476 to 314 mV (Figure 3-5) indicating a change to more reducing conditions. The Eh data are also different to the contaminant and metalloid dynamics experiments where Eh decreased from 504 to 77 mV (Table 3-2).

Inundation Time	Parameter	Units	Coolcha Lagoon (CLG 3.1)
Day 0	Total Fe	mg/kg	4741
	Fe(II)	mg/kg	950
	Sulfate*	mg/kg	4030
	рН		4.66
	Eh	mV	476
Week 7	рН		4.34
	Eh	mV	314
	S <sub>AV</sub>	Wt. %S	<0.01
	S°	Wt. %S	<0.01
	Pyrite-S	Wt. %S	0.10
	Dissolved S <sup>2-</sup>	µg/L	36

Table 3-3 Summary of monosulfide formation potential data for the Coolcha Lagoon surface
soil material CLG 3.1 after 7 weeks (3.6 g/L sucrose).

\*completed during Phase 1.

After 7 weeks, acid volatile sulfide ( $S_{AV}$ ) and elemental sulfur ( $S^0$ ) were both <0.01 % (Table 3-3). It appears, therefore, that monosulfide formation has not occurred in this sample during the tests. The sample originally contained 0.17 %  $S_{CR}$  (pyrite-S +  $S_{AV}$ ) (Grealish *et al.* 2010) and it, therefore, appears that pyrite has not formed in the sample during the experiment. Dissolved sulfide was present at low concentration suggesting sufficiently reducing nature of the soils. The low pH (possibly due to the presence of added sucrose) may be a factor in slowing the changes to reducing conditions compared to the contaminant and metalloid dynamics tests.



Figure 3-5 pH and Eh dynamics during monosulfide formation potential tests in surface soil sample CLG 3.1 from Coolcha 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 (ANZECC/ARMCANZ 2000), 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 reactive metal and metalloid concentrations were all below sediment quality guidelines and soil ecological investigation level values (Table 3-1). The concentrations for most reactive metals and metalloids are relatively low, but relatively high for aluminium (AI), iron (Fe) and manganese (Mn) (Table 3-1). Although concentrations do not exceed sediment quality guidelines and soil ecological investigation level concentrations, they 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** method 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 soil water pH was variable in the samples studied, but increased over time throughout the 35 day period. All samples showed a significant decrease in Eh (Figure 3-1), and for one sample, this was sufficient to allow iron to be soluble. Iron concentrations increased over time in CLG 3.1, and appear to be strongly controlled by the decrease in Eh. Manganese was very low in samples from profile CLG 1, and the moderately low Eh (similar to CLG 3 for the most part) suggests that manganese has limited availability in this part of the wetland. The hazards associated with metal and metalloid release are probably related to the dissolution of iron and manganese compounds. The trends for most metals are similar to manganese, whilst those for the metalloids are more similar to iron (Figure 3-1 to Figure 3-3). The solubility of these elements are controlled by pH and Eh. The dominant control on the hazards of metals is likely to be pH initially, however with an increase in pH and trend towards more reducing conditions Eh will become the dominant control. For the metalloids, it appears that redox processes are the dominant influence, and these may continue to be a problem at higher pH.

The degree to which samples exceed guideline concentrations has been used to assign a degree of hazard (Table 3-4). For some samples which required dilution, the detection limits were slightly above ANZECC/ARMCANZ environmental protection guideline values due to required dilution. Antimony (Sb), for example, was below detection limit for all samples (detection limit varying between 1 and 10  $\mu$ g l<sup>-1</sup>) as was chromium (Cr) and copper (Cu) in a few samples. It is therefore not possible to group these in Table 3-4, although it can be concluded that they either sit in the 'No hazard' or 'Low Hazard' grouping. The data are shown in Appendix 1 which displays the detection limits for individual analyses.

