Assessment of Acid Sulfate Soil Materials (Phase 2): Fivebough and Tuckerbil Swamps

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Cover Photograph:

Typical landscape in the Fivebough Swamp. Photograph taken at Site RSFS 6 in the Fivebough Swamp.
Photographer: Mark Southwell.

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EXECUTIVE SUMMARY

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). An initial Phase 1 acid sulfate soil investigation of the Fivebough and Tuckerbil Swamps Ramsar wetland in July 2008 showed acid sulfate soils to be a priority concern within this wetland (Ward *et al.* 2010a). Based on Phase 1 recommendations, a Phase 2 investigation was undertaken for the Fivebough and Tuckerbil Swamps Ramsar wetland to determine the nature, severity and the specific risks associated with acid sulfate soil materials. Phase 2 activities included soil laboratory analysis, a risk assessment, and interpretation and reporting, including discussion on broad acid sulfate soil management options.

An examination of the sulfur species within a soil profile from the Tuckerbil Swamp found the reduced inorganic sulfur fraction in the surface soil (i.e. 0.02% S) was entirely in the form of pyrite (FeS_2). The x-ray diffraction (XRD) data was in agreement with the sulfur species data in that the surface soil materials examined did not contain any identifiable retained acidity (such as jarosite and similar relatively insoluble hydroxy-sulfate compounds). The soil materials in the profile from the Tuckerbil Swamp had minimal net acidities, except for the surface layer which had a moderate net acidity of 26 mole H^+/tonne.

The x-ray fluorescence (XRF) spectrometry data for two Tuckerbil Swamp soil materials showed the total concentrations for most elements are in the normal range for soils, and elements which have an ANZECC sediment quality guideline are below the sediment quality guideline (SQG) trigger value. However, the contaminant and metalloid release data showed many metals/metalloids examined exceeded the ANZECC water quality guidelines (ANZECC/ARMCANZ 2000).

The contaminant and metalloid dynamics tests were undertaken to assess the release of metals during a water extraction, and to assess changes with time as saturated soils by incubating soil materials for periods of 1, 14 and 56 days. Additional sampling intervals of 7, 21 and 35 days were undertaken for a surface soil material to gain further understanding of the kinetics of contaminant release. The degree to which metal and metalloid concentrations exceed ANZECC/ARMCANZ water quality guideline values for environmental protection was used to characterise the degree of hazard. For Tuckerbil Swamp, the contaminant and metalloid dynamics test over 56 days showed that under the experimental conditions all metals and metalloids examined (with the exception of manganese (Mn) and selenium (Se)) were found to exceed the ANZECC water quality guidelines. The guidelines for aluminium (Al), chromium (Cr) and iron (Fe) were exceeded by more than 100 times, with many of the metals/metalloids being largely released within 14 days of inundation. A maximum concentration after seven days of inundation with the majority of the metals/metalloids associated with the surface soil material suggests that they may have been released as a consequence of redox processes.

Many of the contaminants also exceeded the ANZECC water quality guidelines using the 24 hour rapid metal release test, with the surface soil material exceeding the guidelines by more than 10 times for cobalt (Co) and copper (Cu). The data also showed NO_x (taken as nitrate for this comparison) concentrations were 20-70 times greater than the guidelines for lowland rivers, and the filterable reactive phosphorus (FRP) concentrations were 4-10 times greater than the guidelines for lowland rivers.

As shown in the table below, the metals/metalloids found to exceed the ANZECC water quality guidelines represent a low to high hazard, and usually varied depending on the method used. The degree of hazard was predominantly less with the rapid metal release method which measures the release over the initial 24 hours of inundation. The contaminant

and metalloid dynamics method is able to predict the maximum concentration over a longer timeframe.

The monosulfide formation potential data for both the Fivebough and Tuckerbil Swamps surface soil materials clearly showed that sulfate reduction occurred within the seven week inundation period. While monosulfide formation was not observed, an increase in the pyrite content (of up to 0.03% S) occurred with 54% of the soil materials examined Substantial dissolved sulfide concentrations were also measured in some pore-waters. While the sulfate concentration seemed to have limited pyrite formation in some Fivebough Swamp soil materials, the availability of iron may be the limiting factor with some Tuckerbil Swamp soil materials. The pore-water sulfate data after seven weeks of inundation indicates a potential for further pyrite formation had the incubation interval been greater, although iron complexation with organics may possibly limit the rate of pyrite formation. The fact that monosulfidic soil materials (i.e. $S_{AV} \geq 0.01\%$ S) were not observed to form after seven weeks of incubation indicates that the surface soil materials examined from the Fivebough and Tuckerbil Swamps do not represent a de-oxygenation hazard. However, the potential for sulfide formation with several of the soil materials indicates that under suitable geochemical conditions (i.e. near neutral pH) monosulfides may form.

Degree of Hazard	Guideline Threshold	Contaminant and Metalloid Dynamics Test	Rapid Metal Release Test
No Hazard	Value below ANZECC guideline threshold.	Mn, Se	As, Cd, Mn, Pb, Se
Low Hazard	Value exceeds ANZECC guideline threshold, but is less than 10x exceedance.	As, Cd,	Ag, Al*, Cr, Ni, V, Zn
Moderate Hazard	Value exceeds ANZECC guideline threshold by 10x or more, but is less than 100x exceedance.	Ag, Cu, Ni, Pb, Zn	Co, Cu
High Hazard	Value exceeds ANZECC guideline threshold by 100x or more.	Al*, Cr, Fe	None

** Based on aluminium being soluble – at pH > 5.5 this is unlikely.*

A risk assessment framework was applied to determine the specific risks associated with acidification, contaminant mobilisation and de-oxygenation (MDBA 2011). The Phase 2 assessment identified the following risks associated with the presence of acid sulfate soils in the Fivebough and Tuckerbil Swamps Ramsar wetland:

- low/medium acidification risk in the Tuckerbil Swamp,
- medium contaminant mobilisation risk in the Tuckerbil Swamp, and
- low de-oxygenation risk in the Fivebough and Tuckerbil Swamps.

These findings indicate that, if not managed appropriately, the acid sulfate soil materials identified in the Tuckerbil Swamp have the potential to present a medium risk to the environmental values of both the wetland and adjacent waters. This report outlines the variety of management options available to manage acid sulfate soils in inland aquatic ecosystems. The most appropriate management strategies for Fivebough and Tuckerbil Swamps Ramsar wetland would be undertake routine monitoring to determine whether any of the hazards were increasing, and develop an acid sulfate soil management plan. However, 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.

It is important to note that the soil materials collected in July 2008 as part of the Phase 1 assessment only provided a snapshot of the acid sulfate soil materials present and the conditions at selected locations in the wetland. While recent inundation within the wetland may have minimised the risks identified in the short-term, it is also likely that this inundation will lead to further formation of acid sulfate soil materials.

This Phase 2 study only examined contaminant mobilisation in two partially-oxidised layers collected from one site in Tuckerbil Swamp. Further studies would be required to determine how representative these soil materials are of the entire wetland in order to fully assess the risk of contaminant mobilisation.

It is recommended that, within the context of other management objectives for the wetland, consideration be given to undertaking water quality monitoring to identify potential contamination as a result of the disturbance of acid sulfate soils within the wetland. The presence of some medium risks identified in this Phase 2 assessment indicates that management action may be recommended (MDBA 2011).

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 acid sulfate soil materials are present (or absent) 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 14 Ramsar-listed wetland complexes as part of the MDB ASSRAP. Phase 1 investigations identified four of these Ramsar wetlands to be a priority concern at a wetland-scale to warrant further investigation. These wetlands included Fivebough and Tuckerbil Swamps (Figure 1-1), Riverland, Banrock Station wetland complex and Kerang Wetlands. This report outlines the results of Phase 2 activities on selected samples from the Fivebough and Tuckerbil Swamps Ramsar wetland.

Following the Fivebough and Tuckerbil Swamps Ramsar wetland Phase 1 assessment (Ward *et al.* 2010a) and the priority ranking criteria adopted by the Scientific Reference Panel of the MDB ASSRAP (see Table 1-1), selected sites from within the wetland were chosen for Phase 2 detailed assessment. The Phase 1 assessment identified one high priority site based on the presence of a hypersulfidic material and three moderate priority sites based on the presence of hyposulfidic materials with S_{CR} < 0.10% in the Fivebough and Tuckerbil Swamps Ramsar wetland (Ward *et al.* 2010a). In addition, all 13 sampling sites examined had a high priority ranking for Phase 2 detailed assessment based on potential monosulfidic black ooze (MBO) formation hazard (Ward *et al.* 2010a). Phase 2 investigations were carried out on selected samples from all high priority sites identified in the Phase 1 assessment.

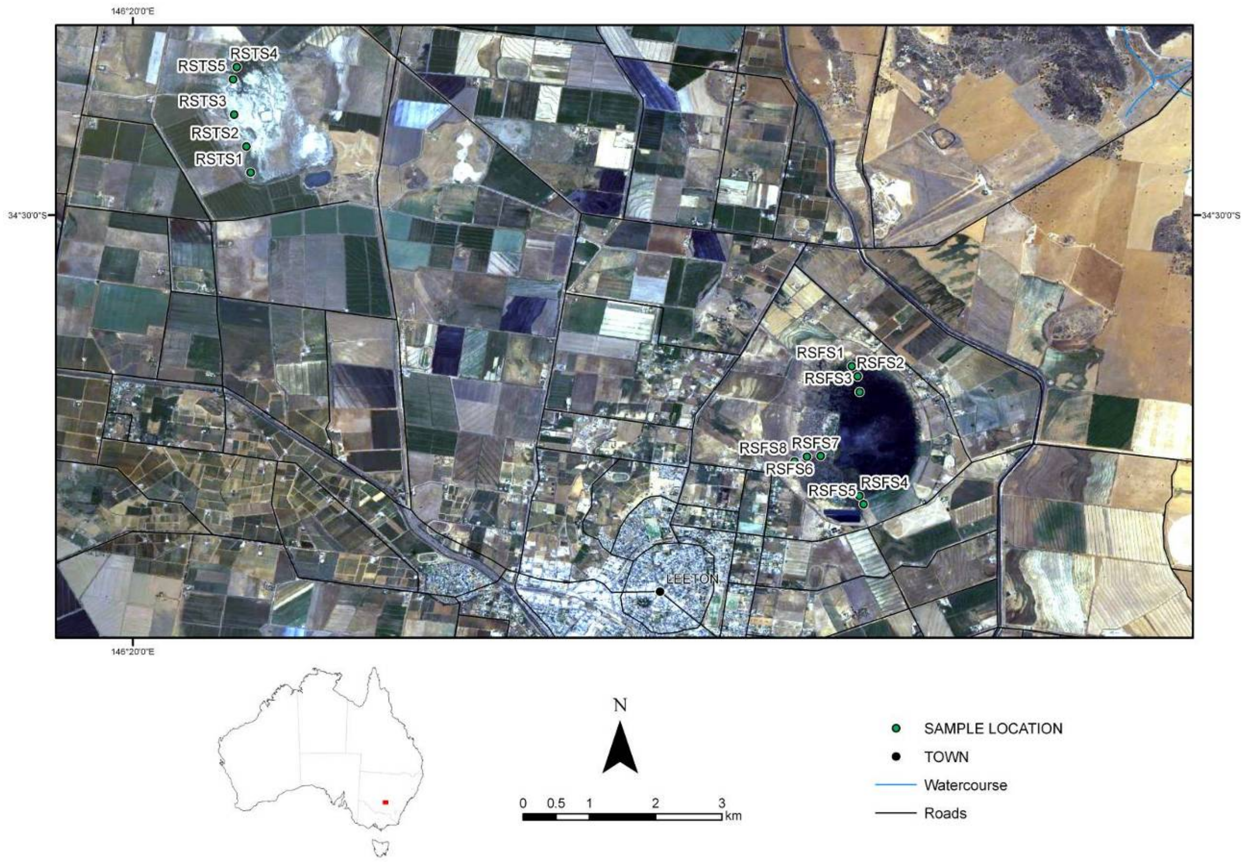

Figure 1-1: Map showing the areas assessed in the Fivebough (RSFS) and Tuckerbil (RSTS) Swamps during the Phase 1 assessment.

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 ≥ 0.10% S.
	All surface soil materials (i.e. within 0-20 cm) with water soluble sulfate (1:5 soil:water) contents ≥ 100 mg SO_4 kg^{-1}.
	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 are given in Table 1-2. Soil samples identified to undergo Phase 2 laboratory analysis are primarily from the surface layer, as this is the soil most likely to have initial contact with water. A list of the samples selected for Phase 2 analysis for the Fivebough and Tuckerbil Swamps Ramsar wetland is presented in Table 1-3.

Table 1-2. Rationale of sample selection for Phase 2 analysis (from MDBA 2010).

Parameter	Samples selected
Sulfur species suite	Conducted on the two uppermost samples where monosulfides are identified.
Rapid metal release	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.
Trace elements by x-ray fluorescence spectroscopy (XRF)	Conducted on a ratio of about 2 samples for every 15 collected. Usually one surface and one deeper sample for a profile along a transect.

Table 1-3. Summary of Fivebough and Tuckerbil Swamps samples analysed for Phase 2 assessment.

Soil Laboratory Test	Fivebough Swamp	Tuckerbil Swamp	[1]n
Sulfur species suite	-	4.3, 4.4, 4.5, 4.6, 4.7	5
Rapid metal release	-	4.3, 4.4	2
Contaminant and metalloid dynamics	-	4.3, 4.4	2
Monosulfide formation potential	1.3, 2.3, 3.3, 4.3, 5.3, 6.3, 7.3, 8.4	1.3, 2.3, 3.3, 4.3, 5.3	13
Mineral Identification by x-ray diffraction (XRD)	-	4.3, 4.4	2
Trace elements by x-ray fluorescence spectroscopy (XRF)	-	4.3, 4.4	2

[1]n = total number of samples analysed.
Sample numbers #.3, #.4, #.5, #.6 and #.7 refer to 0-5 cm, 5-10 cm, 10-20 cm, 20-40 cm and 40-90 cm soil layers, respectively.

2. LABORATORY METHODS

2.1. *Laboratory analysis methods*

2.1.1. Summary of laboratory methods

A list of the parameters measured and each 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, objective for conducting the test and method reference (from MDBA 2010).

Parameter	Objective	Method Reference
Elemental sulfur	Quantify S.	Burton *et al*. (2006)
Acid volatile sulfide	Quantify S in form of FeS minerals.	Hsieh *et al*. (2002)
Retained acidity	Quantify acidity 'stored' in minerals such as jarosite, schwertmannite and other hydroxyl-sulfate minerals.	Ahern *et al*. (2004)
Rapid metal release	Assists with determining impacts on water quality by simulation of rewetting for a 24 hour time frame. Identifies metal release concentrations that may occur in a short time frame.	Simpson *et al*. (2008)
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 6 to 10 week time frame.	MDBA (2010)
Monosulfide formation potential	Determine relative propensity for monosulfides to form following inundation.	MDBA (2010)
Mineral identification by x-ray diffraction	Characterisation and confirmation of minerals present.	MDBA (2010)
Trace elements by x-ray fluorescence spectroscopy	Characterisation and confirmation of geochemistry.	MDBA (2010)

Guidelines on the approaches that were followed as part of this Phase 2 assessment are presented in full in the detailed assessment protocols (see Appendices 5 to 10, MDBA 2010). Further details on the methods followed, and any variations to the methods outlined in the detailed assessment protocols, are presented in Sections 2.1.2 – 2.1.7.

