



Assessment of Acid Sulfate Soil Materials (Phase 2) Taillem Bend wetland, South Australia

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

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Tailem Bend wetland
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EXECUTIVE SUMMARY

An initial Phase 1 acid sulfate soil investigation of the Taillem Bend 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 Taillem Bend 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 were below the sediment quality guidelines (SQG) and soil ecological investigation levels (EIL) for those elements where guidelines are available. Although concentrations of other elements 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 Taillem Bend wetland, aluminium (Al) was 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. The soils displayed little trend in pH throughout the tests, and the pH increased significantly to slightly acidic or neutral pH. High aluminium (Al) was found only in the slightly more acidic surface layer, and it remained high as pH increased, significantly above equilibrium concentrations. It is concluded that much of the aluminium (Al) exists as colloidal particles, thus less toxic than Al^{3+} the dominant form at lower pH. The surface layer also contained the highest iron (Fe), slightly above the ANZECC/ARMCANZ environmental protection guideline. A slight increase in copper (Cu) may be related to the increase in iron (Fe) over the contaminant mobilisation and dynamics tests.

The Taillem Bend wetland has been classified as low 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 **low** risk rating due to **acidification** and a **medium contaminant** risk rating for **soils**. For **surface waters**, the risk is largely dependent on surface and sub-surface hydrology and is thus scenario dependent. Taking into account the range of likely scenarios, from very low flows (highest risk) to very high flows (lowest risk), the risk to surface waters in the wetland has been allocated **low** risk rating for **acidification** and a medium risk rating for **contaminant mobilisation**. The risk associated with **deoxygenation** was determined to be **low** as there was no identified hazard associated with monosulfide formation and no evidence of monosulfides either in the wetland at the time of the Phase 1 field survey or forming during laboratory experiments.

In designing a management strategy for dealing with acid sulfate soils in Taillem Bend 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 risks to the wetland values associated with contaminant mobilisation in Tailern Bend wetland, a monitoring program is recommended during any disturbance to the soils.

1. INTRODUCTION

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

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

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

Following the Taillem Bend wetland Phase 1 assessment (Grealish *et al.* 2011) and the priority ranking criteria adopted by the Scientific Reference Panel of the MDB ASSRAP (see Table 1-1), Taillem Bend wetland was selected for Phase 2 detailed assessment. The Phase 1 assessment sampled 5 profiles (Figure 1-1), and identified 4 high priority sites based on the presence of sulfuric materials, 3 high priority sites based on the presence of hypersulfidic materials, 1 high priority site based on hyposulfidic materials with SCR $\geq 0.10\%$ and no moderate priority sites based on the presence of hyposulfidic materials with SCR $< 0.10\%$. Phase 2 investigations were carried out on selected samples from sites identified in the Phase 1 assessment.

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

Priority	Soil material
High Priority	<p>All sulfuric materials.</p> <p>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).</p> <p>All hyposulfidic materials with S_{CR} contents $\geq 0.10\%$ S.</p> <p>All surface soil materials (i.e. within 0-20 cm) with water soluble sulfate (1:5 soil:water) contents $\geq 100 \text{ mg kg}^{-1} \text{ SO}_4$.</p> <p>All monosulfidic materials.</p>
Moderate Priority	<p>All hyposulfidic materials with S_{CR} contents $< 0.10\%$ S.</p>
No Further Assessment	<p>Other acidic soil materials.</p> <p>All other soil materials.</p>