The data are consistent with the low to high net acidities noted by Grealish *et al.* (2010). The contaminant and metalloid dynamics data suggest that most soils may take some time to recover in terms of acidity, but by day 35 these were only slightly acidic suggesting that the timescales may be shorter than the more acidic wetlands in the Basin. The higher pH in the surface soils of one profile (CLG 1) will help minimise or ameliorate the upward flux of acidity and metals from this area. Higher pH will also limit the solubilities of most trace metals. The main control on metal mobility appears to be pH in Coolcha Lagoon soils, and probably Eh for the metalloids. The source of many metals appears to be closely related to manganese, which may imply a source from manganese oxides/oxyhydroxides, alternatively both may simply be controlled by pH. The metalloids show more similarities to iron, therefore, a link to dissolution of an iron-bearing mineral appears likely. The mobility of both metals and metalloids may be a significant hazard over longer timescales, at least until further reduction into the field of iron sulfide stability, in which case they may be scavenged by precipitating iron sulfides.

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

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

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The monosulfide formation potential tests assist in determining the propensity for monosulfides to form during future inundation. The sample used for this test contained <0.01% acid volatile sulfide ( $S_{AV}$ ). This provides a monosulfide formation potential hazard as 'No hazard' (Table 3-5).

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>

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

## 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, fror	n
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	Consequences category												
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 contaminant 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.

Coolcha Lagoon 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 low to high net acidities in the dry soils of Coolcha Lagoon (Grealish *et al.* 2010) suggest that the acidification hazard is variable. However, the majority of samples had a low to moderate net acidity. This suggests that the recovery of the soils may not be too prolonged, and this is in agreement with the significant increase in pH in the contaminant and metalloid dynamics tests (Figure 3-1). Recovery, however, will depend largely on hydrological conditions e.g. high flows will provide some buffering and allow the acidity flux to move downwards in the soil profile. The acidification hazard is therefore considered to be moderate and probably localised in the wetland.

It is concluded that soil acidification would pose a short-term problem in the soils over much of the wetland as suggested by the measured low pH over the 35 days of the contaminant and metalloid dynamics tests. The wetland was dry during sampling, and due to its location adjacent to the river and connectivity, the likelihood of disturbance is considered almost certain as flows return to normal in the future. The consequences for soil ecology are likely to be short term and localised in nature and the timescale for soil recovery from acidification will probably be of the order of at least months even if there are sufficient flows, as indicated in the contaminant and metalloid dynamics experiments. A minor rating is therefore applied for consequence as short-term damage to soil water chemistry is considered likely. This provides a risk rating for soil acidification of **medium** (Table 4-4). A rating for surface water acidification will depend on surface and sub-surface hydrology. The highest risk is likely to be during low flows where the soil to water ratio is high: acidity will be most concentrated. The minimum risk to surface water acidification is considered lowest where high flows are available to both dilute acidity and transport acidity downwards in the soil profile. Surface water acidification is likely to be lower than soil acidification, due to limited transport and buffering reactions at the soil/water interface (where recovery may be rapid), therefore an insignificant to minor categorisation is given for consequence. The risk rating for surface water acidification is therefore likely to be low to medium (Table 4-4).

### 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) and manganese (Mn) oxides and hydroxides which are important sorbents of metal and metalloids species. The moderate acidification hazard due to the oxidation of sulfide minerals means that metals and metalloids are likely to be present at moderately high concentrations in some soils, depending on availability. The data suggest that iron (Fe) and cobalt (Co) are the elements with the highest hazard, although arsenic (As), manganese (Mn), nickel (Ni) and zinc (Zn) were also relatively high (Table 3-2). The samples showed a trend towards more reducing conditions, and at the pH's observed this was sufficient to mobilise iron in only one sample (CLG 3.1). The risks may be higher for metalloids if the pH increases, as these may be mobile even once pH increases. However, further reduction processes may lead to reincorporation of metals and metalloids into sulfide minerals (following sulfate reduction).

