



Assessment of Acid Sulfate Soil Materials (Phase 2) Wellington North (Murrundi) wetland, South Australia

P. Shand, S. Grocke, A.K. Baker, L. Smith, C. Fiebiger & G. Cozens

Report to the Murray-Darling Basin Authority

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EXECUTIVE SUMMARY

An initial Phase 1 acid sulfate soil investigation of the Wellington North (Murrundi) wetland during September 2008 showed acid sulfate soils to be a priority concern within this wetland complex. Based on Phase 1 recommendations, a Phase 2 investigation was undertaken for the Wellington North (Murrundi) wetland to determine the nature, severity and the specific risks associated with acid sulfate soil materials. The wetland had dried during previous drought conditions, but had partially rewet at the time of sampling.

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

The contaminant and metalloid dynamics tests were undertaken to assess the release of metals during a water extraction, and to assess dynamics in response to saturation over time by incubating soil materials for periods of 1, 7, 14 and 35 days. The degree to which metal and metalloid concentrations exceed ANZECC/ARMCANZ environmental protection guideline values were used to characterise the degree of hazard. For Wellington North (Murrundi) wetland, aluminium (AI) and iron (Fe) were assigned a moderate hazard with concentrations exceeding ANZECC/ARMCANZ environmental protection guidelines by more than 10 times. The dominant control on metal solubility is the pH of the extractions, with the most acidic extractions generally having the highest metal concentrations. The soils displayed little change in pH throughout the tests, but with some remaining very acidic. Over the duration of the period, there was a decrease in Eh, which is thought to be responsible for increasing iron (Fe) over time. Over the period of incubation, the elements arsenic (As), cobalt (Co), chromium (Cr) and vanadium (V) showed a tendency in some samples to increase with time, and this may be related to the reductive dissolution of iron-bearing minerals and solubilisation of adsorbed/absorbed metal species. Lead (Pb) showed an increase in one sample (MUR 2.1) up to 14 days, but decreased by day 35.

The Wellington North (Murrundi) wetland has been classified as medium conservation status by the SA Murray-Darling Basin Natural Resources Management Board (Miles *et al.* 2010). The main hazards considered in this study that may impact on wetland values are acidification, contaminant mobilisation and deoxygenation. The wetland has been allocated a **high** risk rating due to **acidification** and a **high contaminant** risk rating for **soils**. For **surface waters**, the risk is largely dependent on surface and sub-surface hydrology and is thus scenario dependent. Taking into account the range of likely scenarios, from very low flows (highest risk) to very high flows (lowest risk), the risk to surface waters in the wetland has been allocated **medium** to **high** risk rating for both **acidification** and **contaminant mobilisation**. The risk associated with **deoxygenation** was determined to be **low** as there was no identified hazard associated with monosulfide formation and no evidence of monosulfides either in the wetland at the time of the initial field survey or forming during laboratory experiments.

In designing a management strategy for dealing with acid sulfate soils in Wellington North (Murrundi) wetland, other values and uses of the wetland need to be taken into account to

ensure that any intervention is compatible with other management plans and objectives for the wetland.

The wetland soils studied were largely dry at the time of sampling, therefore management options considered should relate to controlling or treating acidification and the protection of connected or adjacent wetlands. Due to the medium to high risks to the wetland values associated with acidification and contaminant mobilisation in Wellington North (Murrundi) wetland, a monitoring program is strongly recommended during any disturbance to the soils.

1. INTRODUCTION

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

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

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

Following the Wellington North (Murrundi) wetland Phase 1 assessment (Fitzpatrick *et al.* 2008) and the priority ranking criteria adopted by the Scientific Reference Panel of the MDB ASSRAP (see Table 1-1), Wellington North (Murrundi) wetland was selected for Phase 2 detailed assessment. The Phase 1 assessment sampled 3 profiles (Figure 1-1), and identified sulfidic material at three different sites with S_{CR} varying from 0.02 to 1.39 %. Phase 2 investigations were carried out on selected samples from high priority sites identified in the Phase 1 assessment.

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

Priority	Soil material
High Priority	All sulfuric materials.
	All hypersulfidic materials (as recognised by either 1) incubation of sulfidic materials or 2) a positive net acidity result with a Fineness Factor of 1.5 being used).
	All hyposulfidic materials with S_{CR} contents $\ge 0.10\%$ S.
	All surface soil materials (i.e. within 0-20 cm) with water soluble sulfate (1:5 soil:water) contents \geq 100 mg kg ⁻¹ SO ₄ .
	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.

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).



Figure 1-1 Wellington North (Murrundi) wetland aerial photograph with Phase 1 sampling sites identified.

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

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

Soil Laboratory Test	Wellington North (Murrundi) wetland samples	Sample depth (cm)	Number of samples analysed
Reactive metals	MUR1.1	0-30	5
	MUR1.2	30-40	
	MUR2.1	0-5	
	MUR2.2	5-10	
	MUR3.1	0-15	
Contaminant and	MUR1.1	0-30	5
metalloid dynamics	MUR1.2	30-40	
	MUR2.1	0-5	
	MUR2.2	5-10	
	MUR3.1	0-15	
Monosulfide formation potential	MUR2.1	0-5	1
Mineral identification by X-ray diffraction (XRD)	N/A		

Table 1-3 Summary of Wellington North (Murrundi) wetland samples analysed for Phase 2 assessment.

2. LABORATORY METHODS

2.1. Laboratory analysis methods

2.1.1. Summary of laboratory methods

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

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

Parameter	Objective
Reactive metals	Assists with determining impacts on water quality by determining weakly to moderately strongly bound metals.
Contaminant and metalloid dynamics	Assists with determining impacts on water quality by simulating longer time frames that create anaerobic conditions. Identifies metal release concentrations that may occur over a 5 week time frame.
Monosulfide formation potential	Determine relative propensity for monosulfides to form following inundation.
Mineral identification by X-ray diffraction (XRD)	Characterisation and confirmation of minerals present.

