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Assessment of Acid Sulfate Soil Materials (Phase 2)
Big Toolunka Flat (12064) wetland, South Australia

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Big Toolunka Flat (12064) wetland
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EXECUTIVE SUMMARY

An initial Phase 1 acid sulfate soil investigation of the Big Toolunka Flat (12064) wetland during March 2010 showed acid sulfate soils to be a priority concern within this wetland complex. Based on Phase 1 recommendations, a Phase 2 investigation was undertaken for the Big Toolunka Flat (12064) wetland to determine the nature, severity and the specific risks associated with acid sulfate soil materials.

The 24 hour **reactive metals** tests were undertaken to determine those metals and metalloids extractable with a moderately strong acid i.e. potentially available from binding sites on soil minerals such as iron (Fe), manganese (Mn) and aluminium (Al) oxides. Although comparisons can be made with soil and sediment quality guidelines, these are defined for total concentrations and not partial extractions. The results showed that concentrations were generally below the sediment quality guidelines (SQG) and soil ecological investigation levels (EIL) for those elements where guidelines are available. Although most metals and metalloids did not breach sediment quality guidelines and soil ecological investigation level trigger values, the concentrations of some elements were high enough that they may impact water quality if mobilised, particularly for 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 was used to characterise the degree of hazard. For Big Toolunka Flat (12064) wetland, iron (Fe) was assigned a moderate hazard with concentrations exceeding ANZECC/ARMCANZ environmental protection guidelines by more than 10 times. Aluminium (Al), cobalt (Co), copper (Cu) and zinc (Zn) were above the guideline values.

The Big Toolunka Flat (12064) wetland has been classified as medium conservation status by the SA Murray-Darling Basin Natural Resources Management Board (Miles *et al.* 2010). The tests undertaken for the subaqueous soils in this wetland are difficult to extrapolate to a case where the soils have dried and oxidised, as the generated acidity depends on a number of complex factors. In addition, it is not possible to predict the potential impacts of metal and metalloid release, as these are present in reduced minerals such as pyrite and thus not easily released until oxidation occurs. Some samples had undergone partial oxidation due to the nature of the experiments undertaken and this suggests that both acidification and metal and metalloid release pose some risk if the wetland were to dry. The main hazards considered in this study that may impact on wetland values are acidification, contaminant mobilisation and deoxygenation. The wetland has been allocated a **low** risk rating due to ***acidification*** and a **low *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 **low** risk rating for ***acidification*** and **low** risk rating for ***contaminant mobilisation***. The risk associated with **deoxygenation** was determined to be **low** as there was no identified hazard associated with monosulfide formation.

In designing a management strategy for dealing with acid sulfate soils in Big Toolunka Flat (12064) 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 was close to full at the time of sampling, therefore management options considered should relate to minimising the formation of acid sulfate soils in inland aquatic ecosystems and to preventing oxidation of acid sulfate soils. Despite the low risks to the wetland values identified during this study for Big Toolunka Flat (12064) wetland, a monitoring program for any localised acidification (and related contaminant release) may be required if the soils were allowed to dry and oxidise.

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 Big Toolunka Flat (12064) wetland Phase 1 assessment (Grealish *et al.* 2010) and the priority ranking criteria adopted by the Scientific Reference Panel of the MDB ASSRAP (see Table 1-1), Big Toolunka Flat (12064) wetland was selected for Phase 2 detailed assessment. The Phase 1 assessment sampled from 8 sites along two transects (Figure 1-1). The Phase 1 assessment identified no high priority sites based on the presence of sulfuric materials, 1 high priority site based on the presence of hypersulfidic materials, 3 high priority sites based on hyposulfidic materials with SCR ≥ 0.10% and 8 moderate priority sites based on the presence of hyposulfidic materials with SCR < 0.10%. Phase 2 investigations were carried out on selected surface soil samples from 2 sites (12046_6 and 12006_8) identified in the Phase 1 assessment (Grealish *et al*. 2010).

The soils sampled were all subaqueous clayey soils. Net acidities were very variable along the length of the wetland, varying overall from -1143 to 89 mol H^+/tonne. However, only five sub-surface soils had positive net acidity. The wetland was well buffered, with ANC varying from 0 to 8.8 % ANC.

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

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

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 near-surface layers, as these are the soils most likely to have initial contact with water. Soil samples from three sites encompassing the length of this narrow wetland (12064_4, 12064_5 and 12064_10) were selected for Phase 2 analyses. A list of the samples selected for Phase 2 analysis for the Big Toolunka Flat (12064) wetland is presented in Table 1-3.