Although the timescales cannot be assessed with existing information, the data suggest that metal availability is significant for some metals. Comparisons with other studies (e.g. Nelwart Lagoon, Shand *et al.* 2010), suggest that at the pH levels noted in the contaminant and metalloid dynamics experiments for most samples, reductive processes may occur rapidly once initiated, and soil recovery may be rapid. A *moderate* rating is applied for consequence due to the presence of a number of metals in deeper acidic soil layers and metalloids in surface soils, along with a likelihood of disturbance of *almost certain* as flows return to normal in the future. This provides a risk rating for contaminant mobilisation in soils of high (Table 4-4).

A rating for surface water impacts from metals and metalloids will depend on surface and sub-surface hydrology. The acidic to circumneutral pH values in this study, however, means that longer term impacts are possible. Chemical reactions with soils and interactions at the soil/water interface are likely to diminish any minor hazards from metal flux. The highest risk is likely to be during low flows where the soil to water ratio is high: metals will be most concentrated. The minimum 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 to moderate* consequence is applied. The risk rating for surface waters from metal mobilisation is therefore considered to be **medium to high** (Table 4-4).

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

Monosulfidic materials are considered the main cause of deoxygenation risk in acid sulfate soils. Monosulfidic black ooze was not identified in the wetland during the Phase 1 survey (Grealish *et al.* 2010). Water soluble sulfate concentrations were high in samples analysed from the wetland (up to 10,636 mg kg<sup>-1</sup> and 4,030 mg kg<sup>-1</sup> for this sample). However, no acid volatile sulfide ( $S_{AV}$ ) was measured from the monosulfide formation potential test, although over longer timeframes and under more reducing conditions there may be potential to form monosulfides. Nevertheless, the consequence is considered to be *insignificant* and therefore the risk associated with deoxygenation from monosulfides is **low**.

Acidifica	tion Risk	Contaminant	Deoxygenation	
Soil	Water	Soil	Water	
Medium	Low-Medium	High	Medium-High	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.

The medium to high risks identified in this study are due to soil and water acidification and metal mobility. The likelihood of water refilling the wetland is high as flows return to normal levels. The limited number of case studies on refilling wetlands makes prediction of risk difficult in terms of determining whether reversible or irreversible damage is likely to occur. However, at the low pH's observed, and significant increase in pH over the 35 day period along with metal and metalloid mobilisation imply that any risks are likely to be significant.

As the wetland has previously dried and undergone oxidation, management options 1 and 2 in Table 5-1 are not relevant to the current study, although minimising further oxidation could have been an option prior to recent high flows down the River Murray. Treatment options currently remain a viable option should water quality impacts e.g. acidification of surface water and/or high metal concentrations be seen. Since the risks are scenario dependent in this medium conservation status wetland, it is recommended that surface water monitoring be undertaken at this wetland. Based on the data from this study and elsewhere (Shand *et al.* 2010), it is likely that soil recovery will be relatively slow in the sub-surface soils as pH is relatively high in three of the four samples. It is anticipated, however, that for deeper soil layers which remain sulfuric, soil acidity may remain for periods of several months. 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> </ul>
2. Preventing oxidation of acid	<ul> <li>Incorporating a more natural flow regime.</li> <li>Preventing oxidation:</li> <li>Koon the acdimente severed by water.</li> </ul>
sultate soils or controlled oxidation to remove acid sulfate soils	<ul> <li>Avoid flow regimes that could re-suspend sediments.</li> <li>Controlled oxidation:</li> </ul>
	<ul> <li>Assess whether neutralising capacity of the sediments and water far exceeds the acidity produced by oxidation</li> </ul>
	<ul> <li>Assess the risk of deoxygenation and metal release. Monitor intervention and have a contingency plan to ensure avoidance of these risks.</li> </ul>
3. Controlling or treating acidification	Neutralise water column and/or sediments by adding chemical ameliorants
	<ul> <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).