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

2.1.2. Reactive metals method

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

2.1.3. Contaminant and metalloid dynamics method

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

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

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

2.1.4. Monosulfide formation potential method

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

The reactive iron (Fe) fraction in field moist sediments was extracted using 1.0 M HCl (Claff *et al.* 2010). The ferrous iron (Fe²⁺) and total iron (Fe²⁺ + Fe³⁺) fractions were immediately fixed following extraction. The ferrous iron trap was made up from a phenanthroline solution with an ammonium acetate buffer (APHA 2005), and the total iron trap also included a hydroxylamine solution (APHA 2005). The iron species were quantified colorimetrically using a Hach DR 2800 spectrophotometer.

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

2.1.5. Mineral identification by x-ray diffraction

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

2.2. Quality assurance and quality control

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

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

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

3. RESULTS AND DISCUSSION

3.1. Summary of soil laboratory results

3.1.1. Reactive metals data

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

The concentrations of metals and metalloids were below sediment quality guideline values and soil ecological investigation levels for these elements where guidelines are available. However, the concentrations of aluminium (AI) and iron (Fe) are considered high for these partial extractions.

Sample	Ag*	AI	As	Cd*	Co	Cr*	Cu	Fe	Mn	Ni	Pb	Sb*	Se*	v	Zn
MUR 1.1	0.92	582	1.6	31	1.8	42	1.9	1489	32	4.7	1.5	< 22	18	11	7.6
MUR 1.2	2.5	701	0.68	37	1.7	59	2.1	748	21	3.9	1.9	< 16	23	7.8	4.1
MUR 2.1	1.9	314	0.45	30	1.9	64	4.1	653	42	4.5	1.9	< 11	30	5.9	5.0
MUR 2.2	3.2	378	0.36	16	1.2	50	2.6	519	9.0	3.6	1.9	< 13	28	6.4	1.6
MUR 3.1	7.4	393	0.84	15	0.78	45	5.3	313	25	3.2	4.3	< 19	63	20	1.4
¹ SQG	1000	-	20	1500	-	80000	65	-	-	21	50	2000	-	-	200
² Soil EIL	-	-	20	3000	-	-	100	-	500	60	600	-	-	50	200

Table 3-1 Wellington North (Murrundi) wetland reactive metals data.

Concentrations in mg kg⁻¹, and µg kg⁻¹ as indicated by asterisk.

* Units are in µg kg⁻¹
< value is below detection limit</p>

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

3.1.2. Contaminant and metalloid dynamics data

The contaminant and metalloid dynamics data for the five Wellington North (Murrundi) wetland soil materials examined are presented in Appendix 2, summarised in Table 3-2 and plotted against time in Figures 3-1 to 3-3. Table 3-2 also compares the pore-water metal contents to the relevant national water quality guideline for environmental protection (ANZECC/ARMCANZ 2000).

Parameter	units	ANZECC Guidelines	Wellington North: Murrundi					
			Min.	Median	Max.			
рН		6.5-8.0	3.9	5.4	6.9			
EC*	µS cm⁻¹	2200	116	273	886			
Eh	mV	-	62	290	527			
Ag	µg l⁻¹	0.05	<0.02	<0.02	0.08			
Al ^A	mg l⁻¹	0.055	<0.05	0.35	3.0			
As ^B	µg l⁻¹	13	0.22	6.3	50			
Cd	µg l⁻¹	0.2	<0.03	0.04	0.22			
Со	µg l⁻¹	2.8	0.12	3.3	12			
Cr ^C	µg l⁻¹	1	<0.3	0.73	2.8			
Cu ^H	µg l⁻¹	1.4	<1.5	<1.5	12			
Fe ^l	mg l⁻¹	0.3	<0.1	1.1	24			
Mn	µg l⁻¹	1700	11	157	577			
Ni ^H	µg l⁻¹	11	0.30	4.8	17			
Pb ^H	µg l⁻¹	3.4	<0.30	<0.6	5.6			
Sb	µg l⁻¹	9	<0.60	<7.5	<7.5			
Se	µg l⁻¹	11	<0.06	0.15	0.45			
V	µg l⁻¹	6	<1.5	9.0	24			
Zn ^H	µg l⁻¹	8	<0.50	2.7	20			

Table 3-2 Summary of contaminant and metalloid dynamics data

ExceededExceededExceededANZECCANZECCANZECCGuideline (x1)Guideline (x10)Guideline (x10)

Notes.

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

* ANZECC water quality upper guideline (125-2200 μ S cm⁻¹) for freshwater lowland rivers in South-east Australia is provided for salinity (there are currently no trigger values defined for 'Wetlands'.)

^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).

¹ Fe Guideline for recreational purposes.

The pH of the soil materials varied significantly from pH < 4.3 to 6.3 on day 1 (Figure 3-1). The pH showed little change over the 35 day period, and remained below the lower ANZECC/ARMCANZ environmental protection guideline of pH 6.5 for most samples. The most acidic sample (MUR 1.2) from the centre of the wetland decreased to pH < 4 by day 35 (Figure 3-1).

The Eh was initially high, but started to show a decrease by day 7, continuing to decrease to day 35 (Figure 3-1). The more acidic samples had the highest SEC, and over the incubation period, there was a slight increase in the more acidic samples and a slight decrease in the higher pH samples (Figure 3-1).

Manganese concentrations were relatively low throughout the time period, and below ANZECC/ARMCANZ environmental protection guideline values in all samples. The decrease in Eh led to a significant release of iron (Figure 3-1) in four of the samples.