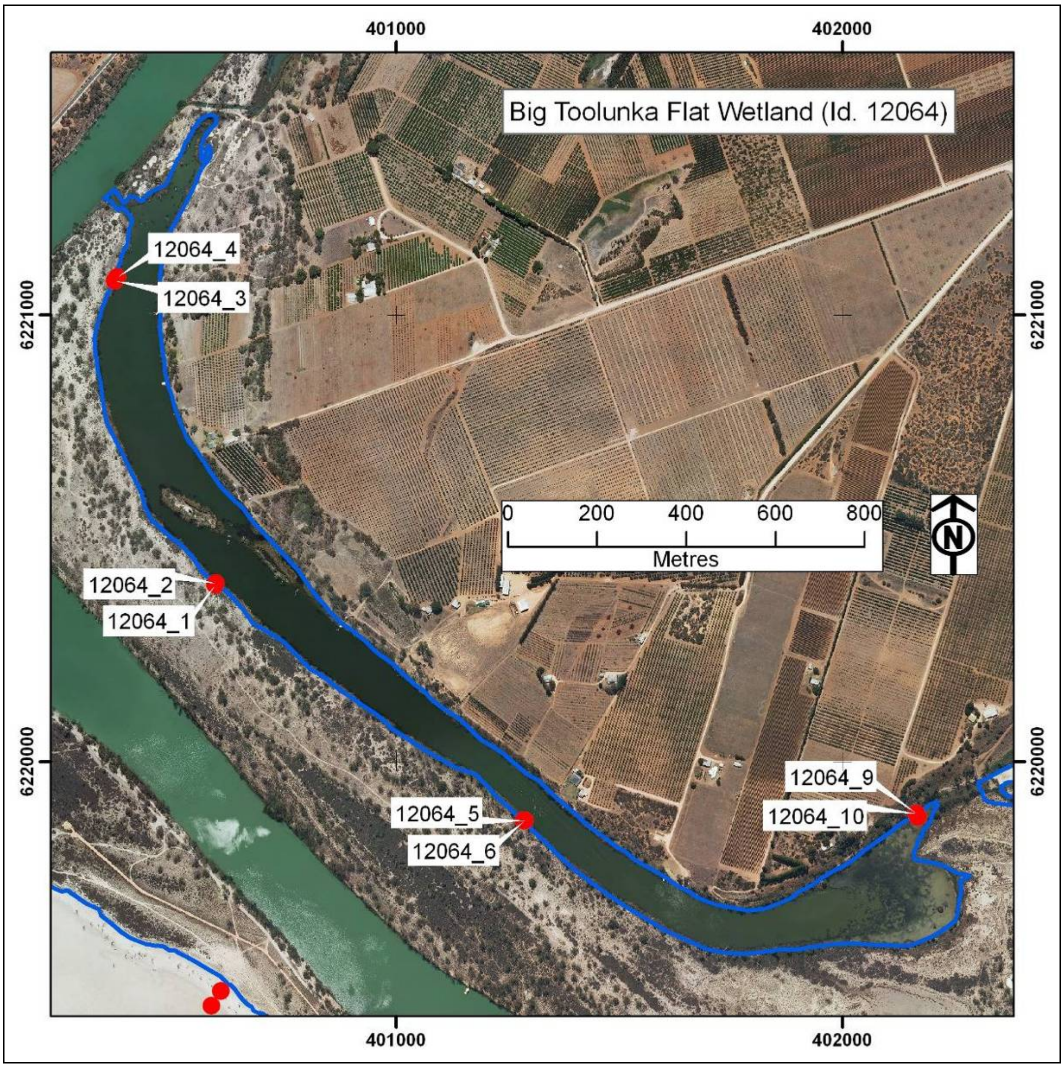

Figure 1-1 Big Toolunka Flat (12064) wetland aerial photograph with Phase 1 sampling sites identified.

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 a limited number of selected crystals and minerals (if present). Most likely to be associated with sulfuric layers to confirm acid mineral presences.
Acid base accounting data	Conducted only on samples from wetlands below Lock 1 and Burnt Creek/Loddon River if not previously analysed and pH_{KCl}<4.5.

Table 1-3 Summary of Big Toolunka Flat (12064) wetland samples analysed for Phase 2 assessment.

Soil Laboratory Test	Big Toolunka Flat (12064) wetland samples	Depth of sample (cm)	Number of samples analysed
Reactive metals	12064_4.1	0-5	6
	12064_4.2	5-10	
	12064_5.1	0-5	
	12064_5.2	5-10	
	12064_10.1	0-3	
	12064_10.2	3-10	
Contaminant and metalloid dynamics	12064_4.1	0-5	6
	12064_4.2	5-10	
	12064_5.1	0-5	
	12064_5.2	5-10	
	12064_10.1	0-3	
	12064_10.2	3-10	
Monosulfide formation potential	-	-	0
Mineral identification by X-ray diffraction (XRD)	-	-	0

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 μm nitro-cellulose filter. The metals examined comprised silver (Ag), aluminium (Al), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), vanadium (V) and zinc (Zn).

2.1.3. Contaminant and metalloid dynamics method

The guidelines for the contaminant and metalloid dynamics method are outlined in Appendix 7 of the detailed assessment protocols (MDBA 2010). The contaminant and metalloid dynamics method was designed to determine the release of metals and metalloids in soils after 24 hours. The data represent the availability of metals and metalloids from a weak extraction (water, and thus easily bioavailable) of saturated soils, and for dry wetland soils, those easily mobilised from mineral surfaces and readily soluble mineral phases (such as salts). The exercise was repeated in a batch process for longer time periods (7 days, 14 days, 35 days). The latter approach was aimed at understanding changes in concentrations over time. This is particularly important for dried soils which have been in contact with the atmosphere. The soil materials and the release/uptake of metals/metalloids are expected to change as the chemical environment changes from oxidising to reducing. The data can be compared to existing water quality guidelines, although care should be taken when extrapolating to surface waters without knowledge of hydrological conditions and natural chemical barriers. The impact on surface waters will be governed by the upward chemical flux which is a function of soil type, water flow, diffusion and the chemistry of the soils near the sediment-water interface.

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

2.1.4. Monosulfide formation potential method

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

The reactive iron (Fe) fraction in field moist sediments was extracted using 1.0 M HCl (Claff *et al.* 2010). The ferrous iron (Fe^{2+}) and total iron ($Fe^{2+} + Fe^{3+}$) 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 generally below sediment quality guideline (SQG) values and soil ecological investigation levels (EIL) for those elements for which guidelines exist (Table 3-1). However, aluminium (Al) and especially iron (Fe) were considered high for this partial extraction.

Table 3-1 Big Toolunka Flat (12064) wetland reactive metals data.

Concentrations in mg kg^{-1}, and μg kg^{-1} as indicated by asterisk.

Sample	Ag*	Al	As	Cd*	Co	Cr*	Cu	Fe	Mn	Ni	Pb	Sb*	Se*	V	Zn
12064_4.1	0.21	199	0.53	11	1.0	41	0.92	676	122	1.1	1.6	< 17	12	2.6	0.86
12064_4.2	0.90	171	0.58	12	2.9	36	1.9	554	90	2.7	1.6	< 18	13	4.2	1.5
12064_5.1	1.5	540	2.2	54	2.5	109	6.1	2198	111	6.6	3.6	< 79	59	21	5.8
12064_5.2	4.1	213	0.68	18	2.2	52	2.1	268	142	2.6	2.5	< 17	37	3.3	0.58
12064_10.1	2.2	125	0.70	12	1.4	50	2.3	759	36	1.8	2.0	< 22	17	3.0	2.4
12064_10.2	1.4	116	0.36	17	0.59	58	1.4	1231	50	1.0	1.5	< 18	13	4.1	1.6
[1]SQG	1000	-	20	1500	-	80000	65	-	-	21	50	2000	-	-	200
[2]Soil EIL	-	-	20	3000	-	-	100	-	500	60	600	-	-	50	200

* Units are in μg kg^{-1}
< value is below detection limit
[1] SQG: Sediment Quality Guideline Value (Australian and New Zealand Guidelines for Fresh and Marine Water Quality 2000)
[2] Soil EIL: Soil – Ecological Investigation Level (NEPC 1999)

3.1.2. Contaminant and metalloid dynamics data

The contaminant and metalloid dynamics data for the six Big Toolunka Flat (12064) wetland soil materials examined are presented in Appendix 2, summarised in Table 3-2 and plotted against time in Figure 3-1 to Figure 3-3. Table 3-2 also compares the pore-water metal contents to the relevant national water quality guideline for environmental protection (ANZECC/ARMCANZ 2000). Due to the high SEC in some samples, dilutions were required prior to metal analysis. For a number of elements the required dilutions resulted in the detection limits being higher than ANZECC/ARMCANZ environmental protection guideline values.