2.1.2. Sulfur species suite method

The guidelines for the sulfur species suite method are outlined in Appendix 5 of the detailed assessment protocols (MDBA 2010). In this Phase 2 assessment the elemental sulfur fraction was extracted using toluene as a solvent and quantified by high-performance liquid chromatography (HPLC) (McGuire and Hamers 2000). Retained acidity (RA) was determined from the difference between 4 M HCl extractable sulfur (S_{HCl}) and 1 M KCl extractable sulfur (S_{KCl}) (Method Code 20J) (Ahern *et al.* 2004). The retained acidity method identifies sulfate in the form of jarosite and similar relatively insoluble iron and aluminium hydroxy-sulfate compounds. Retained acidity was only determined when the sample pH_{KCl} determined in initial Phase 1 assessment was < 4.5.

2.1.3. Rapid metal release method

The guidelines for the rapid metal release method are outlined in Appendix 6 of the detailed assessment protocols (MDBA 2010). Further details of the methodology followed are also outlined in Appendix 3 of this report.

2.1.4. 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). Redox potential (Eh) and pH were determined using calibrated electrodes linked to a TPS WP-80 meter; Eh measurements are presented versus the standard hydrogen electrode. Electrical conductivity (EC) was determined using a calibrated electrode linked to a TPS WP-81 meter. All parameters were measured on filtered (0.45 µm) water samples. In addition to the three sampling intervals (i.e. 24 hours, 14 days and 56 days), sampling was undertaken on three extra intervals (i.e. 7 days, 21 days and 35 days) for sample RSTS 4.3 to gain further understanding of the kinetics of contaminant release.

2.1.5. Monosulfide formation potential method

The guidelines for the monosulfide formation potential method are outlined in Appendix 8 of the detailed assessment protocols (MDBA 2010). Redox potential (Eh) and pH were determined using calibrated electrodes linked to a TPS WP-80 meter; Eh measurements are presented versus the standard hydrogen electrode. The total dissolved iron fraction was analysed by ICP-MS (Inductively Coupled Plasma - Mass Spectrometry) (APHA 3500-Fe) (APHA 2005). Dissolved sulfate was determined by ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry) (APHA 2005). The solid phase elemental sulfur fraction was extracted using toluene as a solvent and quantified by HPLC (McGuire and Hamers 2000). Ferrous iron (Fe (II)) was not measured in this study as the organic substrate was found to interfere with the methodology outlined in the detailed assessment protocols.

In addition to analysing samples after seven weeks, samples were also analysed immediately after inundating the soils (i.e. Day 0) and on selected samples after 2.5 weeks of inundation. The monosulfide formation potential method was also repeated with the addition of excess organic substrate (72 g/L sucrose) and sampling was undertaken on selected samples for up to 9 weeks (i.e. 4, 6, 7 and 9 weeks).

2.1.6. Mineral identification by x-ray diffraction

The guidelines for mineral identification by x-ray diffraction (XRD) are outlined in Appendix 9 of the detailed assessment protocols (MDBA 2010).

2.1.7. Geochemical analysis by x-ray fluorescence spectrometry

The guidelines for geochemical analysis of trace elements by x-ray fluorescence (XRF) spectrometry are outlined in Appendix 10 of 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 followed included the monitoring of blanks, duplicate analysis of at least 1 in 10 samples, and the inclusion of standards in each batch.

Reagent blanks and method blanks were prepared and analysed for each method. All blanks examined here were either at, or very close to, the limits of detection. On average, the frequencies of quality control samples processed were: 10% blanks, ≥ 10% laboratory duplicates, and 10% laboratory controls. The analytical precision was ±10% for all analyses.

3. RESULTS AND DISCUSSION

3.1. Summary of soil laboratory results

3.1.1. Sulfur species suite data

The sulfur species data for the Tuckerbil Swamp soil materials (i.e. RSTS 4.3 – 4.7) are presented in Appendix 1 (Table 8-1) and summarised below in Table 3-1. Pyrite was only observed in the surface layer (i.e. 0-5 cm) at Site 4 with a concentration of 0.02% S. The acid volatile sulfide (S_{AV}) and elemental sulfur (S^{o}) concentrations were below the limit of detection (i.e. < 0.01% S) in all samples. All samples had pH_{KCl} values of > 4.5 (see Ward *et al.* 2010a) indicating that the soil materials did not contain any retained acidity in the form of jarosite and similar relatively insoluble hydroxy-sulfate compounds.

Table 3-1. Summary of sulfur species suite data for the Tuckerbil Swamp soil materials (RSTS 4.3 – 4.7).

Parameter	Units	Minimum	Median	Maximum	[1]n
Pyrite-S	Wt. %S	<0.01	<0.01	0.02	5
S_{AV}	Wt. %S	<0.01	<0.01	<0.01	5
S^{o}	Wt. %S	<0.01	<0.01	<0.01	5
Retained Acidity	mole H^+/t	0.00	0.00	0.00	5

[1] *n: number of samples.*

A summary of the acidity data for the Tuckerbil Swamp soil materials (RSTS 4.3 – 4.7) are presented in Table 3–2. All soil materials had minimal net acidities, except for the surface soil material (RSTS 4.3) which had a moderate net acidity of 25.5 mole H^+/tonne.

Table 3-2. Summary of acidity data for the Tuckerbil Swamp soil materials (RSTS 4.3 – 4.7).

Sample	TAA* (mole H^+/t)	CRS (%S)	ANC* (%$CaCO_3$)	Retained Acidity (mole H^+/t)	Net acidity (mole H^+/t)
RSTS 4.3	13.1	0.02	0.00	0.00	25.5
RSTS 4.4	6.6	<0.01	0.00	0.00	6.6
RSTS 4.5	0.0	<0.01	n.a.	0.00	≤ 0.0
RSTS 4.6	0.0	<0.01	n.a.	0.00	≤ 0.0
RSTS 4.7	0.0	<0.01	n.a.	0.00	≤ 0.0

** Data from the Phase 1 assessment (Ward et al. 2010a)*
n.a. Data only available for sulfidic soil materials when pH_{KCl} ≥ 6.5

3.1.2. Rapid metal release data

The rapid metal release data for Tuckerbil Swamp soil materials (i.e. RSTS 4.3 and 4.4) are presented in Appendix 3 and summarised below in Table 3-3. The rapid metal release method showed the ANZECC water quality guideline trigger values were exceeded for aluminium (Al), cobalt (Co), copper (Cu) and vanadium (V) for both soils and for chromium (Cr), nickel (Ni), silver (Ag) and zinc (Zn) for the surface soil (RSTS 4.3) (see Table 3-3). The surface soil material exceeded ANZECC guidelines by more than 10 times for cobalt (Co) and copper (Cu). The NO_x (taken as nitrate for this comparison) concentrations were 20-70 times greater than the guidelines for lowland rivers, while the filterable reactive phosphorus (FRP) concentrations were 4-10 times greater than the guidelines for lowland rivers. Further details of the results of the rapid metal release are presented in Simpson *et al.* (2010) (see Appendix 3).

Table 3-3. Concentrations of trace metals after the completion of the 24-h rapid metal release tests (from Simpson *et al.* 2010).

	Al	**Mn**	**Ag**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Sb**	**Se**	**V**	**Zn**
Site	**----- mg/L --**		**--Trace metal concentrations in µg/L-----------------------------------**											
RSTS 4.3	**0.14**	1.7	**0.07**	7.2	0.1	**24**	**2.2**	**16**	**21**	1.2	0.6	0.9	**8.6**	**12**
RSTS 4.4	**0.23**	0.5	<0.02	3.8	<0.5	**4.3**	0.6	**8.7**	7.2	<0.4	<0.4	0.7	**6.6**	2
WQG (95%PC)	**0.055**	**1.9**	**0.05**	**13** [b]	**0.2**	**1.4** [c]	**1.0** [d]	**1.4**	**11**	**3.4**	**NV**	**11**	**6.0** [c]	**8.0**
>1×WQG, % [e]	100	0	50	0	0	100	50	100	50	0	NV	0	100	50
>10×WQG, % [e]	0	0	0	0	0	**50**	0	**50**	0	0	NV	0	0	0
>100×WQG, %	0	0	0	0	0	0	0	0	0	0	NV	0	0	0

WQG (95%PC) = ANZECC/ARMCANZ (2000) water quality guideline trigger value for 95% species protection. a Mean and SD calculations use 'Limit of Reporting' (LOR) values are measured value. b As(V) = 13 µg/L (As(III) = 24 µg/L). c Low reliability guideline. d Cr assumes all is as Cr(VI) and NV = no value. e **Blue** when >WQG trigger value, **red** when >10×WQG trigger value, and **black** when >100×WQG trigger value

3.1.3. Contaminant and metalloid dynamics data

The contaminant and metalloid dynamics data for the two Tuckerbil Swamp soil materials examined (i.e. RSTS 4.3 and 4.4) are presented in Appendix 1 (Tables 8-2 and 8-3) and summarised below in Table 3-4. Table 3-4 also compares the pore-water metal contents to the relevant national water quality guideline for environmental protection (ANZECC/ARMCANZ 2000). Results for all parameters measured are presented in Figures 3-1 to 3-4.

Table 3-4. Summary of contaminant and metalloid dynamics data

Parameter	units	ANZECC Guidelines	RSTS 4.3 (0-5 cm)		RSTS 4.4 (5-10 cm)	
			Min.	Max.	Min.	Max.
pH		6.5-8.0	6.44	7.02	6.97	7.15
EC*	µS cm^{-1}	125-2200	352	403	367	446
Eh	mV	-	-16	447	28	437
Ag	µg l^{-1}	0.05	<0.1	0.3	<0.1	1.0
Al[A]	mg l^{-1}	0.055	0.60	263	0.45	527
As[B]	µg l^{-1}	13	<1.0	15	5.5	19
Cd	µg l^{-1}	0.2	<0.1	<0.1	<0.1	0.56
Cr[C]	µg l^{-1}	1	2.9	173	3.3	436
Cu[H]	µg l^{-1}	1.4	5.2	62	4.1	126
Fe	mg l^{-1}	0.3	3.01	134	0.62	384
Mn	mg l^{-1}	1.7	0.08	0.73	0.02	0.88
Ni[H]	µg l^{-1}	11	8.0	87	<1.0	220
Pb[H]	µg l^{-1}	3.4	3.1	79	1.2	61
Se	µg l^{-1}	11	<1.0	1.8	<1.0	1.9
Zn[H]	µg l^{-1}	8	45.6	256	20.2	607

Exceeded ANZECC Guideline (x1) ***Exceeded ANZECC Guideline (x10)*** ***Exceeded ANZECC 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 guidelines for lowland rivers in South-east Australia are provided for salinity (there are currently no trigger values defined for 'Wetlands').*
Values outside the ranges defined in the ANZECC guidelines are indicated with yellow, orange and red background colours.
[A] *Guideline is for Aluminium in freshwater where pH > 6.5.*
[B] *Guideline assumes As in solution as Arsenic (AsV).*
[C] *Guideline for Chromium is applicable to Chromium (CrVI) only.*
[H] *Hardness affected (refer to Guidelines).*

A slight increase in pH was observed following the inundation of both soil materials over the 56 day timeframe of the experiment (Figure 3-1). The pH was within the ANZECC guidelines, except with the surface soil material (i.e. RSTS 4.3) where it was slightly below the pH 6.5 guideline after 24 hours of inundation (Figure 3-1). A decrease in Eh from oxic (>300 mV) to anoxic (<100 mV) conditions was also observed with both soil materials during the inundation experiments (Figure 3-1). The gradual increase in pH with time was a consequence of reduction processes consuming acidity. Previous studies have often found inundation removes the acidity in partially-oxidised sediments as the acidity gets consumed from the reduction of iron (III) oxides, sulfates and other oxidised species by anaerobic bacteria (Dent 1986). The electrical conductivities remained fairly constant or slightly increased during the experiment and remained within the ANZECC guidelines for both soil materials throughout the experiment (Figure 3-1).

It is well established that inundating oxic soils can dramatically alter the mobility of metals and metalloids. The contaminant and metalloid dynamics results for the Tuckerbil Swamp soil materials are presented in Figures 3-2 to 3-4. Under the experimental conditions all metals and metalloids examined (with the exception of manganese (Mn) and selenium (Se)) were found to exceed the ANZECC water quality guidelines during the inundation experiment (Table 3-4). Some metals (i.e. chromium (Cr), copper (Cu), iron (Fe) and zinc (Zn)) were above the ANZECC guideline at all sampling intervals. The water quality guidelines for aluminium (Al), chromium (Cr) and iron (Fe) were exceeded by more than 100 times (Figures 3-2 and 3-3). The elevated aluminium (Al) concentration at a near neutral pH can be attributed a fine particle fraction that passes through the 0.45 µm filter and/or the presence of soluble aluminium (Al) complexes; aluminium (Al) has a low solubility at pH values of greater than 5.5.

The metal/metalloid behaviour during the 56 day inundation period varied between the metals/metalloids examined (Figures 3-2 to 3-4). The magnitude of 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 majority of metals/metalloids showed a maximum concentration after seven days of inundation with the surface soil material (RSTS 4.3) (Figures 3-2 to 3-4). All metals/metalloids (with the exception of cadmium (Cd)) showed a maximum concentration after 24 hours of inundation with the deeper soil material (RSTS 4.4), although the concentrations were only measured on three occasions (i.e. after 24 hours, 14 days and 56 days).

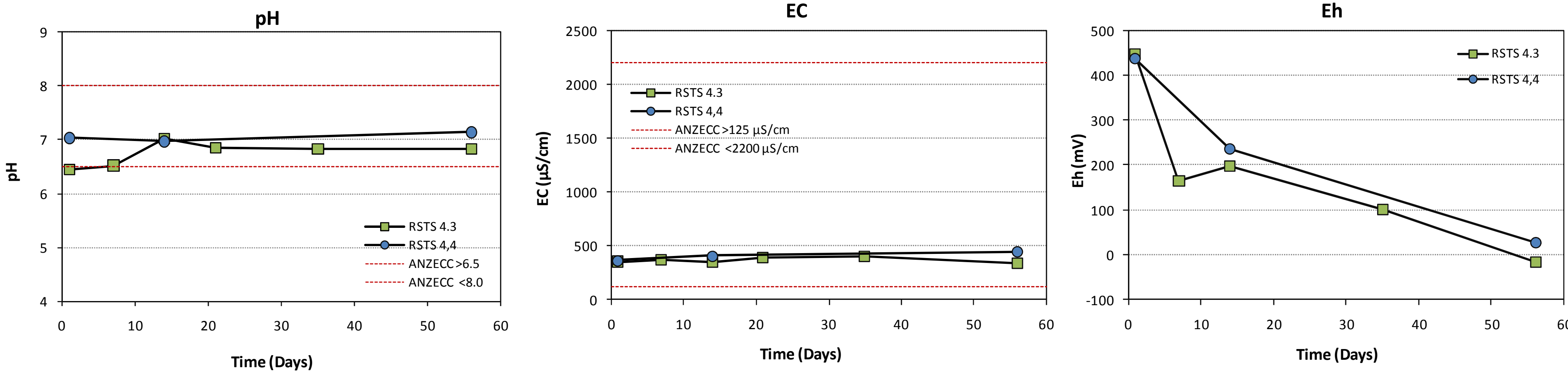

Figure 3-1: pH, EC and Eh dynamics over 56 days for the Tuckerbil Swamp surface soil materials (RSTS 4.3 and 4.4).