A number of other trace elements were significantly above the ANZECC/ARMCANZ environmental protection guidelines including aluminium (AI), arsenic (As), cobalt (Co), chromium (Cr), copper (Cu), vanadium (V) and zinc (Zn). Only aluminium (AI) and iron (Fe) were higher than ten times ANZECC/ARMCANZ environmental protection guidelines (Table 3-2). The concentrations of a number of metals appear to be controlled by pH: most metals showed a decrease in concentration with increasing pH (Figure 3-4), however manganese (Mn) was highest at pH above pH 6.5.

Over the period of incubation, the elements arsenic (As), cobalt (Co), chromium (Cr) and vanadium (V) showed a tendency in some samples to increase with time, and this may be related to the reductive dissolution of iron-bearing minerals and solubilisation of adsorbed/absorbed metal species. Lead (Pb) showed an increase in one sample (MUR 2.1) up to 14 days, but decreased by day 35.

The magnitude of metal mobilisation is affected by many factors that include but are not exclusive to: 1) the abundance and form of metal and metalloid contaminants; 2) the abundance and lability of organic matter; 3) the abundance and reactivity of iron minerals; 4) availability of sulfate; 5) acid/alkalinity buffering capacity; 6) pH; 7) EC; 8) clay content; 9) microbial activity; 10) temperature and 11) porosity (MDBA 2010). The negative correlation of some metals and metalloids with pH suggests pH is a major control on dissolved concentrations. However, the changes in concentration of iron (Fe) and associated metals and metalloids over the time period are largely attributed to a decrease in Eh, allowing iron (Fe) to increase by reductive dissolution of an iron-bearing mineral (iron hydroxysulfate or hydroxide phase). The reductive process thus plays an important role in metal mobilisation, but is strongly modified by the sample pH.

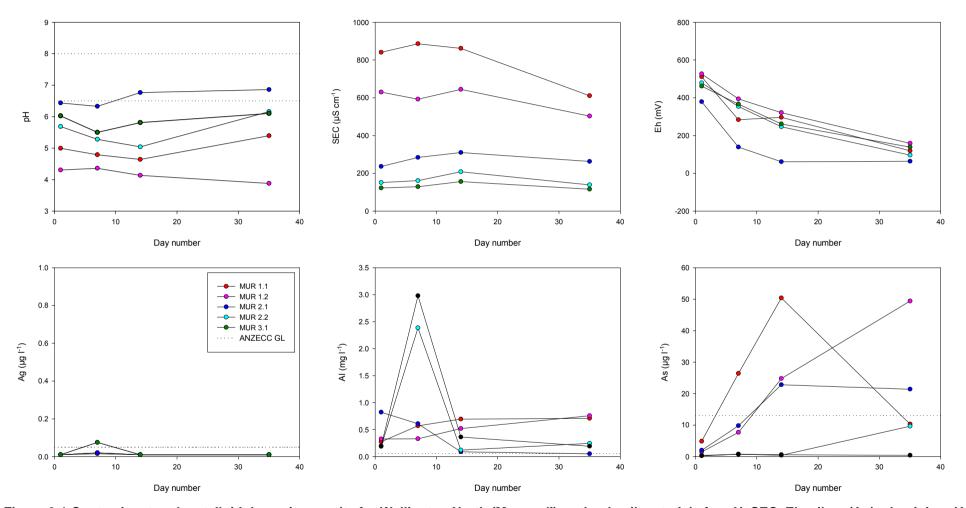


Figure 3-1 Contaminant and metalloid dynamics results for Wellington North (Murrundi) wetland soil materials for pH, SEC, Eh, silver (Ag), aluminium (AI) and arsenic (As).

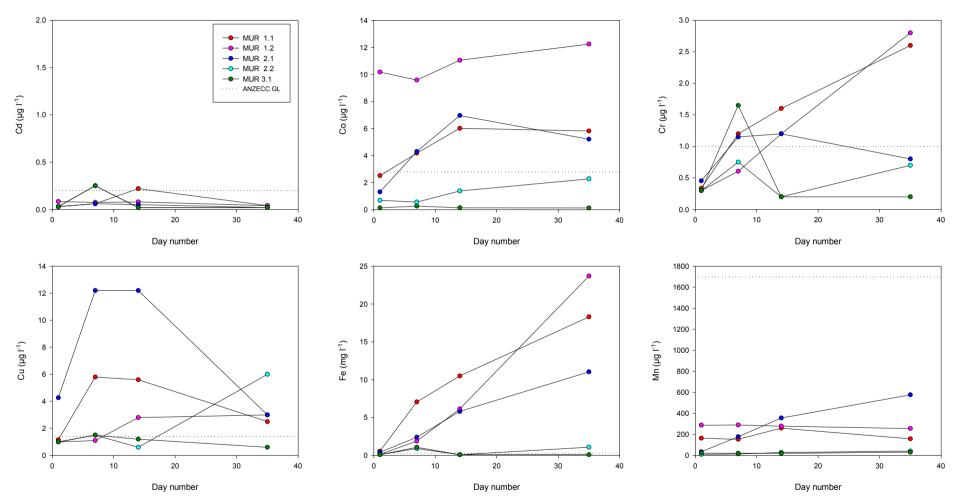


Figure 3-2 Contaminant and metalloid dynamics results for Wellington North (Murrundi) wetland soil materials for cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe) and manganese (Mn).