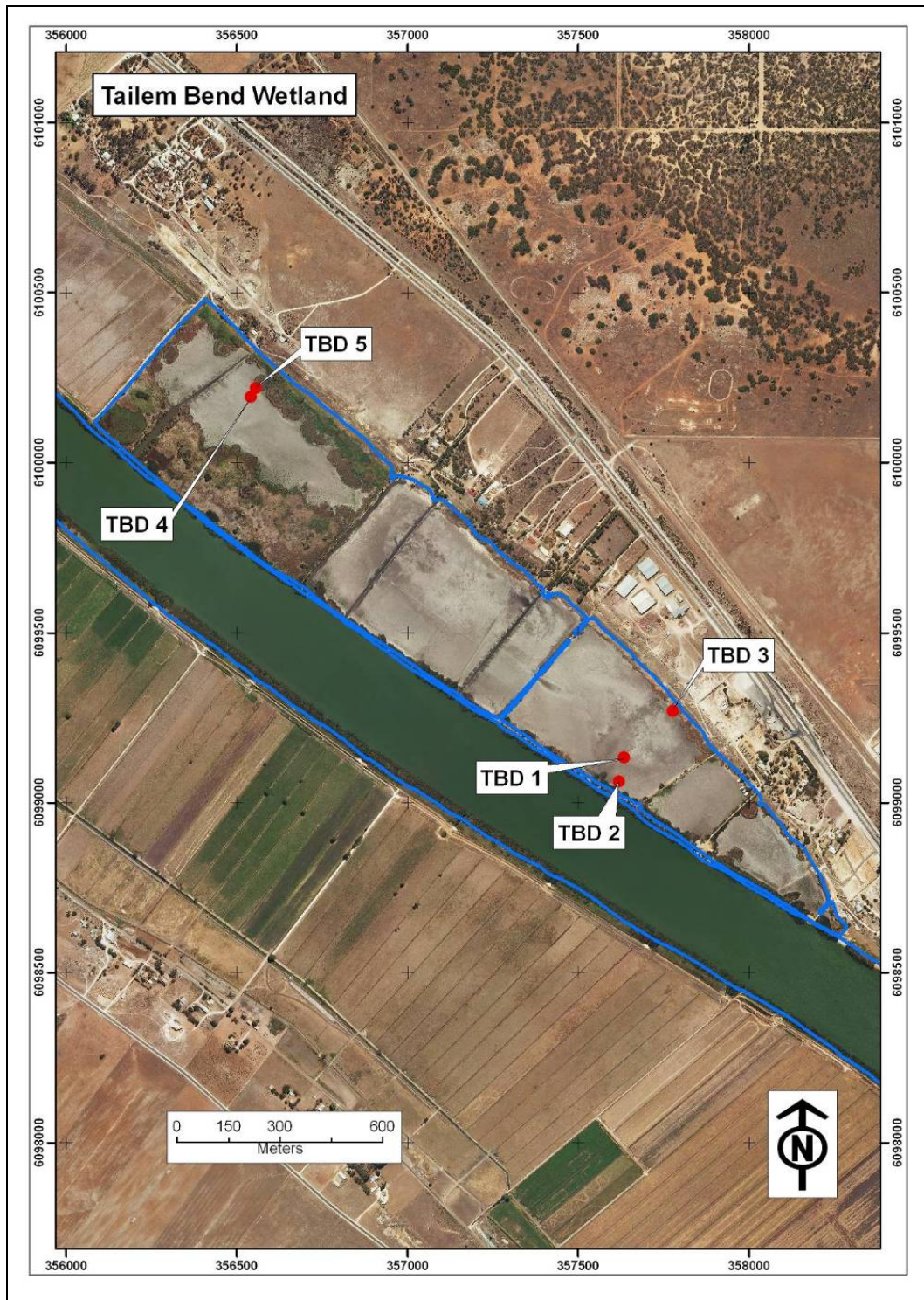


Figure 1-1 Taillem Bend wetland aerial photograph with Phase 1 sampling sites identified.

A summary of the soil laboratory analyses undertaken as part of the Phase 2 assessment and the sample selection criteria for each analysis is given in Table 1-2. Soil samples identified to undergo Phase 2 laboratory analysis are primarily from the surface and near-surface 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 Taillem Bend wetland is presented in Table 1-3.

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

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

Table 1-3 Summary of Taillem Bend wetland samples analysed for Phase 2 assessment.

Soil Laboratory Test	Taillem Bend wetland samples	Sample depth (cm)	Number of samples analysed
Reactive metals	TBD2.1	0-15	2
	TBD4.1	0-10	
Contaminant and metalloid dynamics	TBD2.1	0-15	2
	TBD4.1	0-10	
Monosulfide formation potential	TBD4.1	0-10	1
Mineral identification by X-ray diffraction (XRD)	N/A		

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 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 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 ($\text{Fe}^{2+} + \text{Fe}^{3+}$) 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 $\pm 10\%$ for all analyses. In addition, for all samples, reactive metals and contaminant and metalloid dynamics tests were duplicated. For the reactive metals, two International Standards (Reference Stream Sediment STSD-2 and STSD-3 Canadian Certified Reference Materials) were processed in

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

3. RESULTS AND DISCUSSION

3.1. Summary of soil laboratory results

3.1.1. Reactive metals data

The data are presented on a dry weight basis (mg kg^{-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 (Goody *et al.* 1995). Although guideline values exist for soils and sediments, these are generally for total soil concentrations, and therefore, are not directly appropriate for the data from metal mobilisation studies. Nevertheless, they provide a basis for comparison; and concentrations close to or above guideline values indicate an elevated hazard.