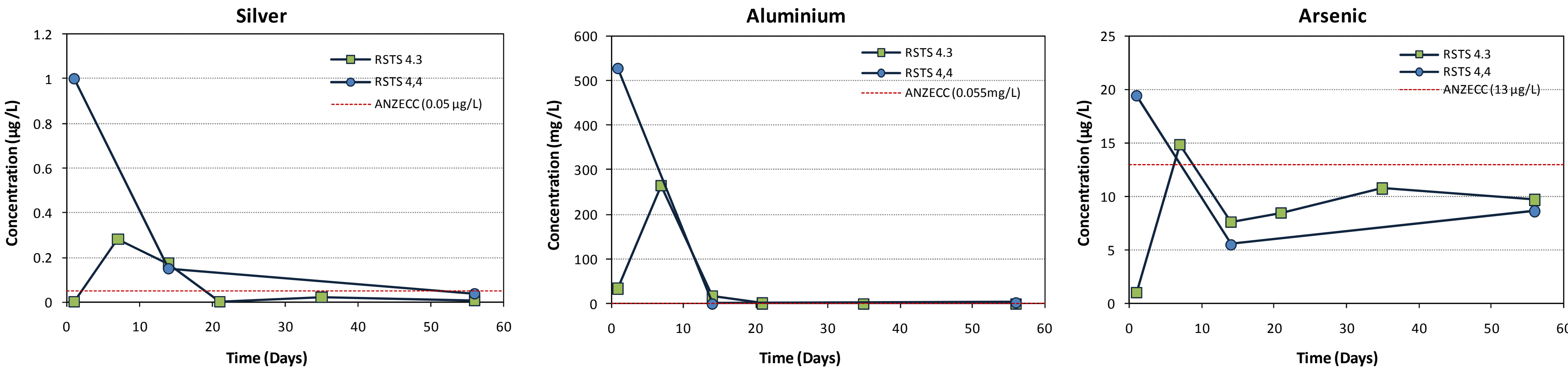

Figure 3-2: Contaminant and metalloid dynamics (Ag, Al and As) over 56 days for the Tuckerbil Swamp surface soil materials (RSTS 4.3 and 4.4).

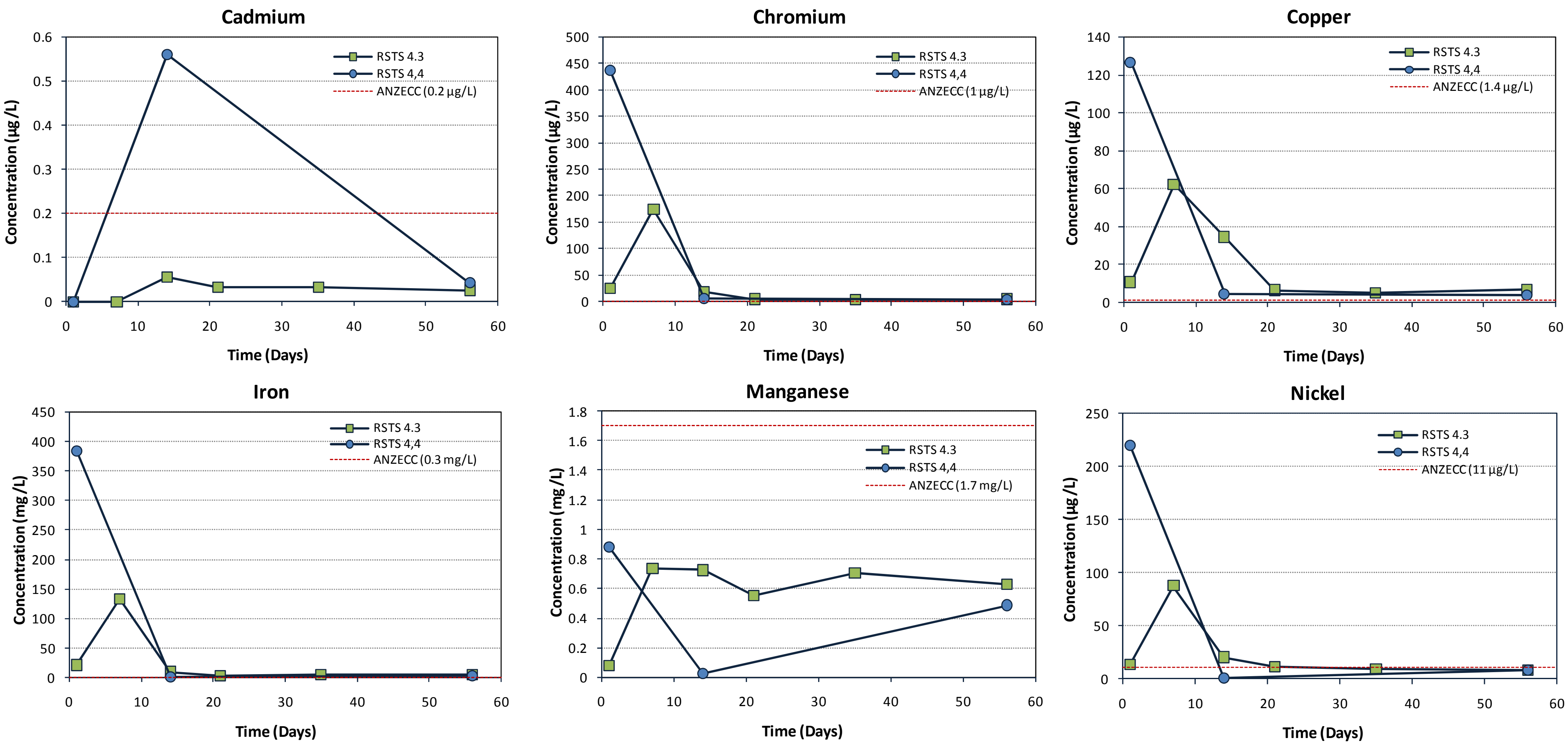

Figure 3-3: Contaminant and metalloid dynamics (Cd, Cr, Cu, Fe, Mn and Ni) over 56 days for the Tuckerbil Swamp surface soil materials (RSTS 4.3 and 4.4).

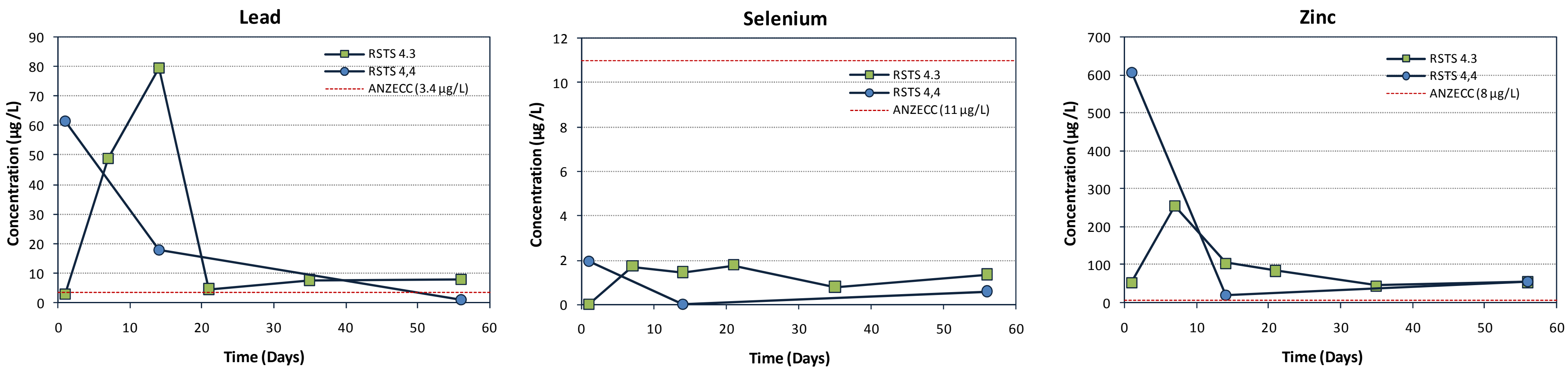

Figure 3-4: Contaminant and metalloid dynamics (Pb, Se and Zn) over 56 days for the Tuckerbil Swamp surface soil materials (RSTS 4.3 and 4.4).

3.1.4. Monosulfide formation potential data

The monosulfide formation potential data for the Fivebough and Tuckerbil Swamps surface soil materials are presented in Appendix 1 (Tables 8-4 to 8-24). The monosulfide formation potential data after seven weeks of inundation are summarised below in Table 3-5.

Table 3-5. Summary of monosulfide formation potential data for the Fivebough and Tuckerbil Swamps surface soil materials after 7 weeks (7.2 g/L sucrose).

Parameter	Units	Minimum	Median	Maximum	[1]n
pH		3.85	4.18	6.11	13
Eh	mV	129	294	319	13
S_{AV}	Wt. %S	<0.01	<0.01	<0.01	13
S^o	Wt. %S	<0.01	<0.01	<0.01	13
Pyrite-S	Wt. %S	<0.01	0.01	0.04	13
Dissolved S^{2-}	mg/L	<0.2	<0.2	1.8	13
SO_4	mg/L	4.66	21.62	300.48	13
Total Fe	mg/L	3.06	45.15	96.58	13

[1] n: number of samples.

The pH of the pore-waters after seven weeks of inundation ranged between 3.85 and 6.11 (Table 8-9, Appendix 1). The pore-water pH was observed to decrease with time with the addition of the two different organic substrate amounts (e.g. Figure 3-5). This decrease in pH may be a consequence of some acidity being released from the soil materials during the inundation experiments and the pore-waters having little buffering capacity. However, it is also possible that fermentation of the organic substrate added (i.e. sucrose) may occur during inundation resulting in acidification of the pore-waters.

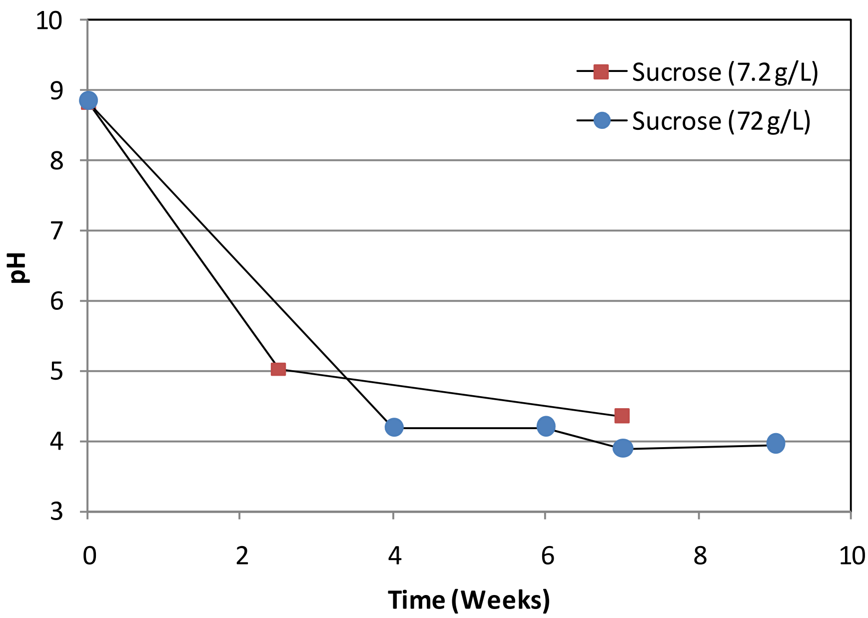

Figure 3-5: pH dynamics during inundation for RSFS 1.3.

A decrease in pore-water Eh was also observed during the inundation experiments (e.g. Figure 3-6), with the Eh of the pore-waters after seven weeks ranging between 129 and 319 mV (Table 8-10, Appendix 1). The Eh range of the pore-waters indicates suboxic-oxic conditions.

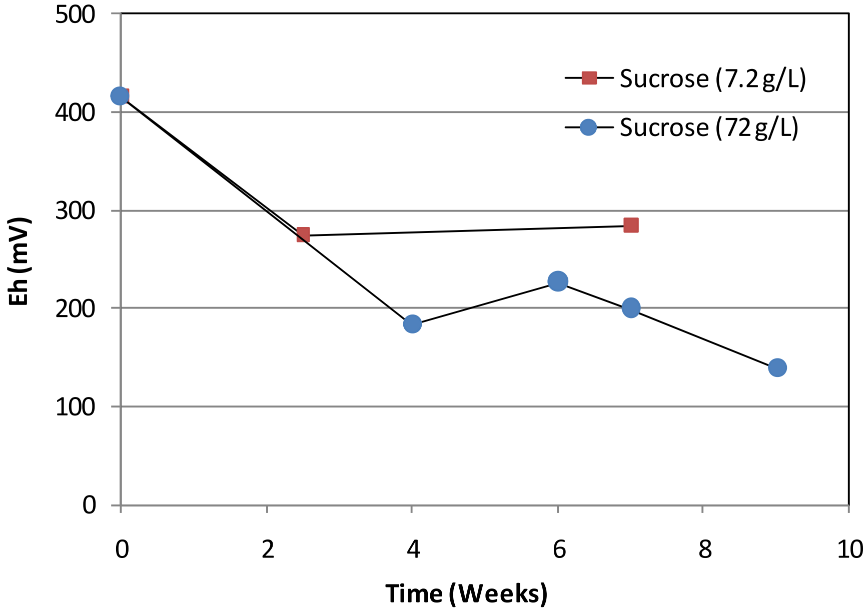

Figure 3-6: Redox potential (Eh) dynamics during inundation for RSFS 1.3.

Acid volatile sulfide (S_{AV}) and elemental sulfur (S^0) did not form in any of the surface soil materials examined after seven weeks of inundation (Tables 8-6 and 8-8, Appendix 1). However, an increase in the pyrite (FeS_2) fraction was observed in several of the soil materials. The Phase 1 assessment of acid sulfate soils in the Fivebough and Tuckerbil Swamps showed the presence of sulfide in the surface soils at three sites (i.e. Sites RSFS 6, RSTS 1 and RSTS 4), with S_{CR} values ranging between 0.01 and 0.02% S (see Ward *et al.* 2010a). After seven weeks of inundation eight of the 13 soil materials (i.e. 62%) contained a detectable pyrite concentration (i.e. ≥ 0.01% S), with a maximum pyrite concentration of 0.04% S (Table 8-7, Appendix 1).

Pyrite formation was observed in four surface soils from Fivebough Swamp (i.e. RSFS 4.3, 5.3, 6.3 and 7.3) and three soils from Tuckerbil Swamp (i.e. RSTS 1.3, 2.3 and 5.3) during the seven week inundation period, with a maximum pyrite increase of 0.03% S. Pyrite formation was not observed in the surface soil at Site RSTS 4 despite the presence of pyrite (i.e. 0.02% S) prior to inundation. The four surface soil materials in which pyrite formed in the Fivebough Swamp were also the soil materials that had the highest sulfate concentrations (i.e. ≥ 327 mg SO_4/kg) (see Ward *et al.* 2010a). Pyrite did not form in any of the soil materials in the Fivebough Swamp with a sulfate concentration of ≤ 163 mg SO_4/kg. However, all surface soils in the Tuckerbil Swamp had high sulfate concentrations (i.e. 287-5,319 mg SO_4/kg) (see Ward *et al.* 2010a) and pyrite formation was only observed in three of the five soils examined. The availability of iron may be the factor limiting sulfide formation in some of the Tuckerbil Swamp surface soil materials.