Table 3-2 Summary of contaminant and metalloid dynamics data

Parameter	units	ANZECC Guidelines	Big Toolunka Flat		
			Min.	Median	Max.
pH		6.5-8.0	**4.6**	**6.3**	**8.2**
EC*	$\mu S\ cm^{-1}$	2200	69	139	276
Eh	mV	-	-46	309	469
Ag	$\mu g\ l^{-1}$	0.05	<0.001	<0.01	<0.02
Al^A	$mg\ l^{-1}$	0.055	<0.05	<0.05	**0.12**
As^B	$\mu g\ l^{-1}$	13	<0.2	0.60	4.8
Cd	$\mu g\ l^{-1}$	0.2	<0.001	<0.04	<0.10
Co	$\mu g\ l^{-1}$	2.8	<0.01	0.08	**13**
Cr^C	$\mu g\ l^{-1}$	1	<0.09	<0.11	0.81
Cu^H	$\mu g\ l^{-1}$	1.4	<0.20	0.42	**2.0**
Fe^I	$mg\ l^{-1}$	0.3	<0.10	<0.10	**11**
Mn	$\mu g\ l^{-1}$	1700	<0.16	192	809
Ni^H	$\mu g\ l^{-1}$	11	<0.5	0.50	5.7
Pb^H	$\mu g\ l^{-1}$	3.4	<0.06	<0.50	<1.0
Sb	$\mu g\ l^{-1}$	9	<0.60	<1.0	<4.0
Se	$\mu g\ l^{-1}$	11	<0.02	0.04	0.24
V	$\mu g\ l^{-1}$	6	<0.10	0.28	4.0
Zn^H	$\mu g\ l^{-1}$	8	<0.30	0.80	**11**

🟨 ***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 upper guideline (125-2200 µS 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).*
[I] *Fe Guideline for recreational purposes*

The pH of the soil materials varied significantly from moderately acidic (pH ca. 5) to circumneutral pH on day 1 (Figure 3-1). Most samples displayed an increase in pH over the 35 days, except for sample 12064_5.1 which remained acidic throughout (Figure 3-1). Since the wetland was close to full and the soil samples were fully saturated during sampling, and given that the pH was slightly acidic to neutral at the time of field sampling, it appears that minor oxidation of sulfides has occurred prior to or during the tests.

The Eh showed an overall decrease over the day 35 period in all samples, from relatively oxidising initially on day one (Figure 3-1). The decrease in Eh was, however, variable with some of the deeper soil layers showing less of a dramatic decrease. Salinities, as indicated by the SEC, were variable but low and all were significantly below the upper ANZECC/ARMCANZ environmental protection guideline (125-2200 µS cm^{-1}) for freshwater lowland rivers in south-east Australia (Figure 3-1).

Iron (Fe) concentrations were very high in two surface samples 12064_5.1 and 12064_10.1, reaching 11 mg l^{-1}. Most other samples remained below detection limit until day 35, where there was small increase (Appendix 2). Manganese (Mn) concentrations were relatively high in three samples, but remained below the ANZECC/ARMCANZ environmental protection guideline values. The data for manganese (Mn) and iron (Fe) are consistent with the reducing conditions expected at the measured pH of the samples.

Aluminium (Al) concentrations were generally below detection limit in some, but not all, of the more acidic samples (Figure 3-1). Arsenic (As) displayed a clear increase in concentrations over time in all samples (Figure 3-1), reaching maxima after 14 days, however, concentrations were significantly lower than the ANZECC/ARMCANZ environmental protection guideline value.

Cobalt (Co) was initially high in the more acidic samples, being higher than the ANZECC/ARMCANZ environmental protection guideline value (Figure 3-2). With time, concentrations decreased and were very low by day 35. Nickel (Ni) showed a similar trend, although concentrations were lower than ANZECC/ARMCANZ environmental protection guideline value over the duration of the tests. A similar trend was noted also for zinc (Zn; Figure 3-3) with all three of these metals displaying contrasting behaviour to iron (Fe). Vanadium (V) was below the ANZECC/ARMCANZ environmental protection guideline values in all samples, but three showed an increase over time (Figure 3-3).

The magnitude of metal mobilisation is affected by many factors that include but are not exclusive to: 1) the abundance and form of metal and metalloid contaminants; 2) the abundance and lability of organic matter; 3) the abundance and reactivity of iron minerals; 4) availability of sulfate; 5) acid/alkalinity buffering capacity; 6) pH; 7) EC; 8) clay content; 9) microbial activity; 10) temperature; and 11) porosity (MDBA 2010). The relationship with pH for metals and metalloids is shown on Figure 3-4. For a number of elements, there appears to be a control by pH, with higher concentrations of manganese (Mn), cobalt (Co), nickel (Ni) and zinc (Zn) at lower pH. For iron (Fe), arsenic (As) and vanadium (V), there is a much closer relationship between low Eh and high concentrations.