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# APPENDICES

# **APPENDIX 1 REACTIVE METALS DATA**

Coolcha Lagoon

Sample	Depth	Analysis	Ag*	AI	As	Cd*	Co	Cr*	Cu	Fe	Mn	Ni	Pb	Sb*	Se*	V	Zn
	0.10	а	5.6	448	0.60	38	1.1	51	2.4	331	60	4.5	1.8	< 1.8	20	7.8	3.5
CLG 1.1	0-10	b	5.6	449	0.60	38	1.1	51	2.4	338	61	4.5	1.8	< 1.8	20	7.8	3.3
01040	10-20	а	5.4	749	0.53	40	0.94	67	1.9	434	48	4.6	1.3	< 2.1	42	8.3	4.2
GLG 1.2		b	5.2	647	0.50	36	0.80	58	1.8	392	41	4.1	1.2	< 2.1	35	10	3.6
	0-5	а	5.0	478	1.7	66	3.9	108	4.4	932	168	6.6	3.3	< 1.7	44	12	6.7
CLG 3.1		b	4.9	483	1.6	66	4.0	114	4.4	907	170	6.7	3.3	< 1.7	46	12	7.1
CLG 3.2	5 10	а	3.9	374	0.96	50	2.0	50	2.1	704	77	5.8	4.8	< 2.1	35	9.9	4.3
	5-10	b	3.9	355	0.92	49	1.9	50	2.3	656	75	6.2	4.9	< 2.1	33	9.4	4.3