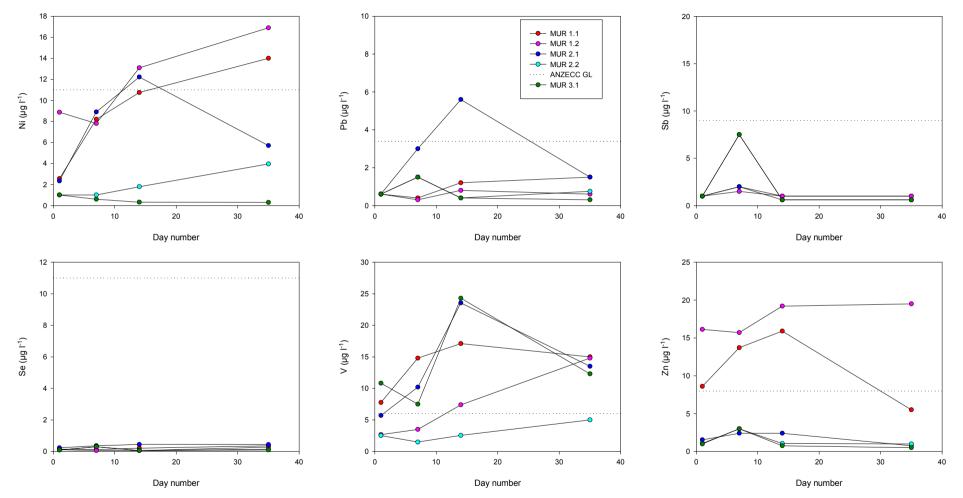


Figure 3-3 Contaminant and metalloid dynamics results for Wellington North (Murrundi) wetland soil materials for nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), vanadium (V) and zinc (Zn).

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

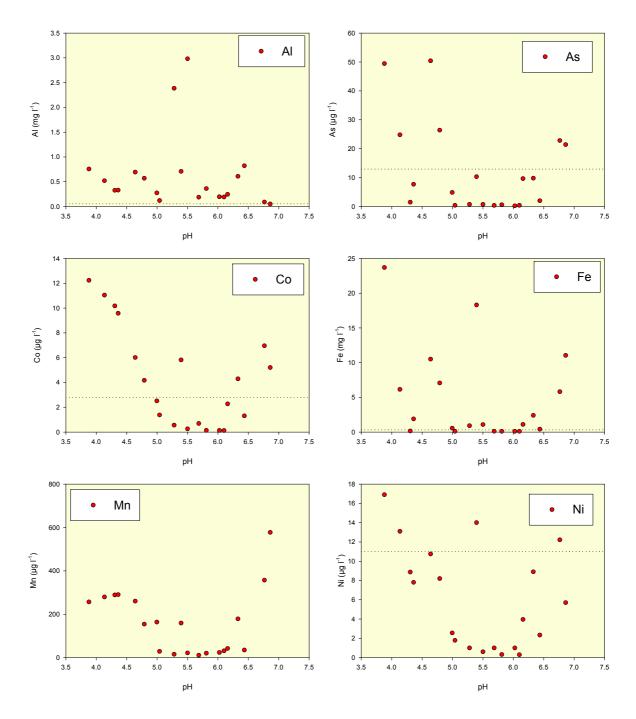


Figure 3-4 Selected trace elements plotted against pH.

3.1.3. Monosulfide formation potential data

The monosulfide formation potential data for sample MUR 2.1 are shown in Table 3-3. The pH of the soil water changed from 6.11 to 4.49 over the seven week incubation period (Figure 3-5). The decrease in pH is different from the contaminant and metalloid dynamics tests, where pH increased and remained relatively high (Figure 3-1). This may be due to fermentation of organic substrate added (sucrose) which caused acidification of the porewaters.

The Eh decreased from 442 to 312 mV indicating a change to slightly more reducing conditions. The Eh data are generally consistent with the contaminant and metalloid dynamics experiments where Eh decreased from 379 to 64 mV.

Table 3-3 Summary of monosulfide formation potential data for the Wellington North (Murrundi)
wetland surface soil material MUR 2.1 after 7 weeks (3.6 g/L sucrose).

Inundation Time	Parameter	Units	Murrundi MUR 2.1
Day 0	Total Fe	mg/kg	4503
	Fe(II) ⁻	mg/kg	839
	Sulfate	mg/kg	
	рН		6.11
	Eh	mV	442
Week 7	рН		4.49
	Eh	mV	312
	S _{AV}	Wt. %S	<0.01
	S°	Wt. %S	<0.01
	Pyrite-S	Wt. %S	0.01
	Dissolved S ²⁻	µg/L	<0.1

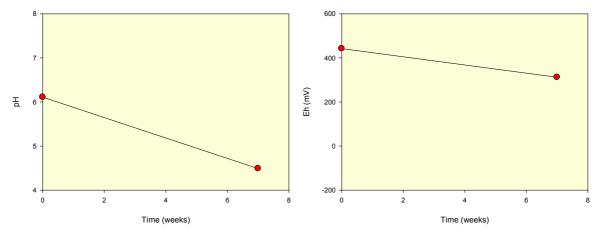


Figure 3-5 pH and Eh dynamics during monosulfide formation potential tests in surface soil sample MUR 2.1 from Wellington North (Murrundi) wetland.

The sample originally contained 0.03% S_{CR} (pyrite-S and S_{AV}) and no ANC (Fitzpatrick *et al.* 2008). After 7 weeks, acid volatile sulfide (S_{AV}) and elemental sulfur (S^0) were both <0.01 %, with pyrite just detectable (Table 3-3). It appears, therefore, that monosulfide formation has not occurred in this sample during the tests. Dissolved sulfide concentrations were also low signifying that the waters are not reducing, in agreement with the Eh data.