Substantial dissolved sulfide (up to 1.8 mg/L) accumulated in some of the pore-waters during the inundation experiments (Table 8-11, Appendix 1). Previous studies have shown that dissolved sulfide is able to accumulate under reducing conditions in acid sulfate soil landscapes where there is limited available iron (e.g. Ward *et al.* 2010b). Pore-waters from the majority of soil materials are observed to have significant soluble iron concentrations after seven weeks of inundation (Table 8-12, Appendix 1). It is therefore most likely that dissolved sulfide is able to accumulate in these pore-waters as the iron present is not able to react with sulfide due to iron complexation with organics. The complexation of the iron would also limit the formation of pyrite and monosulfides.

The sulfate concentration in the pore-waters after seven weeks of inundation ranged between 5 and 300 mg/L (Table 8-11, Appendix 1). Whilst these sulfate concentrations may limit the rate of further sulfate reduction, as the rate of sulfate reduction is generally limited at sulfate concentrations of less than ~500 mg/L SO_4^{2-} (Berner 1984), the threshold sulfate concentration required to prevent sulfate reduction is significantly lower. The threshold sulfate concentration required to induce sulfate reduction ranges between 8 to 40 μM (i.e. 0.08 - 0.42 mg/L SO_4^{2-}) (Holmer and Storkholm 2001). In addition sulfidic sediments have been observed in the Murray-Darling Basin where the sulfate concentration in the water column is > 10 mg/L (e.g. Sullivan *et al.* 2002; Hall *et al.* 2006) suggesting that the pore-water sulfate concentrations observed with the majority of soil materials in this study would not prevent sulfate reduction.

The absence of monosulfides after seven weeks of inundation may indicate that any monosulfides formed may have transformed to pyrite over the seven week inundation period. These findings are in agreement with previous studies that have shown that low pH favours the rapid direct formation of pyrite (e.g. Benning *et al.* 2000; Rickard and Luther III 2007).

The results from this monosulfide formation potential study clearly show that pyrite is able to accumulate under reducing conditions in the presence of organic matter in many of the surface soil materials from both the Fivebough and Tuckerbil Swamps. The sulfate concentrations in the pore-waters after seven weeks of inundation also indicate that there is the potential for more pyrite to form if the soil materials were incubated for more than seven weeks, although iron complexation with organics may possibly limit the rate of pyrite formation. In addition, the potential for sulfide formation in some of the soil materials examined also indicate that under suitable geochemical conditions (i.e. near neutral pH) monosulfides may form.

3.1.5. Mineral identification by x-ray diffraction

The mineralogy of the two Tuckerbil Swamp soil materials examined (i.e. RSTS 4.3 and 4.4) was determined by x-ray diffraction (XRD). The XRD patterns, which include the mineral identification interpretation, are presented in Figures 3-7 and 3-8. The mineralogy of the two samples is very similar with quartz dominant (i.e. >60%) and minor amounts (5-20%) of mica (mostly illite), kaolinite, albite and orthoclase. Smectite and also interstratified layer silicates appear to be present in low concentrations (i.e. <5-20%), but to verify this would require samples to be Ca-saturated.

The XRD data is in agreement with the sulfur species data in that the surface soil materials examined did not contain any identifiable retained acidity (such as jarosite and similar relatively insoluble hydroxy-sulfate compounds).

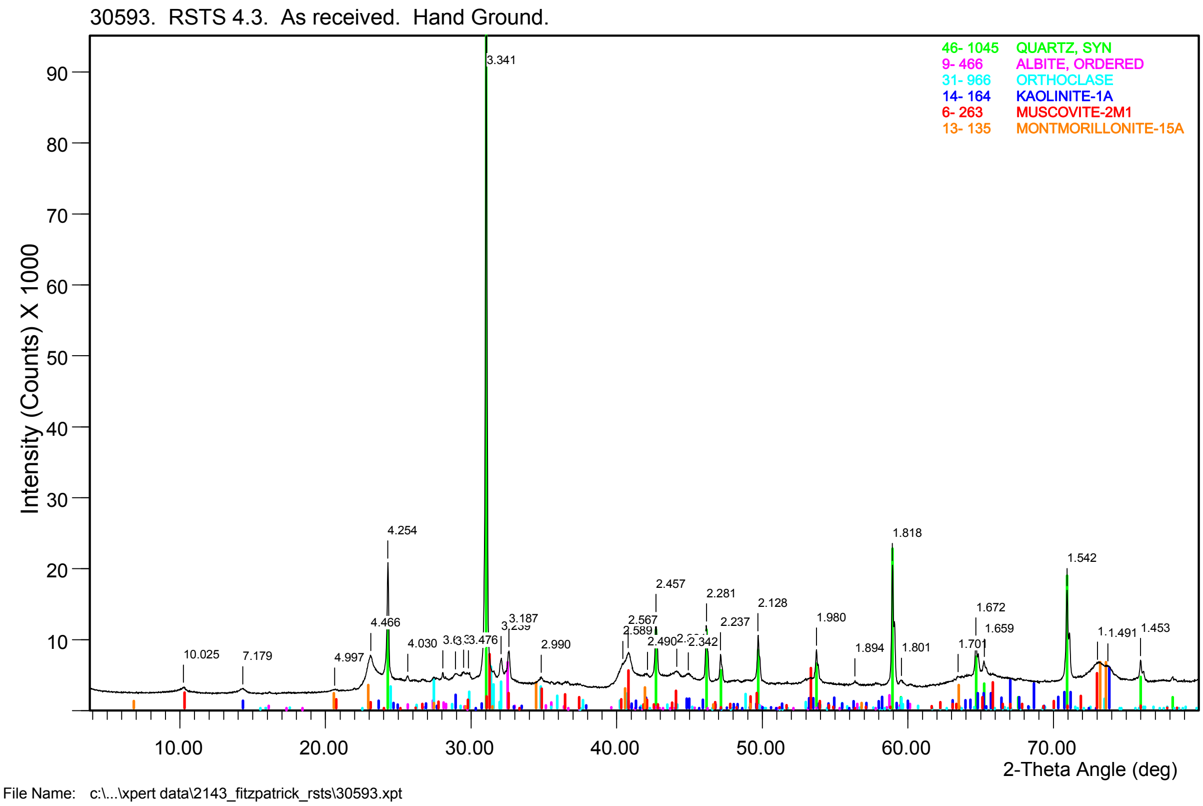

Figure 3-7: X-ray diffraction pattern for RSTS 4.3.

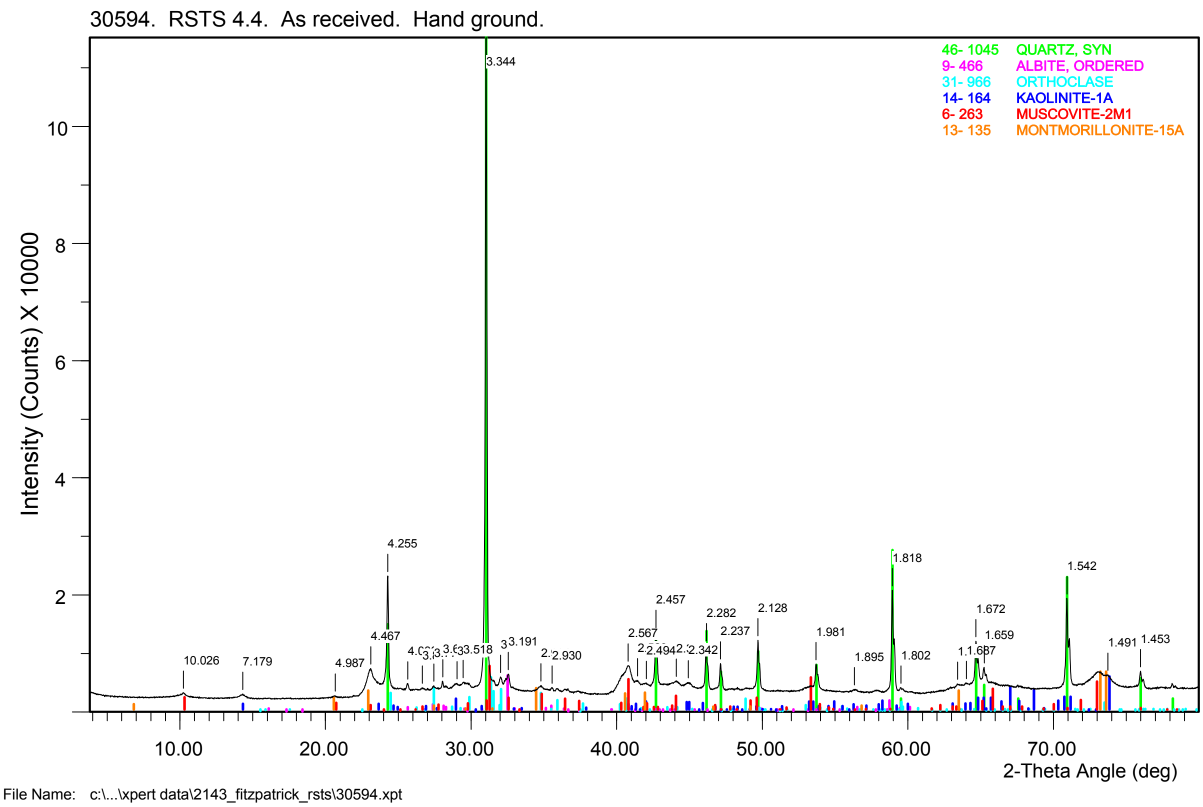

Figure 3-8: X-ray diffraction pattern for RSTS 4.4.

3.1.6. Geochemical analysis by x-ray fluorescence spectrometry

The x-ray fluorescence (XRF) spectrometry data for the two Tuckerbil Swamp soil materials examined (i.e. RSTS 4.3 and 4.4) are presented in Appendix 2 (Table 8-25). For the minor elements, analyses indicate that the concentrations are considered to be in the natural range. All elements which have an ANZECC sediment quality guideline are below the sediment quality guideline (SQG) trigger value. Although there are several anomalies among the minor elements (Table 8-25, Appendix 2), in general total concentrations for most elements are in the normal range for soils (Bowen 1979). The lower limits for detection using XRF analysis for elements such as cadmium (Cd) and mercury (Hg) are too high to be useful and these elements require specialist analysis.

Values for bromide (Br) and iodide (I) are relatively high and probably related to high chloride (Cl) concentrations, which are geochemically related through cyclic salts of marine origin. Manganese (Mn) is also quite high and is probably reinforced in these environments by redox conditions. Rubidium (Rb) and vanadium (V) are anomalously high in concentration for which a geochemical relationship is not known.

3.2. Interpretation and discussion of results

This Phase 2 assessment examined the presence of sulfur species in five soil materials from one site in the Tuckerbil Swamp (i.e. RSTS 4.3 – 4.7). The Phase 1 investigations found low levels of detectable reduced inorganic sulfur (0.02% S) in the surface soil at site 4 (RSTS 4.3; 0-5 cm). Further examination of the sulfur species present showed that the reduced inorganic sulfur fraction was entirely in the form of pyrite (FeS_2). Neither monosulfide nor elemental sulfur was identified within the soil profile at Site 4. Retained acidity in the form of jarosite and similar relatively insoluble hydroxy-sulfate compounds was not present at Site 4 as all soil samples had pH_{KCl} values of > 4.5. All soil materials examined from Site 4 have minimal net acidities, except for the surface layer which had a moderate net acidity (i.e. 26 mole H^+/tonne) (Table 3–2).

The XRD data was in agreement with the sulfur species data in that the two Tuckerbil Swamp soil materials examined (i.e. RSTS 4.3 and 4.4) did not contain any identifiable retained acidity (such as jarosite and similar relatively insoluble hydroxy-sulfate compounds). The XRD patterns also showed the mineralogy of the two soil materials was very similar with quartz dominant (i.e. >60%) and minor amounts (5-20%) of mica (mostly illite), kaolinite, albite and orthoclase. The XRF spectrometry data showed the total concentrations for most elements are in the normal range for soils, and elements which have an ANZECC sediment quality guideline are below the sediment quality guideline (SQG) trigger value.

The monosulfide formation potential data for the Fivebough and Tuckerbil Swamps surface soil materials clearly showed that sulfate reduction occurred within seven weeks of inundation, with the formation of pyrite in seven of the 13 soil materials examined (i.e. 54%). Pyrite formation was observed in four soils collected from the southern region of the Fivebough Swamp (i.e. RSFS 4.3, 5.3, 6.3 and 7.3) and three widely-distributed soils from Tuckerbil Swamp (i.e. RSTS 1.3, 2.3 and 5.3). An increase in the pyrite concentration of up to 0.03% S occurred after seven weeks of inundation. Neither monosulfide nor elemental sulfur was identified in any of the surface soil materials after this timeframe. Substantial dissolved sulfide concentrations were found in some of the pore-waters from both Fivebough and Tuckerbil Swamps.

Pyrite formation was only observed in surface soil materials with elevated soluble sulfate concentrations (i.e. ≥ 327 mg SO_4/kg) in the Fivebough Swamp. However, all surface soils in the Tuckerbil Swamp had high soluble sulfate concentrations and pyrite formation was only observed in three of the five soils examined. The availability of iron may be the factor limiting sulfide formation in some of the Tuckerbil Swamp surface soil materials. The sulfate data after seven weeks of inundation indicates the potential for further pyrite formation had the incubation interval been greater, although iron complexation with organics may possibly limit the rate of pyrite formation.

The monosulfide formation potential test assists in determining the propensity for monosulfides to form following inundation. As monosulfidic soil materials (i.e. S_{AV} ≥ 0.01% S) were not observed to form after the seven week incubation period with any of the Fivebough and Tuckerbil Swamps surface soil materials, these soil materials do not represent a de-oxygenation hazard (see Table 3-6). However, the potential for sulfide formation in several of the soil materials examined indicates that under suitable geochemical conditions (i.e. near neutral pH) monosulfides may form.

Table 3-6. 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_{AV}
Low Hazard	0.01% S_{AV}
Moderate Hazard	0.02% S – 0.04% S_{AV}
High Hazard	≥ 0.05% S_{AV}

The contaminant and metalloid dynamics data for two soils from the Tuckerbil Swamp (i.e. RSTS 4.3 and 4.4) showed all metals and metalloids examined (with the exception of manganese (Mn) and selenium (Se)) exceeded the ANZECC water quality guidelines during the inundation experiments (Table 3–4). The majority of the metals/metalloids showed a maximum concentration after seven days of inundation with the surface soil material (RSTS 4.3) suggesting that the metals/metalloids may have been released as a consequence of redox processes. The process controlling the release of metals/metalloids with the deeper soil material (RSTS 4.4) was not clear.

The rapid metal release experiments for two soils from the Tuckerbil Swamp (i.e. RSTS 4.3 and 4.4) showed the water quality guideline trigger values were exceeded for aluminium (Al), cobalt (Co), copper (Cu) and vanadium (V) for both soils and for chromium (Cr), nickel (Ni), silver (Ag) and zinc (Zn) for the surface soil (RSTS 4.3) (Table 3-3). The surface soil material exceeded the guidelines by more than 10 times for cobalt (Co) and copper (Cu). The NO_x (taken as nitrate for this comparison) concentrations were 20-70 times greater than the guidelines for lowland rivers, while the filterable reactive phosphorus (FRP) concentrations were 4-10 times greater than the guidelines for lowland rivers.

While the contaminant and metalloid dynamics and rapid metal release tests both showed that the ANZECC water quality guidelines were exceeded for many of the metals/metalloids, the degree by which the guidelines were exceeded was usually greater with the contaminant and metalloid dynamics test. The rapid metal release test measures the metals/metalloids released over the initial 24 hours of inundation, whereas the contaminant and metalloid dynamics method is able to predict the maximum concentration over a longer timeframe. The contaminant and metalloid dynamics test indicated that, particularly in the top soil, redox processes were probably largely driving the release of metals/metalloids, with maximum concentrations after at least seven days of inundation.