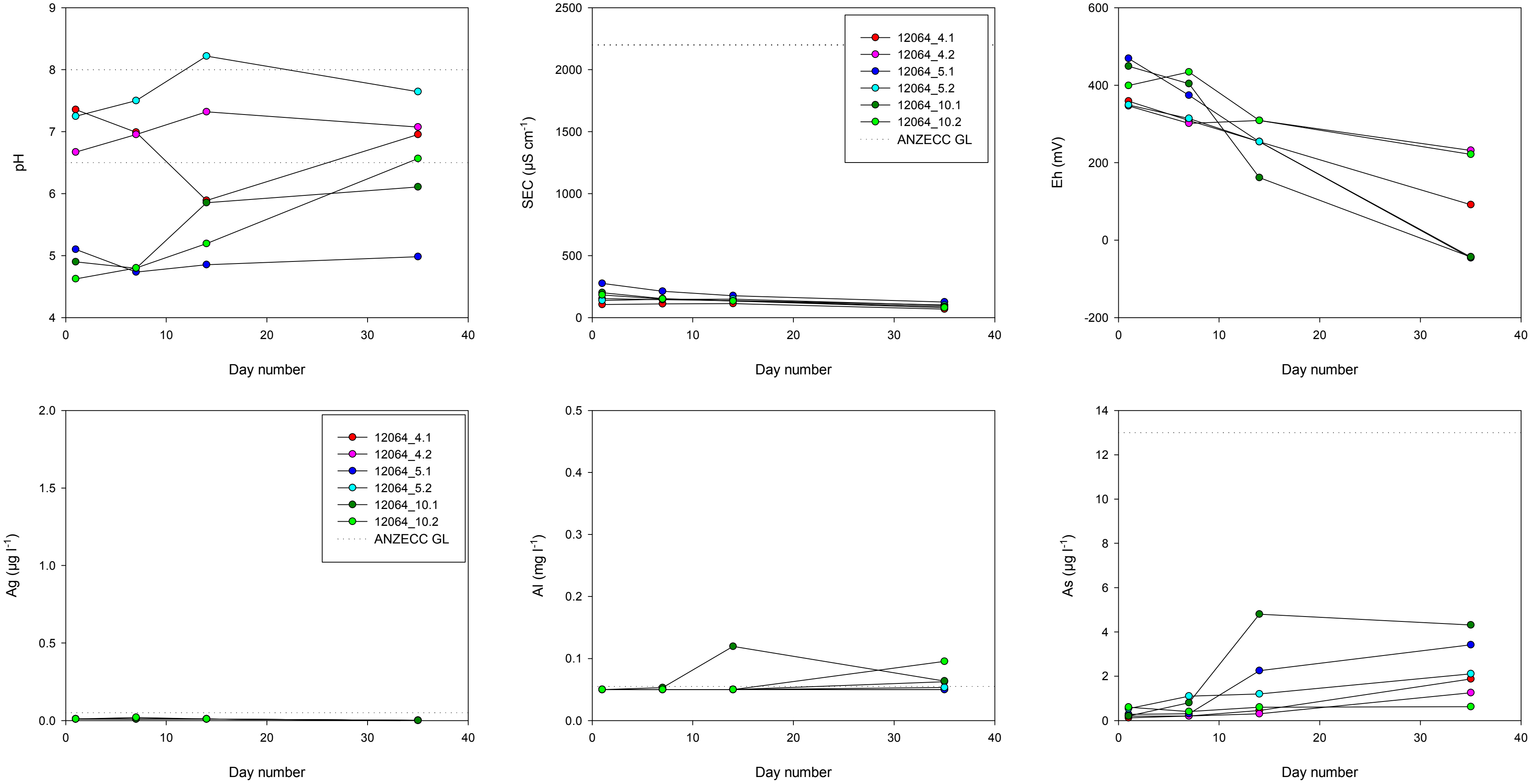

Figure 3-1 Contaminant and metalloid dynamics results for Big Toolunka Flat (12064) wetland soil materials for pH, SEC, Eh, silver (Ag), aluminium (Al) and arsenic (As).

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

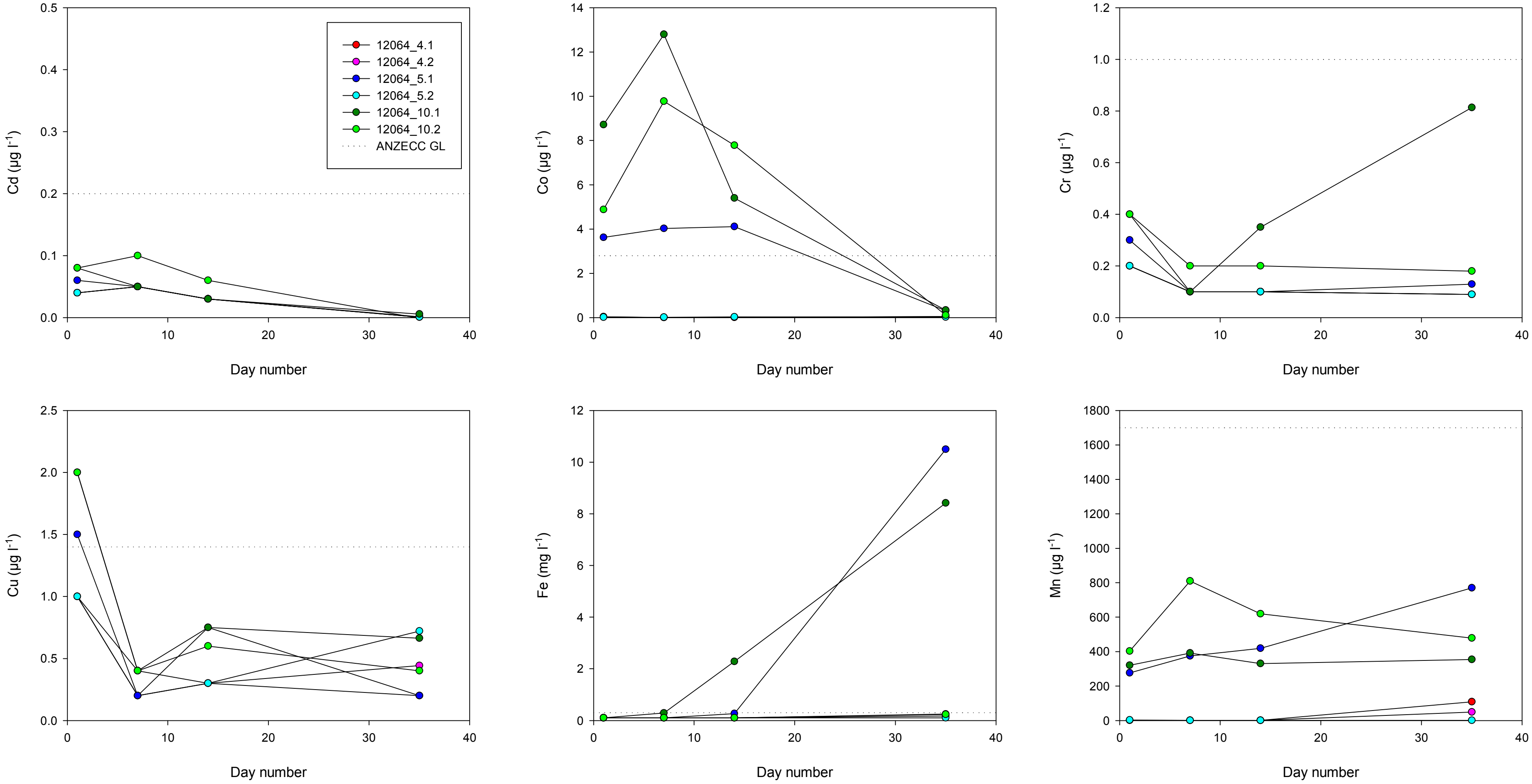

Figure 3-2 Contaminant and metalloid dynamics results for Big Toolunka Flat (12064) wetland soil materials for cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe) and manganese (Mn).