3.1.4. Mineral identification by x-ray diffraction

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

3.2. Interpretation and discussion of results

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

The 24 hour **reactive metals** studies provide an indication of those metals and metalloids which are more strongly bound to minerals (or weakly soluble with an acid extraction), and thus have the potential to be released. The use of a moderately strong acid (HCI) should provide an indication of "stored metals" and metalloids associated with iron (Fe) and manganese (Mn) oxides and organic materials as well as acid soluble minerals. It is commonly found that the concentrations of metals and metalloids released using extractions are much higher than those found in solution (Gooddy *et al.* 1995). Although guideline values exist for soils and sediments (ANZECC/ARMCANZ 2000), these are generally for total soil concentrations, and therefore, are not directly appropriate for the data from metal mobilisation studies. Nevertheless, they provide a basis for comparison; and concentrations close to or above guideline values indicate an elevated hazard.

The metal and metalloid concentrations were all below sediment quality guidelines and soil ecological investigations level values (Table 3-1). However, the concentrations of some metals were moderately high for this partial extraction technique, particularly for aluminium (AI) and iron (Fe), and sufficiently high that many would be of concern for water quality if released.

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

It would appear that reductive processes have begun in the samples with a significant decrease in Eh for most samples, but the pH for some samples remained relatively constant implying significant pH buffering by soil minerals and dissolved species. For a number of elements, the concentrations increased over the 35 day period. Alongside the increase in iron (Fe), this implies a release from an iron-bearing oxyhydroxide or oxyhydroxysulfate mineral phase. The large increases in iron (Fe) concentration and decrease in Eh implies that reductive processes have begun, but not yet to the stage of sulfate reduction. The pH of the solutions, although low, has not allowed very high concentrations of metals apart from aluminium (AI) and iron (Fe). It is thus likely that very high concentrations of metals and

metalloids are not available in the soils, either due to low abundance or insufficient time for release.

The degree to which samples exceed guideline concentrations has been used to assign a degree of hazard (Table 3-4). For some samples which required dilution, the detection limits were slightly above ANZECC/ARMCANZ environmental protection guideline values due to required dilution. Antimony (Sb) was below detection limit for all samples (detection limit varying between 1 and 7.5 μ g l⁻¹). However, it is still possible to group antimony (Sb) in Table 3-4 as the maximum detection limit was less than the guideline value, and as such it can be concluded that antimony (Sb) sits in the No hazard grouping. The data are shown in Appendix 1 which displays the detection limits for individual analyses.

The main hazards in Wellington North (Murrundi) wetland are the moderate hazards for aluminium (AI) and iron (Fe), however increasing concentrations of arsenic (As), chromium (Cr), nickel (Ni) and vanadium (V) are worth noting as the data suggest these may increase further with time in some samples. The data are consistent with the high net acidities noted by Fitzpatrick *et al.* (2010) up to 975 mol H⁺/tonne (median of 164 mol H⁺/tonne), which may mean that the soils will take a significant time to recover. The lack of very high concentrations, however, may suggest that abundances are lower than in nearby wetlands such as Wellington South (Shand *et al.* 2011).

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

Table 3-4 Summary of the degree of hazard associated with the measured contaminant and metalloid concentrations in the Wellington North (Murrundi) wetland.

The monosulfide formation potential test assists in determining the propensity for monosulfides to form during future inundation. The sample used for this test contained no acid volatile sulfide (S_{AV}) or elemental sulfur (S^0) and with chromium reducible sulfur (S_{CR}) only just detectable. The lack of acid volatile sulfide (S_{AV}) ranks the monosulfide formation potential hazard as 'No hazard' (Figure 3-5).

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

Degree of Hazard	Guideline Threshold
No Hazard	< 0.01 % S _{AV}
Low Hazard	0.01 % S _{AV}
Moderate Hazard	> 0.01 – 0.05 % S _{AV}
High Hazard	> 0.05 % S _{AV}

4. RISK ASSESSMENT

4.1. Risk assessment framework

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

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

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

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

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

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

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

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

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

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

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

It is suggested that:

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

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

4.2. Assessment of risks

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

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

The Wellington North (Murrundi) wetland has been classified as medium conservation status by the SA Murray-Darling Basin Natural Resources Management Board (Miles *et al.* 2010).

4.2.1. Risks associated with acidification

The high net acidities in samples from Wellington North (Murrundi) wetland show that the acidification hazard is high. Net acidities were highest in the hypersulfidic soils at depth (MUR 2.4 and 3.2), but were also high in shallow oxidised layers in the centre of the wetland (MUR 1). In the dry interior of the wetland titratable actual acidity dominated the net acidity, whilst closer to the river net acidity was dominated by potential sulfidic acidity (S_{CR}) (MUR 2 and 3).

The probability of soil acidification is considered high as suggested by the measured pH and only minor increase over the 35 days of the contaminant mobilisation and dynamics incubations. Due to the wetlands location adjacent to the river and connectivity, the likelihood of disturbance is considered **almost certain** as flows return to normal in the future. Due to the low hydraulic conductivities in organic clayey soils in this wetland, it is unlikely that soil acidification will be mediated by high flows. The consequences are likely to be significant for soil ecology, but the timescale for soil recovery from acidification cannot be assessed with existing information. Studies in other wetlands e.g. Nelwart Lagoon (Shand et al. 2010) indicate that in areas with strongly acidic soils, the timescale is likely to be months to years. Most samples displayed an increase in pH and combined with the higher pH in some soils and the decrease in Eh, it is likely that recovery will not be as long as for the most acidified wetlands such as Wellington South (Shand et al. 2011). A moderate rating is therefore applied for consequence as short-term damage to soil water chemistry is considered likely. This provides a risk rating for soil acidification of high. A rating for surface water acidification will depend on surface and sub-surface hydrology. The highest risk is likely to be during low flows where the soil to water ratio is high: acidity will be most concentrated. The risk to surface water acidification is considered lowest where high flows are available to both dilute acidity and transport acidity downwards in the soil profile. A minor to moderate consequence rating is therefore suggested. The risk to surface water acidification is therefore likely to vary from medium to high depending on future scenarios (Table 4-4).