Although the contaminant and metalloid dynamics and rapid metal release tests give an indication of the metal/metalloid content of the soil, the overlying water will rarely have the concentration measured in solution during this test due to dilution in the receiving waters. It can therefore be assumed that if a metal/metalloid concentration did not exceed the ANZECC water quality guideline during the test it does not represent an environmental hazard. Thresholds for the degree of hazard associated with the contaminant and metalloid concentrations were developed with respect to the ANZECC guidelines, and a summary of the degree of hazard each of the metals/metalloids pose at the site examined in the Tuckerbil Swamp using the results from both tests is given in Table 3-7. Note the font/background colours presented in Tables 3-3 and 3-4 also correspond to the degree of hazard.

Table 3-7. Summary of the degree of hazard associated with the measured metal and metalloid concentrations.

Degree of Hazard	Guideline Threshold	Contaminant and Metalloid Dynamics Test	Rapid Metal Release Test
No Hazard	Value below ANZECC guideline threshold.	Mn, Se	As, Cd, Mn, Pb, Se
Low Hazard	Value exceeds ANZECC guideline threshold, but is less than 10x exceedance.	As, Cd,	Ag, Al*, Cr, Ni, V, Zn
Moderate Hazard	Value exceeds ANZECC guideline threshold by 10x or more, but is less than 100x exceedance.	Ag, Cu, Ni, Pb, Zn	Co, Cu
High Hazard	Value exceeds ANZECC guideline threshold by 100x or more.	Al*, Cr, Fe	None

** Based on aluminium (Al) being soluble – at pH > 5.5 this is unlikely.*

The metals/metalloids found to exceed the ANZECC water quality guidelines represent a low to high hazard, and usually varied depending on the method used (see Table 3-7). The degree of hazard was predominantly greater with the contaminant and metalloid dynamics test. Manganese (Mn) and selenium (Se) were both observed to be no hazard using both tests, and all metals/metalloids (except for copper (Cu) which had a moderate hazard with both tests) had a greater hazard with the contaminant and metalloid dynamics test. Aluminium (Al), chromium (Cr) and iron (Fe) were the only metals found at concentrations that represent a high hazard (Table 3-7).

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).

In this study a risk assessment framework has been applied 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.

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

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 4-2 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 and acid generating potential of acid sulfate soil materials, 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).

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

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

Likelihood category	Consequences 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

The following sub-sections discuss the risks associated with acidification (Section 4.2.1), contaminant mobilisation (Section 4.2.2) and de-oxygenation (Section 4.2.3) in the Fivebough and Tuckerbil Swamps Ramsar wetland. The risks associated with these hazards are dependent on a variety of factors including the scenario, wetland management regime and the species of aquatic organisms present. While likelihood of a disturbance scenario is taken into account in this risk assessment (see Table 4-2), the sensitivities and tolerances of different species of organism to each hazard has not been included. This risk assessment has primarily used the data obtained from both the Phase 1 and 2 acid sulfate soil assessments to give an overall assessment of each risk to the Fivebough and Tuckerbil Swamps Ramsar wetland and adjacent waters.

4.2.1. Risks associated with acidification

The Phase 1 assessment of acid sulfate soil materials in the Fivebough and Tuckerbil Swamps Ramsar wetland indicated the overall degree of acidification hazard was low (Ward *et al.* 2010a). The Phase 1 assessment found low net acidities were dominant within the wetland, with a single hypersulfidic material in the Tuckerbil Swamp (i.e. RSTS 4.3) having a moderate net acidity.

The Phase 2 sulfur species data for the Tuckerbil Swamp soil materials (i.e. RSTS 4.3 – 4.7) showed the presence of pyritic sulfur in the surface layer at site 4 (RSTS 4.3; 0-5 cm), with no retained acidity in any layers (see Table 3–2). While these findings also indicate the overall degree of acidification hazard is low, the monosulfide formation potential experiments on soil samples from both Fivebough and Tuckerbil Swamps have shown pyrite formation in seven of the 13 surface soil materials examined (i.e. 54%). The maximum pyrite concentration of 0.04% S after the seven week inundation period would suggest a greater potential acidification hazard. The pyrite content of the soil materials may also further increase with longer inundation times.

The degree of damage and impact would largely depend on the amount of pyrite that formed within the wetland over a given period. It is expected that the consequence of an acidification hazard occurring would range from *minor* to *moderate* depending on the amount of pyrite formed. The likelihood of these disturbance scenarios would be *possible*, and therefore there is a *low/medium* risk associated with acidification in the Fivebough and Tuckerbil Swamps Ramsar wetland.

4.2.2. Risks associated with contaminant mobilisation

The contaminant and metalloid dynamics data and the rapid metal release data showed many of the contaminants examined exceeded the ANZECC water quality guidelines. The contaminant and metalloid dynamics data showed three metals (i.e. Al, Cr and Fe) exceeded the ANZECC guidelines by more than 100 times. The metal concentrations that exceeded the guidelines during the contaminant and metalloid dynamics test represented a low to high hazard, with aluminium (Al), chromium (Cr) and iron (Fe) all having a high hazard (see Table 3-7). The rapid metal release data showed the surface soil material exceeded the guidelines by more than 10 times for cobalt (Co) and copper (Cu), and these two metals represent a moderate hazard (see Table 3-7). The rapid metal release data also showed NO_x (taken as nitrate for this comparison) concentrations were 20-70 times greater than the guidelines for lowland rivers, and the FRP concentrations were 4-10 times greater than the guidelines for lowland rivers.

If insufficient dilution of the contaminants was to occur in the receiving waters, there is a *moderate* consequence of a contaminant mobilisation hazard occurring (i.e. short-term damage to wetland values and/or adjacent waters; short-term impact on species and/or drinking water (including stock and domestic) supplies). The contaminant and metalloid dynamics data showed most of the metals/metalloids examined were largely released within 14 days of inundation. This disturbance scenario would be considered *likely*, and therefore there is a *medium* risk associated with contaminant mobilisation in the Fivebough and Tuckerbil Swamps Ramsar wetland.

It should be noted that in this Phase 2 study contaminant mobilisation was only examined in two layers collected from one site in the Tuckerbil Swamp. Further studies would be required to determine how representative these soil materials are of the entire wetland in order to fully assess the risk of contaminant mobilisation.

4.2.3. Risks associated with de-oxygenation

Monosulfidic soil materials pose a de-oxygenation hazard if disturbed. The Phase 2 sulfur species assessment did not identify the presence of monosulfides in any the soil materials examined in the Tuckerbil Swamp. In addition, none of the surface soil materials examined from either the Fivebough Swamp or Tuckerbil Swamp showed detectable monosulfide formation after the seven week timeframe of the monosulfide formation potential experiments. The findings of this study therefore indicate that the de-oxygenation hazard would represent a negligible impact on wetland values and/or adjacent waters and no detectable impacts on species (i.e. *insignificant* consequence of a hazard occurring). The Phase 2 assessment of the soil materials examined has indicated that there is a *low* de-oxygenation risk in the Fivebough and Tuckerbil Swamps Ramsar wetland. However, it is important to note that while the formation of monosulfides was not observed after the seven week inundation period, it is possible that monosulfides may form when some of the soil materials are inundated for a longer timeframe or under different geochemical conditions (i.e. near neutral pH).

A summary of the risks associated with the presence of acid sulfate soils in the Fivebough and Tuckerbil Swamps Ramsar wetland is presented below in Table 4-4.

Table 4-4: Summary of the risks associated with acid sulfate soils in Fivebough and Tuckerbil Swamps Ramsar Wetland.

Hazard	Level of risk
Acidification	Low/Medium risk
Contaminant mobilisation	Medium risk
De-oxygenation	Low risk

5. BROAD ACID SULFATE SOIL MANAGEMENT OPTIONS

This Phase 2 assessment identified the following risks associated with the presence of acid sulfate soils in the Fivebough and Tuckerbil Swamps Ramsar wetland:

- low/medium acidification risk in the Tuckerbil Swamp,
- medium contaminant mobilisation risk in the Tuckerbil Swamp, and
- low de-oxygenation risk in the Fivebough and Tuckerbil Swamps.

The acid sulfate soil materials identified in the Tuckerbil Swamp have the potential to present a medium risk to the environmental values of both the wetland and adjacent waters if not managed appropriately. A variety of options are available to manage landscapes where acid sulfate soil materials are observed. A national guidance document on the management of inland acid sulfate soil landscapes titled "*National guidance for the management of acid sulfate soils in inland aquatic ecosystems*" has recently been released (EPHC & NRMMC 2011). The national guidance document provides a hierarchy of management options for managing acid sulfate soils in inland aquatic ecosystems including:

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

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

5. *Limited further intervention.*

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 possible activities associated with each management objective are summarised in Table 5-1. Further information on each management option is provided in detail in the national guidance document (EPHC & NRMMC 2011).

The presence of acid sulfate soil materials with low/medium acidification and medium contaminant mobilisation risks would suggest that the most appropriate management strategy for the Fivebough and Tuckerbil Swamps Ramsar wetland would be to undertake routine monitoring to determine whether any of the hazards were increasing, and develop an acid sulfate soil management plan. In the event of an increase in the degree of hazard it would be necessary to prevent oxidation of the sulfidic materials present. As outlined in Table 5-1, in order to prevent oxidation it is necessary to keep the sulfidic sediments inundated, and if possible avoid flow regimes that could re-suspend these sediments. In the event of disturbance chemical ameliorants such as lime can be added to neutralise the water column and/or sediments. Details on the ameliorants available including their advantages and disadvantages are provided in the national guidance document (EPHC & NRMMC 2011). Controlled oxidation would not be a recommended management strategy in the Fivebough and Tuckerbil Swamps Ramsar wetland due to the potential risk of contaminant release.

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

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

The Phase 1 acid sulfate soil assessment of the Fivebough and Tuckerbil Swamps Ramsar wetland (Ward *et al*. 2010a) only provided a snapshot of the acid sulfate soil materials present and the conditions at selected locations in the wetland in July 2008. Since sampling the prolonged drought in the Murray-Darling Basin has come to an end and many regions have experienced major flooding. While flooding was probably not strong enough to scour the sulfidic soil materials from the Fivebough and Tuckerbil Swamps Ramsar wetland, inundation of this wetland may have minimised the risks identified in this study in the short-term. However, it is also likely that the recent inundation will lead to further formation of acid sulfate soil materials within the Fivebough and Tuckerbil Swamps Ramsar wetland.

It should be noted that further understanding of the complex interactions between surface water flow, groundwater processes, biogeochemistry and the different pathways for the development of acid sulfate soils in inland aquatic ecosystems is required for satisfactory management and preventative strategies. A more robust understanding of these complex interactions is needed before implementing any new strategies for multiple benefits.

6. CONCLUSIONS AND RECOMMENDATIONS

This report provides the results of a Phase 2 investigation that was undertaken for Fivebough and Tuckerbil Swamps Ramsar wetland to determine the nature, severity and the specific risks associated with acid sulfate soil materials. An examination of the sulfur species within a soil profile from the Tuckerbil Swamp found the reduced inorganic sulfur fraction in the surface soil (i.e. 0.02% S) was entirely in the form of pyrite (FeS_2). The XRD data was in agreement with the sulfur species data in that the surface soil materials examined did not contain any identifiable retained acidity (such as jarosite and similar relatively insoluble hydroxy-sulfate compounds). The soil materials in the profile from the Tuckerbil Swamp had minimal net acidities, except for the surface layer which had a moderate net acidity of 26 mole H^+/tonne.

The XRF data for two Tuckerbil Swamp soil materials showed the total concentrations for most elements are in the normal range for soils, and elements which have an ANZECC sediment quality guideline are below the sediment quality guideline (SQG) trigger value. However, contaminant and metalloid release data showed many metals/metalloids examined exceeded the ANZECC water quality guidelines (ANZECC/ARMCANZ 2000). The contaminant and metalloid dynamics test over 56 days showed that under the experimental conditions all metals and metalloids examined (with the exception of manganese (Mn) and selenium (Se)) were found to exceed the ANZECC water quality guidelines. The guidelines for aluminium (Al), chromium (Cr) and iron (Fe) were exceeded by more than 100 times, with many of the metals/metalloids being largely released within 14 days of inundation. A maximum concentration after seven days of inundation with the majority of the metals/metalloids associated with the surface soil material suggests that they may have been released as a consequence of redox processes.

Many of the contaminants also exceeded the ANZECC water quality guidelines using the 24 hour rapid metal release test, with the surface soil material exceeding the guidelines by more than 10 times for cobalt (Co) and copper (Cu). The data also showed NO_x (taken as nitrate for this comparison) concentrations were 20-70 times greater than the guidelines for lowland rivers, and the filterable reactive phosphorus (FRP) concentrations were 4-10 times greater than the guidelines for lowland rivers.

The metals/metalloids found to exceed the ANZECC water quality guidelines represent a low to high hazard, and usually varied depending on the method used (see Table 3-7). The degree of hazard was predominantly less with the rapid metal release method which measures the release over the initial 24 hours of inundation. The contaminant and metalloid dynamics method is able to predict the maximum concentration over a longer timeframe.

The monosulfide formation potential data for both the Fivebough and Tuckerbil Swamps surface soil materials clearly showed that sulfate reduction occurred within the seven week inundation period. While monosulfide formation was not observed, an increase in the pyrite content (of up to 0.03% S) occurred with 54% of the soil materials examined Substantial dissolved sulfide concentrations were also measured in some pore-waters. While the sulfate concentration seemed to have limited pyrite formation in some Fivebough Swamp soil materials, the availability of iron may be the limiting factor with some Tuckerbil Swamp soil materials. The pore-water sulfate data after seven weeks of inundation indicates a potential for further pyrite formation had the incubation interval been greater, although iron complexation with organics may possibly limit the rate of pyrite formation. The fact that monosulfidic soil materials (i.e. $S_{AV} \geq 0.01\%$ S) were not observed to form after seven weeks of incubation indicates that the surface soil materials examined from the Fivebough and Tuckerbil Swamps do not represent a de-oxygenation hazard. However, the potential for sulfide formation with several of the soil materials indicates that under suitable geochemical conditions (i.e. near neutral pH) monosulfides may form.

A risk assessment framework was applied to determine the specific risks associated with acidification, contaminant mobilisation and de-oxygenation (MDBA 2011). The Phase 2 assessment identified the following risks associated with the presence of acid sulfate soils in the Fivebough and Tuckerbil Swamps Ramsar wetland:

- low/medium acidification risk in the Tuckerbil Swamp,
- medium contaminant mobilisation risk in the Tuckerbil Swamp, and
- low de-oxygenation risk in the Fivebough and Tuckerbil Swamps.

These findings indicate that, if not managed appropriately, the acid sulfate soil materials identified in the Tuckerbil Swamp have the potential to present a medium risk to the environmental values of both the wetland and adjacent waters. This report outlines the variety of management options available to manage acid sulfate soils in inland aquatic ecosystems. The most appropriate management strategies for Fivebough and Tuckerbil Swamps Ramsar wetland would be to undertake routine monitoring to determine whether any of the hazards were increasing, and develop an acid sulfate soil management plan. However, 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.

It is important to note that the soil materials collected in July 2008 as part of the Phase 1 assessment only provided a snapshot of the acid sulfate soil materials present and the conditions at selected locations in the wetland. While recent inundation within the wetland may have minimised the risks identified in the short-term, it is also likely that this inundation will lead to further formation of acid sulfate soil materials.

This Phase 2 study only examined contaminant mobilisation in two partially-oxidised layers collected from one site in Tuckerbil Swamp. Further studies would be required to determine how representative these soil materials are of the entire wetland in order to fully assess the risk of contaminant mobilisation.