The concentrations of metals and metalloids were below sediment quality guideline (SQG) values and soil ecological investigation levels (EIL) for those elements where guidelines are available. The concentrations for most reactive metals and metalloids are relatively low, but relatively high for aluminium (Al) and iron (Fe).

Table 3-1 Taillem Bend wetland reactive metals data.

Concentrations in mg kg^{-1} , and $\mu\text{g kg}^{-1}$ as indicated by asterisk.

Sample	Ag*	Al	As	Cd*	Co	Cr*	Cu	Fe	Mn	Ni	Pb	Sb*	Se*	V	Zn
TBD 2.1	5.8	1009	0.58	20	0.43	97	2.3	532	18	3.0	1.6	< 22	40	11	2.6
TDB 4.1	5.0	1081	1.4	166	0.94	137	3.7	1892	37	6.6	2.7	< 37	53	14	2.7
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 $\mu\text{g kg}^{-1}$

< value is below detection limit

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 two Taillem Bend 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).

Table 3-2 Summary of contaminant and metalloid dynamics data

Parameter	units	ANZECC Guidelines	Taillem Bend		
			Min.	Median	Max.
pH		6.5-8.0	5.4	6.0	7.1
EC*	$\mu\text{S cm}^{-1}$	2200	62	132	301
Eh	mV	-	272	378	467
Ag	$\mu\text{g l}^{-1}$	0.05	<0.01	<0.03	<0.03
Al ^A	mg l^{-1}	0.055	<0.1	0.47	1.4
As ^B	$\mu\text{g l}^{-1}$	13	<2	<2	<2
Cd	$\mu\text{g l}^{-1}$	0.2	<0.2	<0.2	<0.2
Co	$\mu\text{g l}^{-1}$	2.8	0.07	0.18	0.35
Cr ^C	$\mu\text{g l}^{-1}$	1	<0.5	<0.5	<0.5
Cu ^H	$\mu\text{g l}^{-1}$	1.4	<0.2	<2	2.4
Fe ^I	mg l^{-1}	0.3	<0.1	0.21	0.65
Mn	$\mu\text{g l}^{-1}$	1700	<1	12	79
Ni ^H	$\mu\text{g l}^{-1}$	11	<0.5	0.65	2.0
Pb ^H	$\mu\text{g l}^{-1}$	3.4	<2	<2	<2
Sb	$\mu\text{g l}^{-1}$	9	<10	<10	<10
Se	$\mu\text{g l}^{-1}$	11	<0.1	<0.1	<0.1
V	$\mu\text{g l}^{-1}$	6	0.40	4.9	20
Zn ^H	$\mu\text{g l}^{-1}$	8	<1.4	<1.4	3.0

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 ($125\text{-}2200 \mu\text{S cm}^{-1}$) 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).

^I Fe Guideline for recreational purposes.

The pH of the soil materials varied from pH 5.4 to 7.1, with both samples from the profile showing a general increase over the 35 day period (Figure 3-1). Sample TBD 2.1 showed the highest pH change coming within ANZECC/ARMCANZ environmental protection guideline value on day 35, while the other sample (TBD 4.1) was close to the lower ANZECC/ARMCANZ guideline for environmental protection.

The Eh showed only a slight decrease over the day 35 period, remaining relatively oxidising (Figure 3-1). The SEC showed a slight decrease with time, and both samples were fresh.

Manganese (Mn) concentrations were very low throughout the time period, and below ANZECC/ARMCANZ environmental protection guideline values in all samples. Iron (Fe) was

present in sample TBD 2.1, slightly higher than the ANZECC/ARMCANZ environmental protection guideline, but lower in the sample TBD 4.1, consistent with pH and Eh conditions.

Aluminium (Al) was also higher in the TBD 2.1 (Figure 3-1). The only other elements which breached guideline values were copper (Cu) after 14 days in this sample and vanadium (V) throughout (Figure 3-2 and Figure 3-3). Antimony (Sb) was less than detection limit and the other metals and metalloids were present at low concentrations below ANZECC/ARMCANZ guidelines.