4.2.2. Risks associated with contaminant mobilisation

The risks of metal and metalloid mobilisation are controlled primarily by metal abundance and availability, geochemical controls on speciation and transport mechanisms. The master variables pH and Eh exert a direct major influence on the solubility of individual metals and metalloids and minerals such as iron (Fe), iron (Fe) and manganese (Mn) oxides and hydroxides which are important sorbents of metal and metalloids species. The high acidification hazard due to the oxidation of sulfide minerals means that if metals and metalloids have been released from the oxidation of sulfide minerals, they are likely to be mobile. Although reduction processes may lead to reincorporation of metals and metalloids into sulfide minerals (following sulfate reduction), at intermediate redox potentials mobility may be high where iron (Fe) and manganese (Mn) are soluble. The reactive metals and contaminant and metalloid dynamics results attest to the availability and mobility of a number of metals, particularly aluminium (AI) and iron (Fe) but also an increase in several elements was noted e.g. arsenic (As), cobalt (Co), chromium (Cr), nickel (Ni) and vanadium (V) in many samples. At the concentrations measured (>1-10 x ANZECC/ARMCANZ environmental protection guideline values), the consequences are likely to be moderately significant for soil pore-waters and soil/sediment ecology. As in assessing the acidification risk, the timescales cannot be assessed with existing information. However, comparisons with other studies (e.g. Nelwart Lagoon, Shand et al. 2011) suggest that soil recovery in such acidic systems is likely to mean that at least short term impacts are likely. Since pH remained low in soil samples from the middle of the wetland and higher at the margins, a **moderate** rating is applied for consequence as short-term damage to soil ecology is considered likely. This provides a risk rating for contaminant mobilisation in soils of high.

A rating for surface water impacts from metals and metalloids will depend on surface and sub-surface hydrology. The consistently low pH values in this study, however, means that short term impacts are likely if hydrological conditions allow a flux of metals towards overlying surface water. The highest risk is likely to be during low flows where the soil to water ratio is high: metals will be most concentrated. The risk to surface water acidification is considered lowest where high flows are available to both dilute metal and metalloid concentrations and transport these downwards in the soil profile. A minor to moderate consequence rating is therefore suggested. The risk is therefore likely to vary from **medium to high** depending on future scenarios (Table 4-4).

4.2.3. Risks associated with de-oxygenation

Monosulfidic materials are considered the main cause of deoxygenation risk in acid sulfate soils. Monosulfidic black ooze was not observed in the wetland during initial field surveys (Fitzpatrick *et al.* 2008), although the wetland was largely dry and the subaqueous soil that was sampled at the wetland inlet may have been subject to flow disturbance. In addition, soil samples were not analysed for water soluble sulfate concentrations.

The hazard for monosulfide formation potential is 'No hazard' due to the concentration of acid volatile sulfide (S_{AV}) being less than detection limit of 0.01 % S, although the Eh results suggested that conditions were not sufficiently reducing for monosulfide formation. Given that monosulfides were not observed in the wetland and there was no evidence of monosulfides forming during laboratory experiments, the consequence of deoxygenation is considered to be **insignificant**. As such, the risk associated with deoxygenation was determined to be **low** (Table 4-4).

Table 4-4 Summary of risks associated with acid sulfate soil materials in the Wellington North (Murrundi) wetland.

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

5. BROAD ACID SULFATE SOIL MANAGEMENT OPTIONS

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

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

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

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

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

The major risks identified in this study are due to soil and water acidification and contaminant mobilisation. The likelihood of water refilling the wetland is high as flows return to normal levels. The limited number of case studies on refilling wetlands makes prediction of risk difficult in terms of determining whether reversible or irreversible damage is likely to occur. However, short term risks from acid and metal mobilisation are likely if hydrological conditions are such that there is a significant flux of acidity and metals from the soils to the overlying water column.

As the wetland has previously dried and undergone oxidation, management options 1 and 2 in Table 5-1 are not relevant to the current study, although minimising further oxidation could have been an option prior to recent high flows down the River Murray. Treatment options currently remain a viable option should water quality impacts e.g. acidification of surface water and/or high metal concentrations be seen. Since the risks are scenario dependent, it is strongly recommended that surface water and soil pore water monitoring be undertaken at this wetland. Based on the data from this study and elsewhere (Shand et al. 2010), it is likely that soil recovery will be slow. The impacts on surface and sub-surface ecosystems are not well understood and are worthy of further work, particularly long term impacts on ecosystem functionality and diversity.

Management Objective	Activities
1. Minimising the formation of acid	Reduce secondary salinisation through:
sulfate soils in inland aquatic	Lowering saline water tables
ecosystems	 Maintaining the freshwater lens between saline groundwater and the aquatic ecosystem
	 Stopping the delivery of irrigation return water
	 Incorporating a more natural flow regime.
2. Preventing oxidation of acid	Preventing oxidation:
sulfate soils or controlled oxidation	Keep the sediments covered by water
to remove acid sulfate soils	• 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 deoxygenation and metal release. Monitor intervention and have a contingency plan to ensure avoidance of these risks.
3. 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.
4. Protecting adjacent or	Isolate the site
downstream environments if	 Neutralise and dilute surface water
treatment of the affected aquatic ecosystem is not feasible	 Treat discharge waters by neutralisation or biological treatment.
5. Limited further intervention	Assess risk
	Communicate with stakeholders
	Undertake monitoring
	 Assess responsibilities and obligations and take action as required.