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

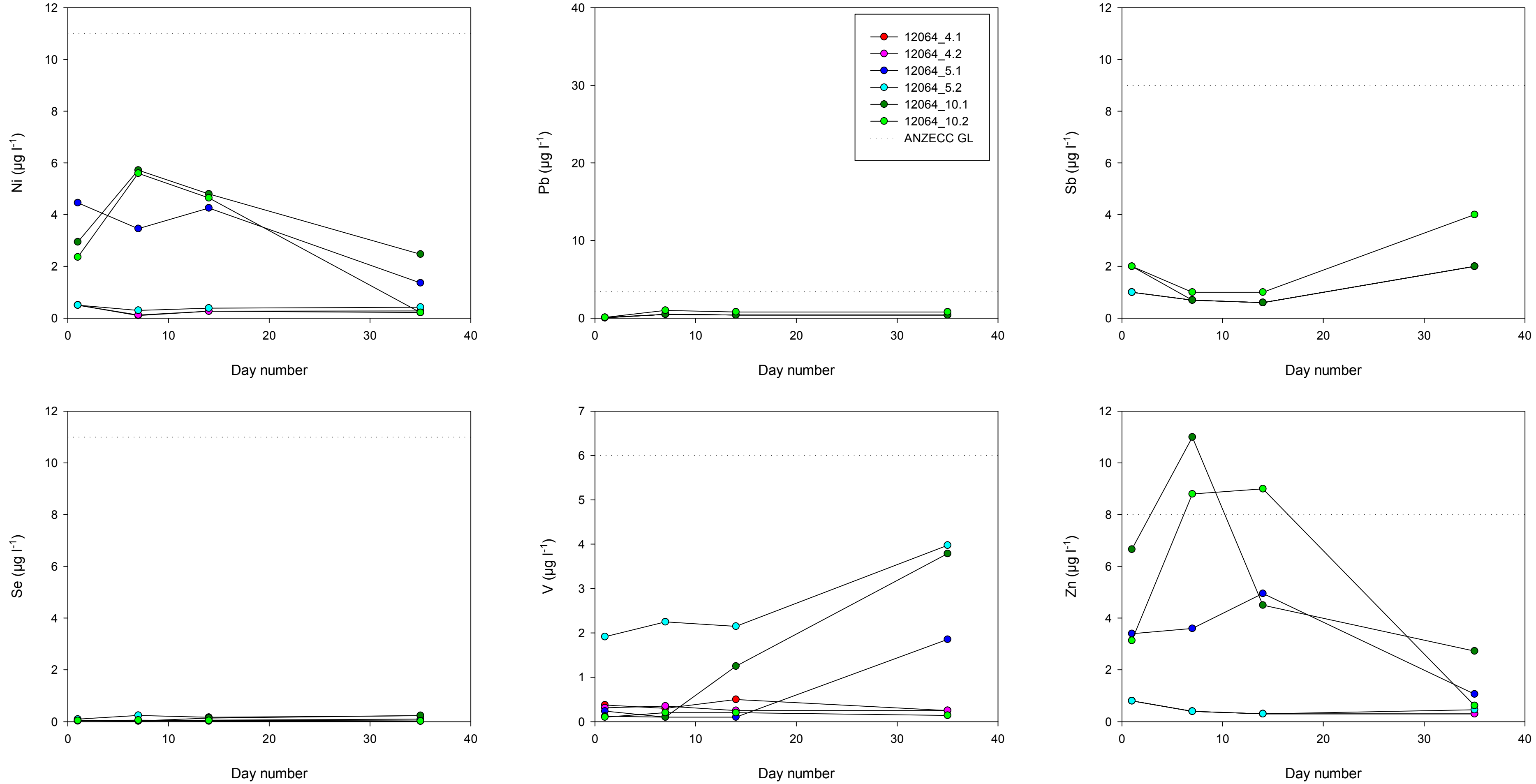

Figure 3-3 Contaminant and metalloid dynamics results for Big Toolunka Flat (12064) wetland soil materials for nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), vanadium (V) and zinc (Zn).

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

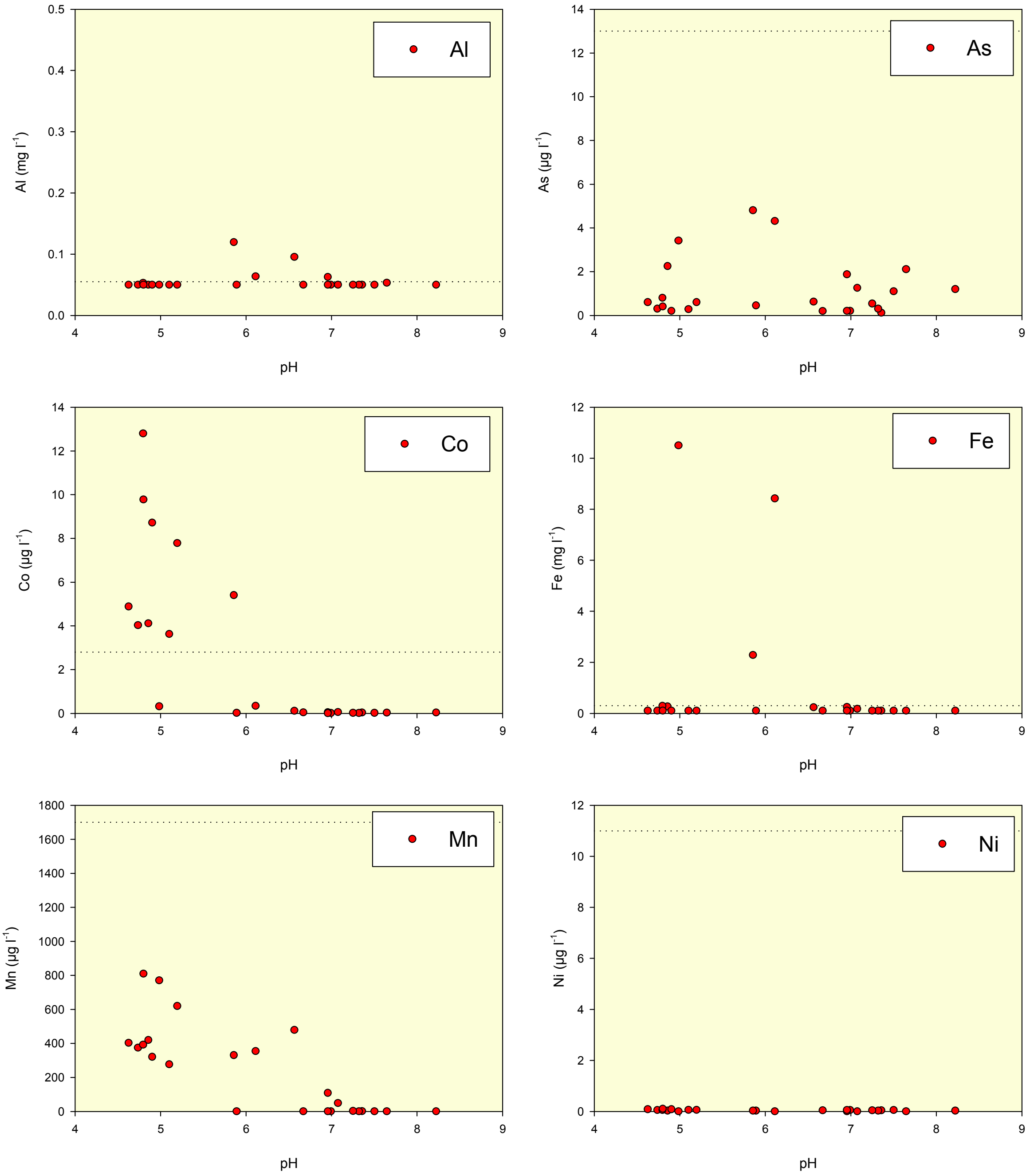

Figure 3-4 Selected trace elements plotted against pH.

3.1.3. Monosulfide formation potential data

No samples were selected from this wetland for monosulfide formation potential studies, as monosulfidic black ooze was not identified at this site.

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 (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 metal and metalloid concentrations were below sediment quality guidelines and soil ecological investigation level values for those elements in which guideline values are available (Table 3-1). Nevertheless, the concentrations of many metals are sufficiently high (mg kg^{-1}) compared to water quality guidelines (generally µg kg^{-1}) that significant release could pose a hazard to soil and surface water quality.