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). There was little correlation of any of the metals and metalloids with pH or Eh over the time period of the incubations (Figure 3-4). The low concentrations of trace elements studied (apart from aluminium (Al) and iron (Fe)), and the lack of correlation with pH and Eh suggests limited abundance of available trace metals, in agreement with the reactive metals tests (section 3.1.1).

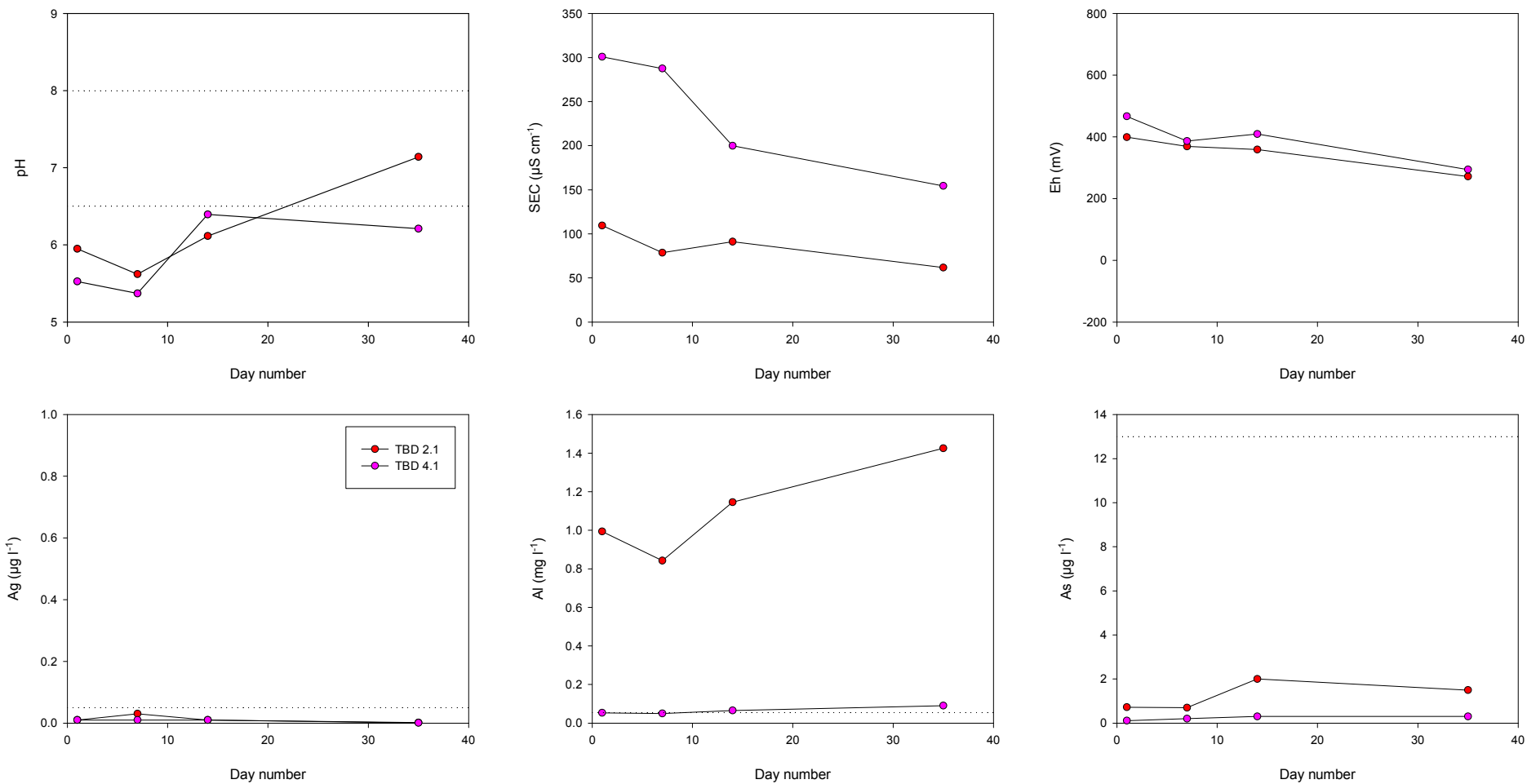


Figure 3-1 Contaminant and metalloid dynamics results for Taillem Bend wetland soil materials for pH, SEC, Eh, silver (Ag), aluminium (Al) and arsenic (As).