It is recommended that, within the context of other management objectives for the wetland, consideration be given to undertaking water quality monitoring to identify potential contamination as a result of the disturbance of acid sulfate soils within the wetland. The presence of some medium risks identified in this Phase 2 assessment indicates that management action may be recommended (MDBA 2011).

7. REFERENCES

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8. APPENDICES

APPENDIX 1. SOIL ANALYTICAL DATA

Table 8-1. Tuckerbil Swamp soil sulfur species suite data.

Site/Sample	Depth (cm)	S_{AV} (Wt. %S)	S^o (Wt. %S)	Pyrite-S (Wt. %S)
RSTS 4.3	0 – 5	<0.01	<0.01	0.02
RSTS 4.4	5 – 10	<0.01	<0.01	<0.01
RSTS 4.5	10 – 20	<0.01	<0.01	<0.01
RSTS 4.6	20 – 40	<0.01	<0.01	<0.01
RSTS 4.7	40 – 90	<0.01	<0.01	<0.01

Table 8-2. Sample RSTS 4.3 contaminant and metalloid dynamics data.

Parameter	units	ANZECC Guidelines	24 hours[#]		7 days		14 days		21 days		35 days		56 days	
			Av.	±	Av.	±	Av.	±	Av.	±	Av.	±	Av.	±
pH		6.5-8.0	6.44	-	6.52	*0.12*	7.02	*0.08*	6.85	*0.08*	6.84	*0.01*	6.84	*<0.01*
EC*	µS cm^{-1}	125-2200	357	-	371	*21*	352	*9*	394	*51*	403	*54*	344	*26*
Eh	mV		447	-	164	*93*	197	*<1*	n.a.	-	101	*17*	-16	*4*
Ag	µg l^{-1}	0.05	<0.1	-	0.3	*0.3*	0.2	*0.1*	<0.1	-	<0.1	-	<0.1	-
Al[A]	mg l^{-1}	0.055	34.6	-	263	*103*	16.2	*4.11*	1.09	*0.29*	0.80	*0.63*	0.60	*0.01*
As[B]	µg l^{-1}	13	1.0	-	14.8	*0.9*	7.6	*1.0*	8.5	*2.0*	10.7	*<1.0*	9.7	*0.4*
Cd	µg l^{-1}	0.2	<0.1	-	<0.1	-	0.1	*0.1*	<0.1	-	<0.1	-	<0.1	-
Cr[C]	µg l^{-1}	1	23.4	-	174	*63.7*	17.9	*0.9*	3.9	*0.8*	2.9	*<1.0*	3.5	*1.1*
Cu[H]	µg l^{-1}	1.4	10.8	-	62.2	*15.4*	34.6	*1.6*	6.6	*0.9*	5.2	*3.3*	7.1	*0.8*
Fe	mg l^{-1}	0.3	21.3	-	134	*33.8*	9.71	*1.58*	3.01	*0.40*	4.96	*0.16*	4.31	*0.10*
Mn	mg l^{-1}	1.7	0.08	-	0.73	*0.24*	0.72	*0.10*	0.55	*0.07*	0.70	*0.07*	0.63	*0.05*
Ni[H]	µg l^{-1}	11	13.4	-	87.3	*26.8*	19.8	*4.1*	10.7	*0.3*	8.9	*0.6*	8.0	*0.9*
Pb[H]	µg l^{-1}	3.4	3.1	-	48.9	*6.3*	79.5	*48.8*	4.7	*<1*	7.8	*5.7*	7.9	*0.1*
Se	µg l^{-1}	11	0.0	-	1.7	*1.7*	1.4	*<0.1*	1.8	*0.1*	<1	-	1.3	*0.2*
Zn[H]	µg l^{-1}	8	54.3	-	256	*73.8*	105	*8.3*	85.6	*4.0*	45.6	*1.3*	55.9	*6.0*

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 guidelines for lowland rivers in South-east Australia is provided for salinity (there are currently no trigger values defined for 'Wetlands').*
Values outside the ranges defined in the ANZECC guidelines are indicated with red text.
The deviation from the mean is represented by '±'.
[#] *Insufficient sample remaining for duplicate analysis.*
[A] *Guideline is for Aluminium in freshwater where pH > 6.5.*
[B] *Guideline assumes As in solution as Arsenic (AsV).*
[C] *Guideline for Chromium is applicable to Chromium (CrVI) only.*
[H] *Hardness affected (refer to Guidelines).*

Table 8-3. Sample RSTS 4.4 contaminant and metalloid dynamics data.

Parameter	units	ANZECC Guidelines	24 hours#		14 days		56 days	
			Av.	±	Av.	±	Av.	±
pH		6.5-8.0	7.04	-	6.97	*0.05*	7.15	*0.06*
EC*	µS cm^{-1}	125-2200	367	-	408	*8*	446	*66*
Eh	mV		437	-	237	*5*	28	*4*
Ag	µg l^{-1}	0.05	1.0	-	0.2	*0.1*	<0.1	-
Al^A	mg l^{-1}	0.055	527	-	0.45	*0.06*	2.47	*2.29*
As^B	µg l^{-1}	13	19.4	-	5.5	*0.7*	8.6	*4.7*
Cd	µg l^{-1}	0.2	<0.1	-	0.6	*<0.1*	<0.1	-
Cr^C	µg l^{-1}	1	436	-	5.5	*1.1*	3.3	*2.0*
Cu^H	µg l^{-1}	1.4	126	-	4.5	*1.5*	4.1	*1.8*
Fe	mg l^{-1}	0.3	384	-	0.63	*0.04*	1.92	*1.56*
Mn	mg l^{-1}	1.7	0.88	-	0.02	*<0.01*	0.48	*0.10*
Ni^H	µg l^{-1}	11	220	-	<1.0	-	7.9	*2.3*
Pb^H	µg l^{-1}	3.4	61.3	-	17.8	*0.7*	1.2	*0.9*
Se	µg l^{-1}	11	1.9	-	<1.0	-	<1.0	-
Zn^H	µg l^{-1}	8	607	-	20.2	*4.9*	56.1	*6.6*

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 guidelines for lowland rivers in South-east Australia is provided for salinity (there are currently no trigger values defined for 'Wetlands'.)*
Values outside the ranges defined in the ANZECC guidelines are indicated with red text.
The deviation from the mean is represented by '±'.
 # Insufficient sample remaining for duplicate analysis.
A Guideline is for Aluminium in freshwater where pH > 6.5.
B Guideline assumes As in solution as Arsenic (AsV).
C Guideline for Chromium is applicable to Chromium (CrVI) only.
H Hardness affected (refer to Guidelines).

Table 8-4. Fivebough and Tuckerbil Swamps monosulfide formation potential data immediately after inundating the soils (7.2 g/L sucrose).

Site/Sample	AVS (%S)	Pyrite (%S)	ES (%S)	pH	Eh (mV)	Total Fe (mg/L)
RSFS 1.3	<0.01	<0.01	<0.01	8.84	416	292.71
RSFS 2.3	<0.01	<0.01	<0.01	8.89	413	11.95
RSFS 3.3	<0.01	<0.01	<0.01	8.41	402	21.50
RSFS 4.3	0.01	0.01	<0.01	7.07	315	113.21
RSFS 5.3	<0.01	<0.01	<0.01	7.59	330	76.46
RSFS 6.3	<0.01	<0.01	<0.01	9.00	345	336.51
RSFS 7.3	0.03	<0.01	<0.01	9.76	342	5.30
RSFS 8.4	<0.01	<0.01	<0.01	9.75	356	27.95
RSTS 1.3	<0.01	<0.01	<0.01	9.46	350	0.33
RSTS 2.3	<0.01	<0.01	<0.01	9.34	351	393.71
RSTS 3.3	<0.01	<0.01	<0.01	8.50	342	0.09
RSTS 4.3	<0.01	0.01	<0.01	6.71	357	129.21
RSTS 5.3	<0.01	0.01	<0.01	6.00	348	14.71

Table 8-5. Fivebough and Tuckerbil Swamps monosulfide formation potential data after 2.5 weeks (7.2 g/L sucrose).

Site/Sample	AVS (%S)	Pyrite (%S)	pH	Eh (mV)	Total Fe (mg/L)
RSFS 1.3	0.01	0.02	5.01	275	10.89
RSFS 4.3	<0.01	<0.01	4.40	105	57.29
RSFS 5.3	<0.01	<0.01	4.52	158	44.93
RSFS 6.3	0.01	<0.01	4.27	202	4.30
RSFS 7.3	<0.01	<0.01	5.85	181	3.76
RSFS 8.4	<0.01	<0.01	4.51	228	2.05
RSTS 3.3	<0.01	<0.01	4.87	172	11.85
RSTS 4.3	<0.01	0.02	4.46	185	29.25
RSTS 5.3	<0.01	0.01	3.99	353	48.54

Table 8-6. Fivebough and Tuckerbil Swamps monosulfide formation potential – acid volatile sulfide (%S) data after 7 weeks.

Site/Sample	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
RSFS 1.3	<0.01		<0.01	
RSFS 2.3	<0.01		<0.01	
RSFS 3.3	<0.01		<0.01	
RSFS 4.3	<0.01		<0.01	
RSFS 5.3	<0.01	<0.01	<0.01	
RSFS 6.3	<0.01		<0.01	
RSFS 7.3	<0.01		<0.01	
RSFS 8.4	<0.01		<0.01	
RSTS 1.3	<0.01		<0.01	
RSTS 2.3	<0.01		<0.01	
RSTS 3.3	<0.01		<0.01	
RSTS 4.3	<0.01		<0.01	
RSTS 5.3	<0.01		<0.01	

Table 8-7. Fivebough and Tuckerbil Swamps monosulfide formation potential – pyrite (%S) data after 7 weeks.

Site/Sample	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
RSFS 1.3	<0.01		<0.01	
RSFS 2.3	<0.01		<0.01	
RSFS 3.3	<0.01		<0.01	
RSFS 4.3	0.03		0.02	
RSFS 5.3	0.02		0.01	
RSFS 6.3	0.04		0.02	
RSFS 7.3	0.01		<0.01	
RSFS 8.4	<0.01		<0.01	
RSTS 1.3	0.03		<0.01	
RSTS 2.3	0.01		<0.01	
RSTS 3.3	<0.01		<0.01	
RSTS 4.3	0.02		<0.01	
RSTS 5.3	0.01		0.01	

Table 8-8. Fivebough and Tuckerbil Swamps monosulfide formation potential – elemental sulfur (%S) data after 7 weeks.

Site/Sample	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
RSFS 1.3	<0.01		<0.01	
RSFS 2.3	<0.01		<0.01	
RSFS 3.3	<0.01	<0.01	<0.01	
RSFS 4.3	<0.01		<0.01	
RSFS 5.3	<0.01		<0.01	
RSFS 6.3	<0.01		<0.01	
RSFS 7.3	<0.01		<0.01	
RSFS 8.4	<0.01		<0.01	
RSTS 1.3	<0.01		<0.01	
RSTS 2.3	<0.01		<0.01	
RSTS 3.3	<0.01		<0.01	
RSTS 4.3	<0.01		<0.01	
RSTS 5.3	<0.01		<0.01	

Table 8-9. Fivebough and Tuckerbil Swamps monosulfide formation potential – pH data after 7 weeks.

Site/Sample	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
RSFS 1.3	4.34		3.89	0.03
RSFS 2.3	4.50		4.01	0.05
RSFS 3.3	4.24	0.15	3.94	0.06
RSFS 4.3	3.94		3.75	0.06
RSFS 5.3	3.98		3.79	0.06
RSFS 6.3	4.18		4.10	0.12
RSFS 7.3	6.11		4.71	0.05
RSFS 8.4	3.91		3.74	0.13
RSTS 1.3	5.70		5.01	0.16
RSTS 2.3	5.02		5.25	0.28
RSTS 3.3	3.96		4.15	0.12
RSTS 4.3	3.85		3.70	-
RSTS 5.3	3.89		3.76	-

Table 8-10. Fivebough and Tuckerbil Swamps monosulfide formation potential – Eh (mV) data after 7 weeks.

Site/Sample	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
RSFS 1.3	285		200	37
RSFS 2.3	246		182	48
RSFS 3.3	312	7	177	52
RSFS 4.3	300		146	45
RSFS 5.3	297		176	47
RSFS 6.3	270		124	52
RSFS 7.3	197		159	56
RSFS 8.4	315		172	79
RSTS 1.3	129		130	39
RSTS 2.3	210		128	45
RSTS 3.3	315		252	43
RSTS 4.3	319		148	-
RSTS 5.3	294		108	-

Table 8-11. Fivebough and Tuckerbil Swamps monosulfide formation potential – dissolved sulfide and sulfate data after 7 weeks (7.2 g sucrose).

Site/Sample	Dissolved sulfide (mg/L)		Sulfate (mg/L)	
	Av.	**±**	**Av.**	**±**
RSFS 1.3	<0.2		6.69	
RSFS 2.3	0.9		10.37	
RSFS 3.3	<0.2		4.66	0.50
RSFS 4.3	0.4		24.20	
RSFS 5.3	<0.2		6.91	
RSFS 6.3	0.7		21.62	
RSFS 7.3	<0.2		77.49	
RSFS 8.4	<0.2		5.40	
RSTS 1.3	1.8		83.58	
RSTS 2.3	<0.2		27.28	
RSTS 3.3	<0.2		300.48	
RSTS 4.3	<0.2		164.34	
RSTS 5.3	0.8		13.69	

Table 8-12. Fivebough and Tuckerbil Swamps monosulfide formation potential – total Fe (mg/L) data after 7 weeks.

Site/Sample	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
RSFS 1.3	35.15		27.90	5.94
RSFS 2.3	45.14		39.64	0.41
RSFS 3.3	26.97	9.50	33.03	0.07
RSFS 4.3	84.61		87.88	3.91
RSFS 5.3	96.58		117.45	7.85
RSFS 6.3	30.19		24.49	0.50
RSFS 7.3	3.06		14.62	4.37
RSFS 8.4	7.23		42.84	29.85
RSTS 1.3	37.82		49.20	1.18
RSTS 2.3	67.71		79.86	31.85
RSTS 3.3	46.21		57.68	5.98
RSTS 4.3	82.78		99.71	-
RSTS 5.3	80.96		176.40	-

Table 8-13. Sample RSFS 1.3 monosulfide formation potential – acid volatile sulfide (%S) data.

Time	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
0 weeks	<0.01		<0.01	
2.5 weeks	0.01		-	-
4 weeks	-	-	<0.01	
6 weeks	-	-	<0.01	
7 weeks	<0.01		<0.01	
9 weeks	-	-	<0.01	

Table 8-14. Sample RSFS 1.3 monosulfide formation potential – pyrite (%S) data.

Time	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
0 weeks	<0.01		<0.01	
2.5 weeks	0.02		-	-
4 weeks	-	-	<0.01	
6 weeks	-	-	<0.01	
7 weeks	<0.01		<0.01	
9 weeks	-	-	<0.01	

Table 8-15. Sample RSFS 1.3 monosulfide formation potential – elemental sulfur (%S) data.

Time	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
0 weeks	<0.01		<0.01	
7 weeks	<0.01		<0.01	
9 weeks	-		<0.01	

Table 8-16. Sample RSFS 1.3 monosulfide formation potential – pH data.

Time	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
0 weeks	8.84		8.84	
2.5 weeks	5.01		-	-
4 weeks	-	-	4.18	0.09
6 weeks	-	-	4.20	0.06
7 weeks	4.34		3.89	0.03
9 weeks	-	-	3.95	0.05

Table 8-17. Sample RSFS 1.3 monosulfide formation potential – Eh (mV) data.