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

The soils had a moderately acidic to circumneutral pH on day one of the contaminant and metalloid dynamics tests. The lower pH values were in those soils identified as hypersulfidic by Grealish *et al*. (2010), and since these were lower than the soils when field sampled, it appears that some oxidation of sulfide minerals has occurred (e.g. by the addition of water to the sample). However, by day 35, most were close to or within the pH range for ANZECC/ARMCANZ environmental protection guideline values. Only one sample, 12064_5.1, remained acidic (Figure 3-1). This sample was identified as hypersulfidic in Phase 1, and had clearly acidified either prior to, or during the contaminant and metalloid dynamics tests. The samples were generally very well buffered with high ANC elsewhere in the wetland (Grealish *et al*. 2010). A number of the samples decreased significantly in Eh to allow manganese (Mn) and iron (Fe) to become soluble. The acidic samples, in particular displayed a large decrease in Eh.

The more acidic soil materials released moderately high concentrations of the trace metals cobalt (Co) and zinc (Zn) and to a lesser degree nickel (Ni), but these decreased over time in those samples where pH increased. Cobalt (Co) also displayed a decrease in the acidic samples over time, possibly due to incorporation into a reduced species such as sulfide minerals. These samples suggest that the availability of most metals and metalloids are limited, as concentrations were not particularly high in the acidic and/or reducing soils. For those samples where Eh was not low enough for iron (Fe) and manganese (Mn) reduction, metal and metalloid release may yet occur if Eh decreases. However, the suggestion of limited availability of many metals and metalloids limits the risk to soil and surface waters. Vanadium (V) did, however, appear to show a consistent increase in some samples, therefore, monitoring should be completed in case conditions change to make vanadium and other elements more mobile.

The degree to which samples exceed guideline concentrations has been used to assign a degree of hazard (Table 3-3). The data are consistent with the generally low (and often negative) net acidities noted by Grealish *et al.* (2011) which suggest that these shallow soils will take little time to recover in terms of any acidification. This appears to be largely confirmed in the contaminant and metalloid dynamics experiments where most samples reached circumneutral to slightly alkaline pH during the experiments (Figure 3-1). The extent of the more acidic surface soil (12064_5.1) is not known, but the sample site was located amongst *Phragmites* reeds at the margin of the wetland and may thus not be representative of the wetland as a whole. The higher pH will limit the solubilities of most trace metals, and the concentrations in this study suggest that mobilisation will be limited and of short duration at the circumneutral pH of most samples. Iron (Fe) has been identified as the main hazard, but its control on a number of metals and metalloids appears to be limited, as discussed above possibly due to limited metal and metalloid availability. At higher pH, the metalloids identified as a hazard in this study (arsenic and vanadium) may be stable due to limited adsorption of oxyanions at high pH. These metalloids may dissolve over longer timescales, at least until very reducing conditions in the field of iron sulfide stability, in which case they may be scavenged by precipitating iron (Fe) sulfides.

Table 3-3 Summary of the degree of hazard associated with the measured contaminant and metalloid concentrations in the Big Toolunka Flat (12064) wetland.

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

The monosulfide formation potential test assists in determining the propensity for monosulfides to form during future inundation. Water soluble sulfate concentrations were generally moderate in most samples, although all were above 100 mg kg^{-1}. Monosulfidic black ooze was not observed at this site and therefore not considered to be a hazard for this wetland.

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.

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 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).

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

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

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

The Big Toolunka Flat (12064) 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 variable net acidities in the shallow samples from Big Toolunka Flat (12064) wetland studied here (-1143 to 89 mol H^+/tonne) suggest that the overall acidification hazard is likely to be minimal over much of the centre of the wetland if kept wet, but that local acidification may occur at the margins in areas such as site 12064_5 where sulfide concentrations are high, or at the terminal end (site 12064_10) where ANC is low, if the soils are allowed to dry. The ageing of soils during Phase 1 broadly agreed with contaminant and metalloid dynamics tests. The acidification hazard is therefore, considered to be variable from very low to high.

The wetland was close to full when the samples were collected, and the risk of acidification is considered minimal under undisturbed conditions. The wetland is close to the river, separated by a narrow inlet at the north, and unmanaged. The likelihood of disturbance is therefore considered ***possible***. The highest risk for acidic soils is likely to be where soils are allowed to dry over extended periods of time, allowing deep cracking of the clay soils. Acidification is illustrated in the contaminant and metalloid dynamics tests and the previous soil ageing tests undertaken during Phase 1 (Grealish *et al*. 2010). The consequences for soil ecology are likely to be significant in the more acidic surface and sub-soils identified and much less in the more alkaline soils with high ANC. The timescale for soil recovery are also likely to vary following any drying. The results from the contaminant and metalloid dynamics experiments suggest that an overall rating for consequence would be ***minor*** if oxidation of the soils occurred. This provides a *risk rating for soil acidification* of **low** if the soils are dried. A rating for surface water acidification will be minimal if no disturbance occurs, and would depend on surface and sub-surface hydrology following any drying period. The minimum risk to surface water acidification would be where high flows were available to both dilute acidity and transport acidity downwards in the soil profile. In the case of Big Toolunka Flat (12064) wetland, acidification of surface water would potentially be an ***insignificant*** (no drying) to ***minor*** (drying and oxidation) rating for consequence. The *risk to surface water acidification* is therefore likely to be **low.**

4.2.2. Risks associated with contaminant mobilisation

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

Although the timescales cannot be assessed with existing information, the data suggest that metal availability is significant for only a few metals, in particular iron (Fe). Comparisons with other studies (e.g. Nelwart Lagoon, Shand *et al.* 2010) suggest that at the pH levels of the surface layers after 35 days of the contaminant and metalloid mobilisation tests, reductive processes may occur rapidly once initiated if there is sufficient organic matter available, and soil recovery may be rapid. The risks of metal and metalloid mobilisation are dependent on the degree of oxidation of soils and the depth to which oxidation occurs, hence related to the time of drying. For the subaqueous soils of Big Toolunka (12064) wetland, the risks due to drying and oxidation cannot be addressed fully as the soils were wet. However, it does appear that some minor oxidation has occurred during the tests which give some insight into metal availability.

The main solutes likely to present a risk under undisturbed conditions are iron (Fe) and possibly the oxyanion forming metalloids arsenic (As) and vanadium (V). In the more acidic soils the metals aluminium (Al), cobalt (Co), copper (Cu) and zinc (Zn) breached ANZECC/ARMCANZ environmental protection guideline values. The full extent of metal and metalloid release under fully oxidising conditions cannot be assessed with existing data, but do appear to pose a significant risk. Taking into account the metal and metalloid mobility assessed and limitations discussed above, a ***minor*** rating is applied for consequence. This provides a risk rating for contaminant mobilisation in soils of **low** (Table 4-4).