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

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APPENDICES

APPENDIX 1 REACTIVE METALS DATA

Wellington North (Murrundi) wetland

Sample	Depth	Analysis	Ag*	AI	As	Cd*	Со	Cr*	Cu	Fe	Mn	Ni	Pb	Sb*	Se*	v	Zn
	0.00	а	1.1	601	1.6	33	1.9	40	2.0	1418	33	5.0	1.6	< 22	16	12	7.6
MUR 1.1	0-30	b	0.73	564	1.6	30	1.7	44	1.9	1560	31	4.3	1.5	< 22	19	11	7.6
	20.40	а	2.6	742	0.71	38	1.8	65	2.2	828	23	4.1	2.0	< 16	25	8.7	4.3
MUR 1.2	30-40	b	2.4	661	0.64	35	1.5	52	2.1	669	19	3.6	1.8	< 16	21	6.8	4.0
	0.5	а	2.0	315	0.46	30	1.9	65	4.6	664	42	4.6	1.9	< 11	32	6.0	5.5
MUR 2.1	0-5	b	1.8	312	0.45	30	1.9	63	3.7	642	43	4.5	1.9	< 11	28	5.9	4.5
	F 40	а	3.5	399	0.39	18	1.2	53	2.9	523	9.5	4.1	2.2	< 13	30	7.3	1.7
MUR 2.2	5-10	b	2.9	357	0.32	15	1.1	47	2.4	514	8.5	3.1	1.7	< 13	26	5.6	1.4
	0.45	а	6.8	398	0.81	14	0.68	45	5.5	316	22	2.6	4.2	< 19	59	18	1.3
MUR 3.1	0-15	b	8.1	389	0.87	16	0.87	45	5.1	309	27	3.7	4.5	< 19	66	21	1.6

Units are mg kg⁻¹ unless indicated otherwise as below

* Units are in µg kg⁻¹

< value is below detection limit

APPENDIX 2 CONTAMINANT AND METALLOID DYNAMICS DATA

Wellington North (Murrundi) wetland

Comple	Dev	Depth	Analysis	Eh	EC	mLl	Ag	AI	As	Cd	Со	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Se	v	Zn
Sample	Day	cm		mV	µS/cm	рН	µg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
		1	а	519	881	4.65	<0.01	0.34	4.8	< 0.03	3.5	0.37	1.2	0.64	201	3.5	<0.6	<1	0.15	8.3	11
	1		b	504	801	5.34	<0.01	0.22	5.0	< 0.03	1.5	< 0.3	1.1	0.46	127	1.7	<0.6	<1	0.15	7.2	6.0
		-	а	289	1133	4.36	< 0.02	0.53	28	< 0.06	6.9	1.2	3.6	12	266	10.0	<0.4	<2	0.08	8.8	22
MUR 1.1	7	0-30	b	279	639	5.22	< 0.02	0.61	25	< 0.06	1.5	1.2	8.0	2.1	42	6.4	0.40	<2	0.16	21	5.6
		0.00	a	299	825	4.59	< 0.01	0.70	47	0.40	6.3	1.6	5.6	11	261	11	0.80	<1	0.18	16	16
	14		b	294	898	4.69	< 0.01	0.69	54	< 0.04	5.7	1.6	5.6	10	260	10	1.6	<1	0.24	18	16
		_	a	124	576	5.38	< 0.01	0.79	11	< 0.04	5.9	2.8	3.0	19	152	15	1.8	<1	0.40	17	5.0
	35		b	114	645	5.41	< 0.01	0.63	9.6	< 0.04	5.8	2.4	2.0	18	166	13	1.2	<1	0.32	13	6.0
			a	529	549	4.40	< 0.01	0.23	1.1	0.07	7.0	< 0.3	<1	<0.1	219	6.0	< 0.6	<1	0.08	1.8	12
	1		b	524	711	4.21	< 0.01	0.42	1.8	0.10	13	< 0.3	<1	0.19	358	12	< 0.6	<1	0.15	3.5	21
	_	1	a	354	650	4.18	< 0.02	0.52	15	0.12	13	1.0	2.0	3.7	281	12	< 0.4	<2	< 0.08	6.0	23
MUR 1.2	7	30-40	b	434	535	4.54	< 0.01	0.14	0.40	0.03	6.6	0.21	0.20	< 0.1	299	3.2	<0.2	<1	< 0.04	1.0	8.0
-	4.4		а	319	674	4.12	<0.01	0.54	26	0.08	12	1.2	3.2	6.3	309	14	<0.8	<1	0.06	7.8	21
	14		b	324	615	4.15	<0.01	0.50	24	0.08	10	1.2	2.4	6.0	250	12	<0.8	<1	0.06	7.0	17
	35		а	159	434	3.91	<0.01	0.76	54	< 0.04	11	2.8	3.0	23	238	16	<0.6	<1	0.32	15	18
	35		b	159	572	3.85	<0.01	0.75	45	0.04	13	2.8	3.0	25	276	18	<0.6	<1	0.24	14	21
	1		а	394	252	6.59	<0.01	0.71	1.8	< 0.03	1.0	0.36	2.6	0.35	34	1.6	<0.6	<1	0.22	4.9	<1
	-		b	364	220	6.28	<0.01	0.94	2.2	< 0.03	1.6	0.54	6.0	0.49	36	3.1	<0.6	<1	0.26	6.5	2.1
	7		а	144	289	6.29	<0.02	0.56	9.8	< 0.06	4.2	1.1	13	2.5	178	8.8	3.2	<2	0.36	10	2.4
MUR 2.1	'	0-5	b	134	279	6.37	<0.02	0.66	9.8	<0.06	4.3	1.2	12	2.3	179	9.0	2.8	<2	0.36	10.0	2.4
	14		а	74	326	6.73	<0.01	0.08	21	0.06	6.8	1.2	11	5.8	346	12	5.2	<0.6	0.45	20	1.8
		4	b	49	295	6.80	< 0.01	0.10	25	0.04	7.1	1.2	14	5.9	368	12	6.0	<0.6	0.45	27	3.0
	35		a	79	270	6.89	< 0.01	< 0.05	23	< 0.02	6.1	0.80	3.0	14	643	6.4	1.5	<0.6	0.48	14	1.0
			b	49	255	6.83	< 0.01	< 0.05	20	< 0.02	4.3	0.80	3.0	8.4	511	5.0	1.5	<0.6	0.40	13	0.50
	1		a	489	173	4.90	< 0.01	0.13	0.35	< 0.03	0.89	< 0.3	<1	< 0.1	15	<1	< 0.6	<1	0.09	1.3	1.0
		4	b	469	129	6.47	< 0.01	0.25	0.42	< 0.03	0.48	< 0.3	<1	0.11	6.7	<1	< 0.6	<1	0.10	3.8	1.1
MUR 2.2	7	5-10	a b	339 369	163 160	5.34	<0.1 <0.05	<u>2.9</u> 1.9	<1 <0.5	<0.3 <0.2	0.40	<0.7 0.80	<2 <1	1.1 0.70	14 17	0.80	<2 <1	<10 <5	<0.4 <0.2	<2 1.0	4.0 <2
WUR 2.2		5-10	a	244	196	5.22 5.10	<0.05	0.05	0.20	<0.2	1.9	<0.2	<0.4	<0.1	32	2.2	<0.4	<0.6	0.06	1.0	0.90
	14		a b	244	222	4.98	<0.01	0.05	0.20	<0.02	0.82	<0.2	0.80	<0.1	25	1.3	<0.4	<0.6	0.06	3.9	1.2
			a	99	137	6.07	<0.01	0.13	9.0	<0.02	2.1	0.60	6.0	0.74	37	3.6	0.60	<0.6	0.00	4.8	1.2
	35		b	94	141	6.25	<0.01	0.24	10	<0.02	2.1	0.80	6.0	1.4	47	4.3	0.00	<0.6	0.12	5.2	1.0
			а	464	127	5.55	< 0.01	0.15	0.22	< 0.03	0.12	< 0.3	<1	<0.1	23	<1	<0.6	<1	0.09	9.7	<1
MUR 3.1	1	0-15	b	459	119	6.50	< 0.01	0.24	0.21	< 0.03	0.13	< 0.3	<1	< 0.1	23	<1	< 0.6	<1	0.09	12	<1
	7		a	364	104	5.49	< 0.1	4.4	<1	< 0.3	0.30	2.1	<2	1.6	17	0.80	<2	<10	<0.4	8.0	<4
	7		b	369	155	5.51	<0.05	1.6	<0.5	<0.2	0.20	1.2	<1	0.55	26	0.40	<1	<5	<0.2	7.0	<2