Time	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
0 weeks	416		416	
2.5 weeks	275		-	-
4 weeks	-	-	184	4
6 weeks	-	-	227	
7 weeks	285		200	37
9 weeks	-	-	139	11

Table 8-18. Sample RSFS 1.3 monosulfide formation potential total – Fe (mg/L) data.

Time	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
0 weeks	292.71		292.71	
2.5 weeks	10.89		-	-
4 weeks	-	-	13.03	
6 weeks	-	-	18.50	
7 weeks	35.15		27.90	5.94
9 weeks	-	-	38.43	1.47

Table 8-19. Sample RSFS 8.4 monosulfide formation potential – acid volatile sulfide (%S) data.

Time	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
0 weeks	<0.01		<0.01	
2.5 weeks	<0.01		-	-
4 weeks	-	-	<0.01	
6 weeks	-	-	<0.01	
7 weeks	<0.01		<0.01	
9 weeks	-	-	<0.01	

Table 8-20. Sample RSFS 8.4 monosulfide formation potential – pyrite (%S) data.

Time	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
0 weeks	<0.01		<0.01	
2.5 weeks	<0.01		-	-
4 weeks	-	-	-	
6 weeks	-	-	<0.01	
7 weeks	<0.01		<0.01	
9 weeks	-	-	<0.01	

Table 8-21. Sample RSFS 8.4 monosulfide formation potential – elemental sulfur (%S) data.

Time	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
0 weeks	<0.01		<0.01	
7 weeks	<0.01		<0.01	
9 weeks	-		<0.01	

Table 8-22. Sample RSFS 8.4 monosulfide formation potential – pH data.

Time	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
0 weeks	9.75		9.75	
2.5 weeks	4.51		-	-
4 weeks	-	-	3.87	0.03
6 weeks	-	-	3.91	0.07
7 weeks	3.91		3.74	0.13
9 weeks	-	-	3.77	0.05

Table 8-23. Sample RSFS 8.4 monosulfide formation potential – Eh (mV) data.

Time	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
0 weeks	356		356	
2.5 weeks	228		-	-
4 weeks	-	-	175	4
6 weeks	-	-	253	
7 weeks	315		172	79
9 weeks	-	-	165	10

Table 8-24. Sample RSFS 8.4 monosulfide formation potential – total Fe (mg/L) data.

Time	Sucrose added (7.2 g/L)		Sucrose added (72 g/L)	
	Av.	**±**	**Av.**	**±**
0 weeks	27.95		27.95	
2.5 weeks	2.05		-	-
4 weeks	-	-	20.84	
6 weeks	-	-	12.17	
7 weeks	7.23		42.84	29.85
9 weeks	-	-	48.36	28.48

APPENDIX 2. GEOCHEMISTRY DATA (X-RAY FLUORESCENCE)

Table 8-25. Summary of trace element data for the Tuckerbil Swamp soil materials by x-ray fluorescence.

Element	Units	ANZECC Sediment Quality Guidelines*		[1] LLD	RSTS 4.3	RSTS 4.4
		SQG-Low (Trigger value)	SQG-High			
Ag	(ppm)	1	3.7	3	<3	<3
As	(ppm)	20	70	1	8	9
Ba	(ppm)			10	225	268
Bi	(ppm)			3	<3	<3
Br	(ppm)			1	56	13
Cd	(ppm)	1.5	10	3	<3	<3
Ce	(ppm)			14	60	69
Co	(ppm)			4	14	15
Cr	(ppm)	80	370	2	56	67
Cs	(ppm)			7	<7	11
Cu	(ppm)	65	270	1	25	27
Ga	(ppm)			1	14	18
Ge	(ppm)			1	<1	2
Hf	(ppm)			7	<7	<7
Hg	(ppm)	0.15	1	11	<11	<11
I	(ppm)			6	18	<6
La	(ppm)			12	52	50
Mn	(ppm)			6	368	398
Mo	(ppm)			1	<1	<1
Nb	(ppm)			1	10	13
Nd	(ppm)			8	25	33
Ni	(ppm)	21	52	2	18	19
Pb	(ppm)	50	220	2	16	14
Rb	(ppm)			2	92	113
Sb	(ppm)	2	25	7	<7	<7
Sc	(ppm)			3	10	13
Se	(ppm)			1	<1	<1
Sm	(ppm)			9	<9	<9
Sn	(ppm)			3	<3	<3
Sr	(ppm)			1	86	77
Ta	(ppm)			5	<5	<5
Te	(ppm)			6	<6	<6
Th	(ppm)			3	11	15
Tl	(ppm)			2	4	5
U	(ppm)			2	3	<2
V	(ppm)			5	76	94
Y	(ppm)			1	19	27
Yb	(ppm)			8	<8	<8
Zn	(ppm)	200	410	2	62	64
Zr	(ppm)			1	176	256

** The ANZECC sediment quality guidelines (SQG) are for total metal concentrations (ANZECC/ARMCANZ 2000).*

[1] LLD: lower limit of detection for the method.

APPENDIX 3. CSIRO ACID, METAL AND NUTRIENT MOBILISATION REPORT

Acid, metal and nutrient mobilisation from two Fivebough & Tuckerbil soils

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www.csiro.au

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1. EXECUTIVE SUMMARY

Rapid metal release tests

Rapid metal release tests were completed on two soils from wetlands at Fivebough & Tuckerbil in order to assess the availability of nutrient and trace metals and metalloids of concern. The elutriate waters exceeded the water quality guideline (WQG) trigger values for Al, Co, Cu and V for both soils and for Ag, Cr, Ni and Zn for one of the two soils. One soil elutriate water exceeded WQGs by 10× for Co and Cu. The NOx (taken as nitrate for this comparison) concentrations in the elutriate waters were 20-70× greater than the guidelines for lowland rivers, while the FRP concentrations were 4-10× greater than the guidelines for lowland rivers. If these two soils were considered representative of the entire wetland, the results suggest that NOx, but not FRP release may not be of potential concern to the environment. Generalisations about potential metal release from the Fivebough & Tuckerbil wetland soils are not possible based on this small data set.

1.1 Rapid release test methods

The rapid metal release tests were undertaken using the protocols for laboratory analysis prescribed for the 'Detailed Assessment of Acid Sulfate Soils in the Murray-Darling Basin' (Murray–Darling Basin Authority (2010).

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

The soils were resuspended (50 g dry weight in 500 mL Nalgene bottles – 50 mL headspace) by rolling the bottles containing soil and water at 100 rpm on a purpose built bottle roller. The water quality parameters measure were, pH, redox potential (Eh), conductivity (EC) and dissolved oxygen, both at the start and finish of all tests. After 24 h, the waters will be centrifuged before sample collection. Alkalinity, nutrient (N and P) and major ion analyses were performed on unfiltered samples (centrifuged and no visible suspended solids present) and dissolved metals analyses were made on <0.45 µm filtered samples so that they can be accurately compared to the water quality guidelines. The full set of analyses on water samples at the end of the tests comprised (i) alkalinity (ii) dissolved organic carbon, (iii) the major anions/nutrients (Cl, NO_2, NO_3, reactive-P (PO_4), and SO_4, (iv) the major cations Na, K, Ca, Mg, and (v) the trace metals or metalloids Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, V, Zn.

Replicate tests and analyses were be undertaken for approximately 10% of samples. For the majority of the chemical analyses, NATA-accredited laboratories were used, including ALS Environmental (Brisbane) for water alkalinity and anions (including N and P nutrients) and

CSIRO Centre for Environmental Contaminants Research in Sydney for dissolved metals analyses in water and soils and also for the acid, metal and nutrient mobilisation tests.

Table 1. Methods used for analyses of water

Analyte	Method
Dissolved metals by ICP-AES	Dissolved metals were measured by ICP-AES (CIROS, SPECTRO). The sample is converted to an aerosol and transported into the plasma. Atoms and ions of the plasma are excited and emit light at characteristic wavelengths. The light emitted by the sample passes through the entrance slit of the spectrometer. The different wavelengths are measured and converted to a signal and quantified by comparison with standards.
Dissolved metals by ICP-MS	Dissolved metals were measured by ICP-MS (Agilent 7500 CE). Analyte species originating in a liquid are nebulised by a Micromist nebuliser and a cooled double-pass spray chamber. The ions are detected by an electron multiplier. The ions are quantified by comparison with prepared standards.
Alkalinity and Acidity as calcium carbonate	APHA 21st ed., 2320 B This procedure determines alkalinity by both manual measurement and automated measurement (e.g. PC Titrate) using pH 4.5 for indicating the total alkalinity end-point. Acidity is determined by titration with a standardised alkali to an end-point pH of 8.3.
Major anions - filtered	APHA 21st ed., 4500 Cl - B. Automated Silver Nitrate titration.
Chloride	APHA 21st ed., 3120; USEPA SW 846 - 6010 The ICP AES technique ionises filtered sample atoms emitting a characteristic spectrum. This spectrum is then compared against matrix matched standards for quantification.
Nitrite and nitrate as N	APHA 21st ed., 4500 NO_3^- I. Nitrate is reduced to nitrite by way of a cadmium reduction column followed by quantification by FIA. Nitrite is determined separately by direct colourimetry and result for Nitrate calculated as the difference between the two results.
Reactive phosphorus - filtered	APHA 21st ed., 4500 P-E Water samples are filtered through a 0.45um filter prior to analysis. Ammonium molybdate and potassium antimonyl tartrate reacts in acid medium with othophosphate to form a heteropoly acid -phosphomolybdic acid - which is reduced to intensely coloured molybdenum blue by ascorbic acid. Quantification is achieved by FIA.
Total organic carbon (TOC)	APHA 21st ed., 5310 B, The automated TOC analyzer determines Total and Inorganic Carbon by IR cell. TOC is calculated as the difference.
Moisture content	A gravimetric procedure based on weight loss over a 12-24 h drying period at 110±5ºC.
Paste pH, conductivity	Paste pH (USEPA 600/2-78-054): pH determined on a saturated paste by ISE. Electrical Conductivity of Saturated Paste (USEPA 600/2-78-054) - conductivity determined on a saturated paste by ISE.

	Depth, cm			**pH**		**Sulfate**	**TAA (to pH6.5)**	**Reduced Inorganic Sulfur**
Sample	**Upper**	**Lower**	**pH_W**	**pH_{KCl}**	**pH_{Fox}**	**($mgSO_4$/kg)**	**(mole H+ /tonne)**	**(%S_{Cr})**
RSTS 4.3	0	5	6.06	5.5	2.8	3033	13.05	0.015
RSTS 4.4	5	10	7.41	5.8	8.5	3318	6.56	<0.01

2. Rapid metal release tests

Rapid metal release tests were used to assess soils under standard laboratory conditions for their ability to release metals, metalloids and chemical compounds which have potential to be a hazard. These rapid metal release tests were undertaken on two samples using deionised water.

The general water quality parameters, alkalinity, and major anion and cation concentrations from the two rapid release tests are shown in Table 1. Due to there being just two samples, a detailed interpretation of the results in relation to each entire wetland is not justified. The significance of the single result for soils is compared to the results for soils tested for other wetlands (e.g. Banrock, Chowilla, Kerang) or soils from Lake Albert and Alexandrina.

The pH of the elutriate waters from the two rapid metal release test samples were slightly acidic, but both waters had a moderate amount of alkalinity (32-36 mg $CaCO_3$/L) (Table 2). One of soils had negligible oxygen demand, however the soil which released the greater amount of TOC caused the dissolved oxygen (DO) to drop to 2.5 mg/L, indicating that this soil had a significant biological oxygen demand.

The ANZECC/ARMCANZ (2000) trigger values for salinity for South Australia wetlands range from 300 to 1000 µS/cm. It is recognised that wetlands in particular can have substantially higher salinity due to saline groundwater intrusion. Background specific electrical conductance in many wetlands is likely to already substantially exceeds these trigger values. The specific electrical conductance (SEC) of the two rapid release test waters were near 1000 µS/cm. .

Compared to background chloride and sulfate concentrations in the River Murray (100-150 mg Cl/L, 20-30 mg SO_4/L), the two soil elutriate waters had chloride concentrations close to this range, but the sulfate concentrations were an order of magnitude greater (Table 2). In 2008, concentrations of chloride and sulfate in wetlands at Jury Swamp, Paiwalla, Riverglades ranged from 100 and 5000 mg/L and 50 to 2000 mg/L, respectively. In the 2008 rapid release tests; chloride concentrations were similar to background River Murray concentrations (100-150 mg/L) for the Swanport wetland, and about two-fold higher in Ukee and Jury Swamp; the highest sulfate concentration was in the Swanport wetland remobilisation sample (1930 mg/L), followed by Ukee (1360 mg/L) and Jury Swamp (790 mg/L). With the exception of Swanport, these were within the range of sulfate concentrations in the background River Murray water (20-30 mg/L), suggesting that release of sulfate from these ASS was negligible.

There are no ANZECC/ARMCANZ (2000) guidelines for nitrate or phosphate for wetlands, however the trigger values for nitrate and FRP filterable reactive phosphate in lowland rivers are 100 µg/L and 40 µg/L, respectively. For the two Fivebough & Tuckerbil soil elutriates, the NOx (taken as nitrate for this comparison) concentrations were 20-70× greater than the guidelines for lowland rivers, while the FRP concentrations were 4-10× greater than the guidelines for lowland rivers. If these two soils were considered representative of the entire wetland, the results suggest that NOx, but not FRP release may not be of potential concern to the environment. For comparison, in the 45 wetland soil samples studied by Simpson et al. (2008), the highest nitrate concentration was 2.91 mg/L in Ukee, and the highest phosphate concentration was 0.1 mg/L in Riverglades, suggesting that ASS may contribute to nutrients in the wetlands. In 2008, concentrations of NOx and FRP in wetlands at Jury Swamp, Paiwalla, Riverglades ranged from <0.005 to 1.0 mg/L and <0.01 to 2.5 mg/L, respectively.

Comparison of mean±SD and maximum pH, SEC and concentrations of alkalinity, major anions and cations, nitrate (represented by NOx) and phosphate (FRP) are made between the elutriates from Banrock, Chowilla and Kerang wetland soils in Table 3. Within a factor of 2-3, many of these parameters were within a similar range.

Table 2. pH, redox potential (Eh), conductivity and dissolved oxygen (DO), and concentrations of alkalinity, acidity, sulfate, chloride, nitrite+ nitrate, phosphate, total organic carbon and major cations at the completion of the 24-h rapid release tests.

Site	pH	Eh mV	SEC mS/cm	DO mg/L	Alkalinity mg CaCO3/L	NOx mg/L		FRP mg/L
RSTS 4.3	5.8	574	1.2	2.5	36	36		300
RSTS 4.4	6.3	583	0.90	6.2	32	32		282
	Major anions and cations in mg/L							
	SO4	**Cl**	**Na**	**K**	**Ca**	**Mg**	**Al**	**Fe**
RSTS 4.3	300	140	200	28.1	32.2	23.3	0.14	0.60
RSTS 4.4	282	72.9	150	19.5	20.2	12.9	0.23	0.18

NOx = Nitrate+Nitrite-N, FRP = Filterable reactive phosphate, TOC = total organic carbon

Table 3. Comparison with rapid metal-release data for other wetland soils samples tested in 2010 and results for wetlands studied in 2008 (Simpson *et al*., 2008).