A rating for surface water impacts from metals and metalloids will also depend on the degree of drying and oxidation, and also on surface and sub-surface hydrology. The varying pH values by day 35 in the contaminant and metalloid dynamics tests undertaken in this study, however, mean that longer term impacts are unlikely. The risks for surface waters will relate to those metals and metalloids discussed above. Chemical reactions with soils and interactions at the soil/water interface are likely to diminish hazards from upward soil metal flux. The highest risk is likely to be following drying and during low flows where the soil to water ratio is high: metals will be most concentrated. The risk to surface metal and metalloid flux is considered lowest where high flows are available to both dilute metal and metalloid concentrations and transport these downwards in the soil profile. Due to enhanced mobility of metalloids at higher pH, the hazard cannot be assumed to be insignificant with the limited time series data available in this study, hence an ***insignificant to minor*** rating for consequence is applied. The risk to surface waters from metal mobilisation is therefore considered to be **low** (Table 4-4). The Phase 1 study sampled two soil pit-waters and noted high concentrations above ANZECC/ARMCANZ environmental protection guidelines for the nutrients ammonium (NH_4) and phosphate (PO_4) as well as high aluminium (Al) and zinc (Zn).

4.2.3. Risks associated with de-oxygenation

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

Table 4-4 Summary of risks associated with acid sulfate soil materials in the Big Toolunka Flat (12064) wetland.

Acidification Risk		Contaminant mobilisation		Deoxygenation
Soil	*Water*	*Soil*	*Water*	
Low	Low	Low	Low	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.

Big Toolunka Flat (12064) wetland was close to capacity at the time of sampling. The first two options in Table 5-1 provide the best options for minimising damage to ecosystem health and costs. Low risks to wetland values from acid sulfate soil materials were identified in this study. The contaminant and metalloid dynamics results suggest that the availability of metals and metalloids, with the exception of iron (Fe) is low, most likely due to their incorporation in reduced mineral phases such as pyrite. Although, the data are limited in addressing metal and metalloid release during drying of the wetland, the results do suggest that oxidation will lead to the release of a number of metals such as cobalt (Co) and zinc (Zn). While the risks were low, it is possible that options 3-4 i.e. controlling or treating localised acidification (and related contaminant release) may be required if the soils were allowed to dry and oxidise.

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

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

Management Objective	Activities
1. 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.
2. 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 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 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.
5. Limited further intervention	• Assess risk • Communicate with stakeholders • Undertake monitoring • Assess responsibilities and obligations and take action as required.

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APPENDICES

APPENDIX 1 REACTIVE METALS DATA

Big Toolunka Flat (12064) wetland

Sample	Depth	Analysis	Ag*	Al	As	Cd*	Co	Cr*	Cu	Fe	Mn	Ni	Pb	Sb*	Se*	V	Zn
12064_4.1	0-5	a	< 0.21	224	0.62	15	1.0	51	0.87	861	137	1.2	1.6	< 17	14	3.2	0.85
		b	0.21	173	0.45	7.2	0.96	32	0.97	490	107	1.1	1.6	< 17	10	2.1	0.87
12064_4.2	0-5	a	0.45	188	0.56	7.9	1.1	36	1.8	470	83	1.7	1.8	< 18	9.0	2.5	1.1
		b	1.3	155	0.59	16	4.7	36	2.0	639	98	3.7	1.3	< 18	18	5.9	1.9
12064_5.1	0-5	a	2.0	468	2.2	45	2.3	99	5.6	2445	106	5.1	3.3	< 79	59	20	5.1
		b	< 0.99	611	2.1	64	2.6	119	6.5	1950	116	8.1	4.0	< 79	59	22	6.4
12064_5.2	5-10	a	4.4	213	0.62	12	1.8	48	1.9	253	89	2.3	2.4	< 17	26	3.0	0.50
		b	3.9	214	0.73	24	2.7	57	2.2	283	194	2.8	2.5	< 17	48	3.6	0.65
12064_10.1	0-3	a	3.3	119	0.69	8.4	1.3	50	2.3	772	35	1.1	1.9	< 22	17	2.7	2.3
		b	1.1	130	0.71	15	1.5	50	2.4	747	37	2.5	2.2	< 22	17	3.3	2.5
12064_10.2	3-10	a	1.8	112	0.27	10	0.45	60	1.4	1495	50	0.91	1.4	< 18	12	4.5	0.90
		b	0.92	121	0.44	23	0.72	55	1.5	967	50	1.1	1.6	< 18	14	3.7	2.2