Sample	Day	Depth cm	Analysis	Eh mV	EC μS/cm	рН	Ag μg/L	Al mg/L	As μg/L	Cd µg/L	Co μg/L	Cr μg/L	Cu μg/L	Fe mg/L	Mn μg/L	Ni μg/L	Pb μg/L	Sb μg/L	Se μg/L	ν µg/L	Zn μg/L
	14		а	259	165	5.52	<0.01	0.29	0.60	<0.02	0.14	<0.2	2.0	<0.1	22	0.35	<0.4	<0.6	0.06	23	0.90
	14		b	264	148	6.10	<0.01	0.44	0.60	<0.02	0.13	<0.2	0.40	<0.1	19	0.28	<0.4	<0.6	0.06	25	0.60
	35		а	129	114	6.18	<0.01	0.19	0.40	<0.02	0.10	<0.2	0.60	<0.1	29	0.30	<0.3	<0.6	0.12	16	<0.5
	- 30		b	149	118	6.02	<0.01	0.19	0.40	<0.02	0.14	<0.2	<0.6	<0.1	34	0.30	<0.3	<0.6	0.08	9.0	<0.5

< value is below detection limit

APPENDIX 3 MONOSULFIDE FORMATION POTENTIAL DATA

Wellington North (Murrundi) wetland

MBO Format	ion Potent	tial (MBO FP) - DAY 0					IRON	DATA			DAY 0								
				Т	otal Reactiv	e Fe (mg/k	g)		Fe(II) (mg/kg)				Eh (ı	nV)		pH			
Sample No.	org	Site Name	Site ID	Replicate	Replicate	Mean	+/-	Replicate	Replicate	Mean	+/-	Replicate	Replicate	Mean	+/-	Replicate	Replicate	Mean	+/-
				1	2			1	2			1	2			1	2		
12	csiro	Wellington North - Murrundi	MUR2.1	4584	4421	4503	82	1105	574	839	266	435	449	442	7	6.07	6.14	6.11	0.03
32	-	Blank	-	0.3	0.1	0.2	0.1	<0.1	<0.1	<0.1	<0.1	183	186	185	2	6.17	6.10	6.14	0.04
MBO Format	ion Potent	ial (MBO FP) - DAY 0				IRON	DATA						DA	AY 0					

				IKON DATA								DATO							
				Total Reactive Fe (mg/kg)			Fe(II) (mg/kg)				Eh (mV)				pН				
Sample No.	org	Site Name	Site ID	Replicate	Replicate	Mean	+/-	Replicate	Replicate	Mean	+/-	Replicate	Replicate	Mean	+/-	Replicate	Replicate	Mean	+/-
				1	2			1	2			1	2			1	2		
12	csiro	Wellington North - Murrundi	MUR2.1	4584	4421	4503	82	1105	574	839	266	435	449	442	7	6.07	6.14	6.11	0.03
32	-	Blank	-	0.3	0.1	0.2	0.1	<0.1	<0.1	<0.1	<0.1	183	186	185	2	6.17	6.10	6.14	0.04

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