Banrock (2010)	**pH**	**SEC, mS/cm**	**Alkalinity**	**SO4**	**Cl**	**NOx**	**FRP**	**TOC**	**Ca**	**Mg**	**Fe**
						mg/L					
Maximum	7.5	13	64	3000	4570	9.8	1.3	392	813	350	88
Mean (n=15)	5.4	3.1	27	500	880	1.5	0.3	72	141	80	10
SD	1.3	4.1	23	735	1370	2.8	0.4	104	229	105	25
Chowilla (2010)											
Maximum	8.0	4.6	46	652	10500	25.9	3.8	148	672	944	74
Mean (n=46)	6.1	0.37	16	80	510	1.8	0.7	25	41	54	15
SD	1.0	0.89	13	150	2100	4.5	0.9	26	126	187	17
Kerang (2010)											
Maximum	8.4	26	85	4010	10800	27.6	2.0	134	956	557	41
Mean (n=27)	7.0	4.0	36	540	1500	2.4	0.5	33	108	83	10
SD	1.3	7.5	26	1070	2900	5.9	0.6	31	244	140	14

2.1.1 Trace metals

The trace metal/metalloid concentrations from the rapid metal release tests are shown in Table 4. Also shown are the maximum, mean±standard deviation, and percent of tests exceeding the ANZECC/ARMCANZ (2000) water quality guideline trigger vales for 95% species protection. Generalisations about potential metal release from the Fivebough & Tuckerbil wetland soils are not possible based on this small data set. The elutriate waters exceeded the WQGs for Al, Co, Cu and V for both soils and for Cr, Ni and Zn for one of the two soils (Table 4). The RSTS 4.3 soil elutriate waters exceeded WQGs by 10× for Co and Cu.

A comparison with rapid metal-release data (mean±SD, maximum) for other wetland soils samples tested in 2010 and results for wetlands studied in 2008 (Simpson et al. (2008) is shown in Table 5. In the 2008 study the elutriate waters from the rapid metals release tests of exceeded the WQGs for most metals in greater than 50% of the waters from wetland soil samples. There were also some very high metal releases, e.g. 460 mg Al/L, 60 mg Mn/L, 14 mg Zn/L, 6.9 mg Ni/L, 4.4 mg Co/L for one sample. For the wetland soils from Fivebough & Tuckerbil, and those from Banrock, Chowilla and Kerang, the elutriate metals were generally not as great as those observed for the wetland soils studied in 2008 or for soils from Lake Albert and Alexandrina.

It is important to note that the elutriate waters produced from the rapid metal mobilisation tests were expected to result in a worst case scenario for rapid metal release from most of these soils (undertaken using high concentrations of suspended solids (100 g/L) with the soils shaken for 24 h). As demonstrated previously (Simpson et al., 2008, 2010), there are a number of processes that will result in significant attenuation of these dissolved concentrations, including precipitation and re-adsorption processes.

Table 4. Concentrations of trace metals at the completion of the 24-h rapid release tests

	Al	Mn	Ag	As	Cd	Co	Cr	Cu	Ni	Pb	Sb	Se	V	Zn
Site	**----- mg/L -----**		**-----Trace metal concentrations in µg/L-----**											
RSTS 4.3	**0.14**	1.7	**0.07**	7.2	0.1	**24**	**2.2**	**16**	**21**	1.2	0.6	0.9	**8.6**	**12**
RSTS 4.4	**0.23**	0.5	<0.02	3.8	<0.5	**4.3**	0.6	**8.7**	7.2	<0.4	<0.4	0.7	**6.6**	2
WQG (95%PC)	**0.055**	**1.9**	**0.05**	**13 [b]**	**0.2**	**1.4 [c]**	**1.0 [d]**	**1.4**	**11**	**3.4**	**NV**	**11**	**6.0 [c]**	**8.0**
>1×WQG, % [e]	100	0	50	0	0	100	50	100	50	0	NV	0	100	50
>10×WQG, % [e]	0	0	0	0	0	**50**	0	**50**	0	0	NV	0	0	0
>100×WQG, %	0	0	0	0	0	0	0	0	0	0	NV	0	0	0

WQG (95%PC) = ANZECC/ARMCANZ (2000) water quality guideline trigger value for 95% species protection. a Mean and SD calculations use 'Limit of Reporting' (LOR) values are measured value. b As(V) = 13 µg/L (As(III) = 24 µg/L). c Low reliability guideline. d Cr assumes all is as Cr(VI) and NV = no value. e **Blue** when >WQG trigger value, **red** when >10×WQG trigger value, and **black** when >100×WQG trigger value

Table 5. Comparison with rapid metal-release data for other wetland soils samples tested in 2010 and results for wetlands studied in 2008, and soils from the Murray River and Lower Lakes (Simpson *et al*., 2008; Baker et al., 2010).

	Al	Mn	Ag	As	Cd	Co	Cr	Cu	Ni	Pb	Se	V	Zn
	----- mg/L -----		---------------------------------Trace metal concentrations in µg/L----------------------------										
WQG *	**0.055**	**1.9**	**0.05**	**13**	**0.2**	**1.4**	**1**	**1.4**	**11**	**3.4**	**11**	**6**	**8**
Banrock (2010)													
Maximum	250	41.9	0.09	150	2.3	2200	38	48	640	30	2.6	120	2300
Mean (n=15) a	**14**	**5.1**	0.03	**17**	**0.6**	229	**5**	**17**	**97**	**4**	0.7	**23**	**217**
SD	38	10.6	0.02	37	0.7	563	10	14	173	8	0.7	33	586
Chowilla (2010)													
Maximum	49	5.31	0.50	99	1.7	70	39	96	81	60	1.7	270	200
Mean (n=46)	**11**	0.58	0.04	**14**	**0.5**	**12**	**8**	**24**	**15**	**14**	0.4	**55**	**28**
SD	10	1.02	0.07	17	0.3	12	8	22	14	15	0.4	58	31
Kerang (2010)													
Maximum	50	2.47	0.43	42	0.6	39	24	75	58	51	6.4	240	50
Mean (n=27)	**13**	0.43	**<0.1**	**14**	<0.2	**9**	**6**	**21**	**14**	**10**	1.2	**48**	**14**
SD	16	0.61	0.10	11	0.1	11	8	21	16	15	1.4	67	16
Fivebough & Tuckerbil (2010)													
Maximum	0.23	1.7	0.070	7.2	0.50	24	2.2	16	21	1.2	0.90	8.6	12
Mean (n=2)	**0.19**	1.1	0.045	5.5	**0.30**	**14**	**1.4**	**12**	**14**	0.8	0.80	**7.6**	7.0
SD	0.06	0.8	0.035	2.4	0.28	14	1.1	5.2	10	0.6	0.14	1.4	7.1
[f] **2008 Wetlands (n=19): Ekee (n=7), Jury Swamp (n=4), Morgan (n=4), Paiwilla (n=1), Swanport (n=2)**													
Maximum	460	60	0.12	51	20	4400	120	220	6900	7.4	4.9	1130	14000
Mean (n=27)	**50**	**7.8**	0.016	10	**2.8**	**485**	**18.2**	**44**	**754**	1.2	0.78	**142**	**1400**
SD	124	15.9	0.029	14	5.9	1140	31	65	1800	1.9	1.10	285	3532
[f] **2008 Murray River (n=13): Non-wetland sites near river edge (n=10), Lake Albert (n=8), lake Alexandrina (n=7) (n=1), Swanport (n=2)**													
Maximum	37	3.9	0.05	15	2.6	370	28	200	710	17	0.62	150	520
Mean (n=27)	**4.1**	1.7	0.010	3.3	**0.4**	**66**	**3.7**	**29**	**99**	1.9	0.25	**20**	**97**
SD	10	1.5	0.015	4	0.8	108	8	57	201	4.6	0.15	43	169
[f] **2008 Lower Lakes (n=15): Lake Albert (n=8), lake Alexandrina (n=7)**													
Maximum	37	7.5	0.06	32	5	1200	20	170	780	8.5	1.1	230	950
Mean (n=27)	**8**	**2.8**	0.024	9	**1.5**	**204**	**3.4**	**29**	**228**	2.6	0.30	**25**	**191**
SD	13	2.2	0.019	9	1.6	297	6	49	229	3.1	0.26	64	253
2010 Lower Lakes (n=35): Lake Albert (n=19), lake Alexandrina (n=16)													
Maximum	1200	1700	0.22	380	61.0	5650	720	970	8430	2.6	2.0	510	3200
Mean (n=27)	**47**	**86**	0.03	**20**	**3.0**	**245**	**30**	**49**	**326**	0.7	0.4	**38**	**250**
SD	211	285	0.04	65	10.3	959	121	163	1420	0.7	0.5	101	607

* WQG (95%PC) = ANZECC/ARMCANZ (2000) water quality guideline trigger value for 95% species protection. a Mean and SD calculations use 'Limit of Reporting' (LOR) values are measured value. b As(V) = 13 µg/L (As(III) = 24 µg/L). c Low reliability guideline. d Cr assumes all is as Cr(VI) and NV = no value. e **Blue** when >WQG trigger value, **red** when >10×WQG trigger value, and **black** when >100×WQG trigger value. f In the 2008 studies, only soils with pH <6 were tested.

It is difficult to make generalisations about the Fivebough & Tuckerbil wetlands based on just the two soils tested. In the studies of the more acidic soils, in lakes Alexandrina and Albert, Simpson et al. (2008) and Baker et al. (2010) consistently observed trends of increasing metals and metalloids concentrations with decreasing soil pH. In the study by Simpson et al. (2008), the strong relationships between pH of the soils, the water upon soil resuspension and the concentrations of dissolved metals were used to create models for the rapid release of Al, Zn, Cu, V, and Cr versus pH (using data from lakes, rivers and wetlands). Similar relationships were observed in 2010 for soils from lakes Alexandrina and Albert (Baker et al., 2010). For the Chowilla, Kerang wetland soils, for many of the samples their was considerable divergence from these relationships for a number of the metals (e.g. Cr, V) Figure 4). In Figure 4 the rapid-release results for the Fivebough & Tuckerbil wetland soils are compared with results from other wetland soils with pH >4.5 (44 Chowillas, 27 Kergangs and 15 Banrock wetland) and contrasted with the results of soils from lakes Albert and Alexandrina.

Overall, while the metal/metalloid release occurring from the acidic soils from the lower lakes region and wetland soils with pH <4.5 appears to be driven mostly by soil pH, the metal/metalloid release from the less acidic wetland soils appears to be significantly influenced by Al and Fe colloids for Cr, Cu and V and organic complexation/colloids for Co, Mn, Ni and Zn (see the accompanying Fivebough & Tuckerbil Phase 2 Report).

Summary

The rapid release from soils into deionised water of metals, metalloids and chemical compounds which have potential to be a hazard was assessed for two soils from wetlands at Fivebough & Tuckerbil. The elutriate waters exceeded the water quality guideline (WQG) trigger values for Al, Co, Cu and V for both soils and for Ag, Cr, Ni and Zn for one of the two soils. One soil elutriate water exceeded WQGs by 10× for Co and Cu. The NOx (taken as nitrate for this comparison) concentrations in the elutriate waters were 20-70× greater than the guidelines for lowland rivers, while the FRP concentrations were 4-10× greater than the guidelines for lowland rivers. If these two soils were considered representative of the entire wetland, the results suggest that NOx, but not FRP release may not be of potential concern to the environment. Generalisations about potential metal release from the Fivebough & Tuckerbil wetland soils are not possible based on this small data set.

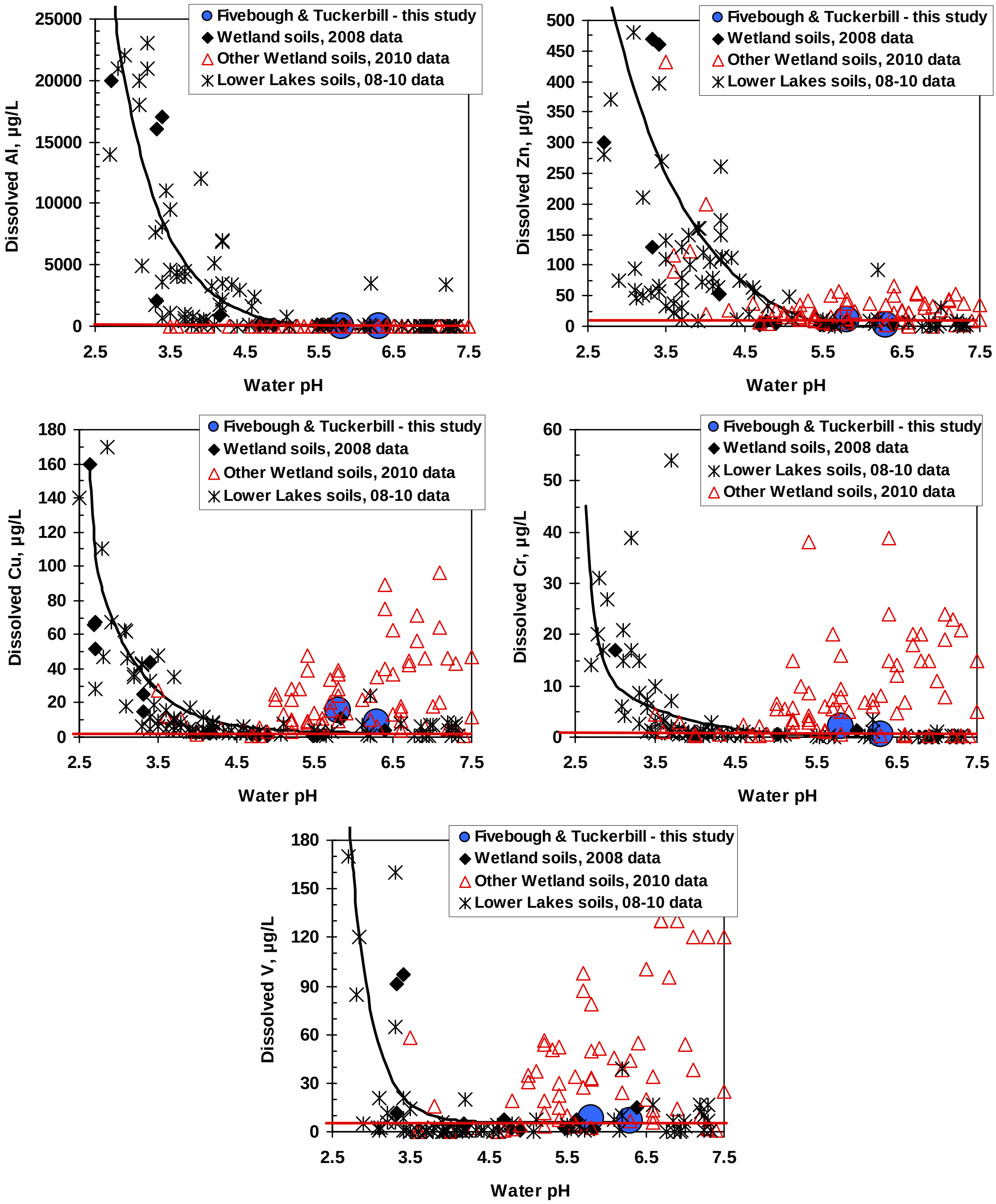

Figure 1. Comparison between the dissolved Al, Zn, Cu, V, and Cr concentrations measured in the rapid-release tests undertaken for Fivebough & Tuckerbill soils (●-enlarged), other wetland soils tested in 2008 (◆) and 2010 (△), and soils from lakes Albert and Alexandrina (✳,08, 09, 2010 data). The **black curve** is the model from Simpson et al. (2008). The **red lines** are water quality guidelines for 95% species protection.

2.1.2 References

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