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**

Coolcha Lagoon

Sample	Davi	Depth	Analysis	Eh	EC		Ag	AI	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Se	v	Zn		
	Day	cm		mV	µS/cm	рн	µg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L		
	4		а	444	124	5.90	<0.01	0.13	0.25	< 0.03	0.10	<0.3	<1	<0.1	9.4	<1	<0.6	<1	0.09	1.3	<1		
	1		b	449	96	6.03	<0.01	0.17	0.47	< 0.03	0.10	< 0.3	<1	<0.1	7.7	<1	<0.6	<1	0.12	1.6	<1		
	-		а	499	99	5.90	<0.01	0.39	0.80	< 0.03	0.20	0.28	0.80	0.22	11	0.88	<0.2	<1	0.08	3.2	0.40		
CLG 1.1	1	0-10	b	479	96	5.88	< 0.02	0.58	0.80	<0.06	0.16	0.20	0.80	0.33	10	0.80	<0.4	<2	<0.08	3.2	<0.8		
			а	479	85	6.08	<0.01	0.18	1.2	< 0.03	0.29	0.20	1.2	<0.1	23	1.2	<0.4	<0.6	0.12	6.7	1.8		
	14		b	474	83	6.05	<0.01	0.43	1.5	< 0.03	0.48	0.50	1.8	0.21	27	1.7	0.40	<0.6	0.14	8.0	3.0		
	05		а	279	102	6.57	<0.01	0.26	3.3	< 0.01	0.48	0.32	1.5	0.16	28	1.8	<0.4	<2	0.15	3.7	0.95		
	35		b	274	97	6.49	<0.01	0.31	7.6	< 0.01	0.79	0.49	2.3	0.19	40	2.7	<0.4	<2	0.18	3.9	1.3		
	4		а	459	183	5.47	< 0.01	0.20	0.22	< 0.03	0.04	< 0.3	<1	<0.1	5.8	<1	<0.6	<1	1.1	3.7	<1		
	1		b	459	160	6.10	<0.01	0.18	0.31	< 0.03	0.05	< 0.3	<1	<0.1	15	<1	<0.6	<1	1.1	3.2	<1		
	7				а	464	204	5.90	<0.01	0.35	0.60	< 0.03	0.06	0.07	0.20	0.20	8.2	0.40	<0.2	<1	0.80	6.4	<0.4
CLG 1.2	1	10-20	b	459	197	6.03	<0.01	0.45	0.50	< 0.03	0.07	0.14	0.40	0.21	5.6	0.48	<0.2	<1	0.76	8.0	<0.4		
	1/	-	а	469	165	6.12	<0.01	0.14	0.30	< 0.03	0.07	<0.1	< 0.3	<0.1	14	0.36	<0.4	<0.6	1.0	5.9	< 0.3		
	14		b	464	159	5.94	<0.01	0.06	0.30	<0.03	0.06	<0.1	<0.3	<0.1	12	0.36	<0.4	<0.6	1.1	6.3	<0.3		
	35		а	294	188	6.06	<0.01	0.26	0.59	<0.01	0.06	0.12	0.94	0.15	2.9	0.55	<0.4	<2	0.67	8.0	0.61		
			b	289	175	6.13	<0.01	0.22	0.60	<0.01	0.07	0.16	0.63	0.14	2.8	0.50	<0.4	<2	0.59	8.5	0.43		
	1		а	479	346	4.47	<0.05	0.09	1.8	0.22	26	<2	<5	0.58	2027	18	<3	<5	0.95	<2	18		
			b	489	350	4.64	< 0.05	0.10	1.8	< 0.2	31	<2	<5	0.68	2498	23	<3	<5	1.0	<2	25		
	7		а	444	748	4.36	< 0.05	< 0.05	9.0	<0.2	36	<0.4	<1	6.2	2204	30	<1	<5	0.60	<1	24		
CLG 3.1		0-5	b	464	/31	4.38	< 0.05	< 0.05	11	< 0.2	35	<0.4	<1	6.0	2188	28	<1	<5	0.40	<1	18		
	14		a	384	489	5.25	<0.01	<0.05	52	< 0.2	38	<0.5	<2	11	2502	33	<2	<3	1.2	2.5	28		
	35	ł	D	329	500	5.35	<0.01	<0.05	56	< 0.2	40	< 0.5	<2	14	2594	35	<2	<3	1.1	3.0	26		
		35				a b	79	092 765	0.37	<0.01	<0.05	20	<0.05	3.7	0.77	<1	13	1072	0.4	<2	<10	0.40	3.U 3.Q
			0	/4	544	5.00	<0.01	<0.05	0.42	<0.05 0.06	5.5	<0.5	<2	<0.1	547	9.4	~2	<10	0.59	J.0	<u>~</u> 2		
	1		a h	499 500	308	5.09	<0.02	<0.05	<0.42	0.00	5.0	<0.0	~2	<0.1	557	4.9	<1	<2	0.31	<0.0	53		
		+	2	449	885	4 4 2	<0.02	<0.05	0.20	<0.10	0.56	<0.0	0.20	<0.1	210	1.0	<0.2	<1	0.37	1.0	3.6		
CIG32	7	5-10	b a	464	636	4 61	<0.01	<0.05	0.20	<0.03	27	0.07	0.20	<0.1	319	4.2	<0.2	<1	0.24	0.80	2.8		
020 0.2		0 10	a	459	896	4.87	<0.01	<0.00	<0.6	<0.06	9.3	<0.07	<0.6	<0.1	896	12	<0.2	<1	0.36	1.0	9.0		
	14		b	469	915	5.35	< 0.01	< 0.05	<2	< 0.2	10	< 0.5	<2	< 0.1	1071	12	<2	<3	0.50	1.0	10.0		
	0.5	1	a	219	943	4.83	< 0.01	< 0.05	<0.6	0.11	23	<0.2	< 0.4	<0.1	1915	22	<0.8	<4	0.36	0.90	15		
	35		b	214	817	5.86	<0.01	<0.05	<2	<0.05	15	<0.5	<1	<0.1	1310	15	<2	<10	0.38	0.69	9.9		

< value is below detection limit

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

### Coolcha Lagoon

MBO Format	tion Potent	tial (MBO FP) - DAY 0				IRON	DATA			DAY 0									
				Total Reactive Fe (mg/kg)					Fe(II) (	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		
21	csiro	Coolcha Lagoon	CLG3.1	4725	4756	4741	16	983	917	950	33	463	489	476	13	4.67	4.65	4.66	0.01
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

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		
21	csiro	Coolcha Lagoon	CLG3.1	0.00	0.00	<0.01	<0.01	0.11	0.09	0.10	0.01	0.00	0.00	<0.01	<0.01	4.31	4.37	4.34	0.03	290	337	314	24	<0.1	71.7	35.8	35.8
32	csiro	Blank														5.45	5.42	5.44	0.02	325	338	331	6	< 0.1	< 0.1	< 0.1	< 0.1

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