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

Big Toolunka Flat (12064) wetland

Sample	Day	Depth cm	Analysis	Eh mV	EC µS/cm	pH	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	V µg/L	Zn µg/L
12064_4.1	1	0-5	a	359	104	7.94	<0.01	<0.05	0.11	<0.04	0.03	<0.2	<1	<0.1	0.98	<0.5	<0.06	<1	0.06	0.28	<0.8
			b	359	110	6.77	<0.01	<0.05	0.12	<0.04	0.03	<0.2	<1	<0.1	0.89	<0.5	<0.06	<1	0.03	0.47	<0.8
	7		a	309	102	6.93	<0.01	<0.05	<0.2	<0.05	0.01	<0.1	0.20	<0.1	<0.2	0.08	<0.5	<0.7	<0.03	0.20	<0.4
			b	309	121	7.05	<0.01	<0.05	<0.2	<0.05	0.01	<0.1	0.20	<0.1	<0.2	0.12	<0.5	<0.7	<0.03	0.40	<0.4
	14		a	259	121	3.69	<0.01	<0.05	<0.3	<0.03	0.02	<0.1	<0.3	<0.1	0.72	0.24	<0.4	<0.6	<0.02	0.40	<0.3
			b	249	106	8.09	<0.01	<0.05	0.60	<0.03	0.02	<0.1	<0.3	<0.1	0.16	0.30	<0.4	<0.6	0.02	0.60	<0.3
	35		a	94	60	6.82	<0.001	0.08	1.2	<0.001	0.03	<0.09	<0.2	0.13	90	0.15	<0.4	<2	0.01	0.39	0.30
			b	89	79	7.09	<0.001	<0.05	2.6	<0.001	0.07	<0.09	<0.2	0.36	126	0.28	<0.4	<2	0.02	0.11	<0.3
12064_4.2	1	0-5	a	349	148	6.63	<0.01	<0.05	0.20	<0.04	0.06	<0.2	<1	<0.1	0.52	<0.5	<0.06	<1	0.03	0.23	<0.8
			b	344	158	6.71	<0.01	<0.05	0.19	<0.04	0.03	<0.2	<1	<0.1	0.77	<0.5	<0.06	<1	0.02	0.39	<0.8
	7		a	304	152	6.97	<0.01	<0.05	<0.2	<0.05	<0.01	<0.1	<0.2	<0.1	<0.2	0.12	<0.5	<0.7	<0.03	0.30	<0.4
			b	299	139	6.94	<0.01	<0.05	<0.2	<0.05	<0.0	<0.1	0.20	<0.1	<0.2	0.12	<0.5	<0.7	<0.03	0.40	<0.4
	14		a	309	145	8.10	<0.01	<0.05	0.30	<0.03	<0.01	<0.1	<0.3	<0.1	0.24	0.24	<0.4	<0.6	0.06	0.20	<0.3
			b	309	132	6.54	<0.01	<0.05	<0.3	<0.03	0.01	<0.1	<0.3	<0.1	<0.08	0.30	<0.4	<0.6	0.04	0.30	<0.3
	35		a	229	103	7.11	<0.001	<0.05	2.0	<0.001	0.07	<0.09	<0.2	0.25	71	0.24	<0.4	<2	0.04	0.13	<0.3
			b	234	101	7.04	<0.001	<0.05	0.54	0.00	0.04	<0.09	0.69	<0.1	26	0.31	<0.4	<2	0.02	0.37	<0.3
12064_5.1	1	0-5	a	479	289	4.40	<0.01	<0.05	0.37	<0.08	5.5	<0.4	<2	<0.1	381	7.3	<0.1	<2	<0.04	0.11	5.5
			b	459	262	5.80	<0.01	<0.05	0.19	<0.04	1.7	<0.2	<1	<0.1	172	1.7	<0.06	<1	0.02	0.37	1.3
	7		a	384	220	4.48	<0.01	<0.05	<0.2	<0.05	5.3	<0.1	0.20	<0.1	484	4.1	<0.5	<0.7	<0.03	<0.1	4.4
			b	364	206	4.99	<0.01	<0.05	0.40	<0.05	2.8	<0.1	0.20	<0.1	263	2.8	<0.5	<0.7	<0.03	<0.1	2.8
	14		a	159	169	5.73	<0.01	<0.05	2.1	<0.03	2.1	<0.1	0.60	0.35	340	2.9	<0.4	<0.6	0.06	<0.1	3.0
			b	349	186	3.98	<0.01	<0.05	2.4	<0.03	6.1	<0.1	0.90	0.18	499	5.6	<0.4	<0.6	0.06	<0.1	6.9
	35		a	-31	123	6.13	<0.001	<0.05	2.9	<0.001	0.12	<0.09	<0.2	7.4	1009	0.47	<0.4	<2	0.08	1.7	<0.3
			b	-61	128	3.84	<0.001	<0.05	4.0	0.00	0.51	0.17	<0.2	14	532	2.3	<0.4	<2	0.11	2.0	1.8
12064_5.2	1	5-10	a	349	139	7.58	<0.01	<0.05	0.52	<0.04	0.02	<0.2	<1	<0.1	2.0	<0.5	<0.06	<1	0.10	2.2	<0.8
			b	349	140	6.92	<0.01	<0.05	0.56	<0.04	0.01	<0.2	<1	<0.1	3.3	<0.5	<0.06	<1	0.09	1.6	<0.8
	7		a	319	145	7.80	<0.01	<0.05	1.2	<0.05	0.02	<0.1	0.40	<0.1	0.40	0.32	<0.5	<0.7	0.24	2.3	<0.4
			b	309	152	7.20	<0.01	<0.05	1.0	<0.05	0.02	<0.1	0.40	<0.1	<0.2	0.28	<0.5	<0.7	0.24	2.2	<0.4
	14		a	259	145	8.23	<0.01	<0.05	1.2	<0.03	0.04	<0.1	0.30	<0.1	0.96	0.36	<0.4	<0.6	0.18	2.3	<0.3
			b	249	154	8.21	<0.01	<0.05	1.2	<0.03	0.02	<0.1	0.30	<0.1	0.16	0.42	<0.4	<0.6	0.16	2.0	<0.3
	35		a	-56	100	8.07	<0.001	0.06	2.1	<0.001	0.02	<0.09	0.72	<0.1	0.75	0.33	<0.4	<2	0.22	3.6	<0.3
			b	-31	99	7.22	<0.001	<0.05	2.1	<0.001	0.02	<0.09	0.72	<0.1	0.46	0.52	<0.4	<2	0.23	4.3	0.61
12064_10.1	1	0-3	a	449	214	4.72	<0.01	<0.05	<0.2	<0.08	8.3	<0.4	<2	<0.1	324	2.6	<0.1	<2	<0.04	0.10	6.0
			b	449	189	5.08	<0.01	<0.05	<0.2	<0.08	9.2	<0.4	<2	<0.1	317	3.3	<0.1	<2	<0.04	0.14	7.3
	7		a	394	149	4.78	<0.01	<0.05	0.80	<0.05	13	0.10	0.40	0.28	381	5.8	<0.5	<0.7	0.03	0.10	11
			b	414	157	4.81	<0.01	0.06	0.80	<0.05	12	0.10	0.40	0.30	403	5.7	<0.5	<0.7	0.03	<0.1	11

Sample	Day	Depth cm	Analysis	Eh mV	EC µS/cm	pH	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	V µg/L	Zn µg/L
	14		a	174	131	5.31	<0.01	0.14	4.8	<0.03	5.8	0.30	0.60	2.2	334	5.0	<0.4	<0.6	0.14	1.1	3.9
			b	149	140	6.40	<0.01	0.10	4.8	<0.03	5.0	0.40	0.90	2.4	327	4.6	<0.4	<0.6	0.14	1.4	5.1
	35		a	-41	92	6.11	<0.001	0.06	4.7	<0.001	0.35	0.86	0.79	9.2	370	2.6	<0.4	<2	0.23	4.0	2.3
			b	-46	87	6.11	<0.001	0.07	3.9	0.01	0.32	0.77	0.53	7.7	339	2.3	<0.4	<2	0.23	3.5	3.1
12064_10.2	1	3-10	a	399	196	4.59	<0.01	<0.05	0.64	<0.08	5.8	<0.4	<2	0.11	417	2.7	<0.1	<2	<0.04	<0.1	3.2
			b	399	171	4.66	<0.01	<0.05	0.56	<0.08	4.0	<0.4	<2	<0.1	389	2.0	<0.1	<2	<0.04	<0.1	3.1
	7		a	424	150	4.89	<0.02	<0.05	<0.4	<0.1	8.3	<0.2	<0.4	<0.1	859	4.7	<1	<1	<0.06	<0.2	7.2
			b	444	152	4.71	<0.02	<0.05	<0.4	<0.1	11	<0.2	<0.4	<0.1	760	6.5	<1	<1	<0.06	<0.2	10
	14		a	299	135	4.54	<0.01	<0.05	<0.6	<0.06	8.4	<0.2	<0.6	<0.1	625	5.3	<0.8	<1	<0.04	<0.2	9.0
			b	319	134	5.85	<0.01	<0.05	<0.6	<0.06	7.2	<0.2	<0.6	<0.1	613	4.0	<0.8	<1	<0.04	<0.2	9.0
	35		a	219	81	5.75	0.00	0.07	0.65	0.00	0.11	<0.18	<0.4	0.17	498	0.24	<0.8	<4	<0.02	<0.14	0.64
			b	224	81	7.38	0.00	0.12	<0.6	0.00	0.11	<0.18	<0.4	0.29	459	0.19	<0.8	<4	<0.02	<0.14	<0.6

< value is below detection limit

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