Note: silver (Ag) and arsenic (As) were < detection limit in some samples, data represent detection limits which vary according to required dilutions.

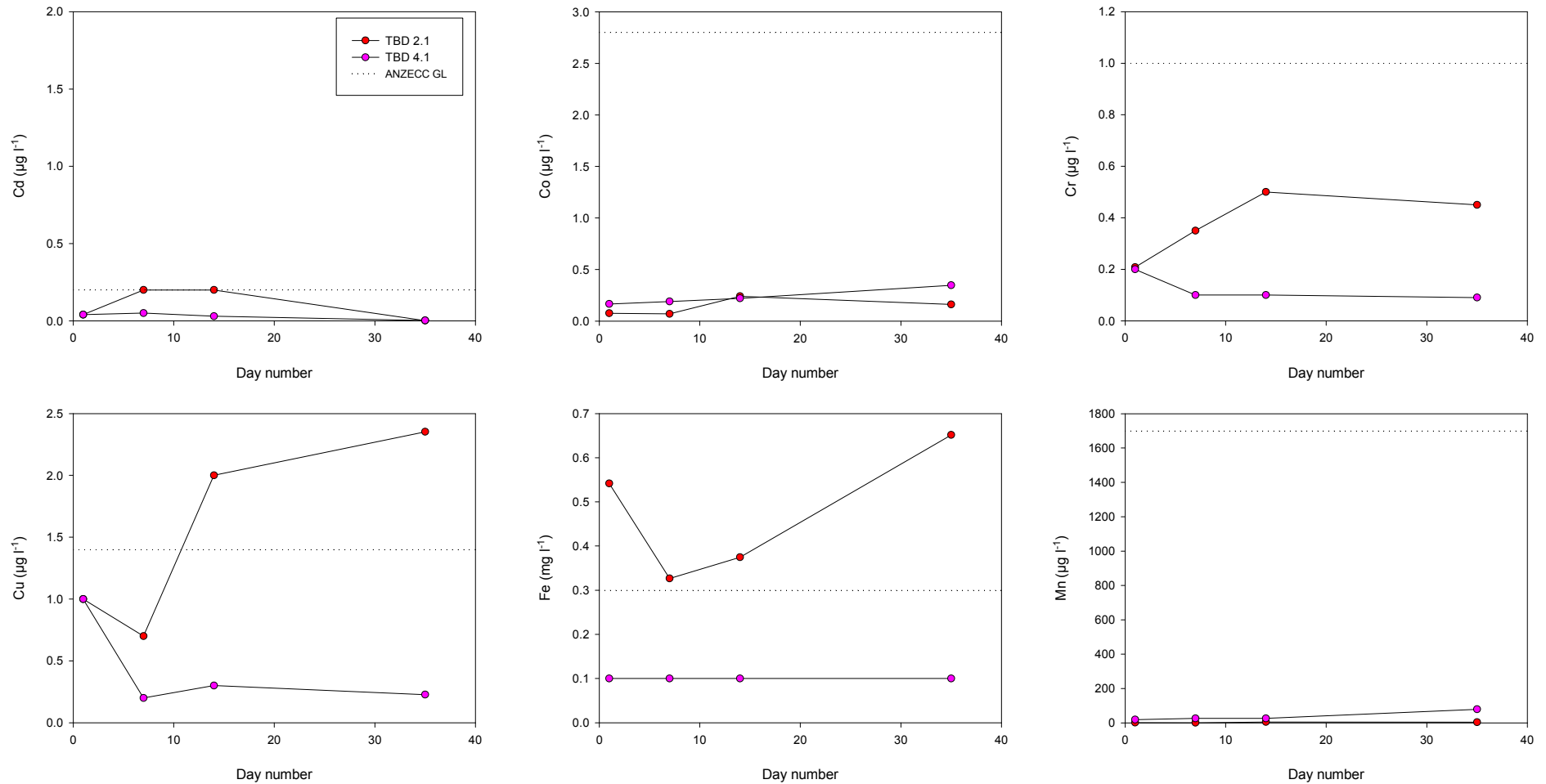


Figure 3-2 Contaminant and metalloid dynamics results for Taillem Bend wetland soil materials for cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe) and manganese (Mn).

Note: cadmium (Cd) and chromium (Cr) were < detection limit in some samples, data represent detection limits which vary according to required dilutions.

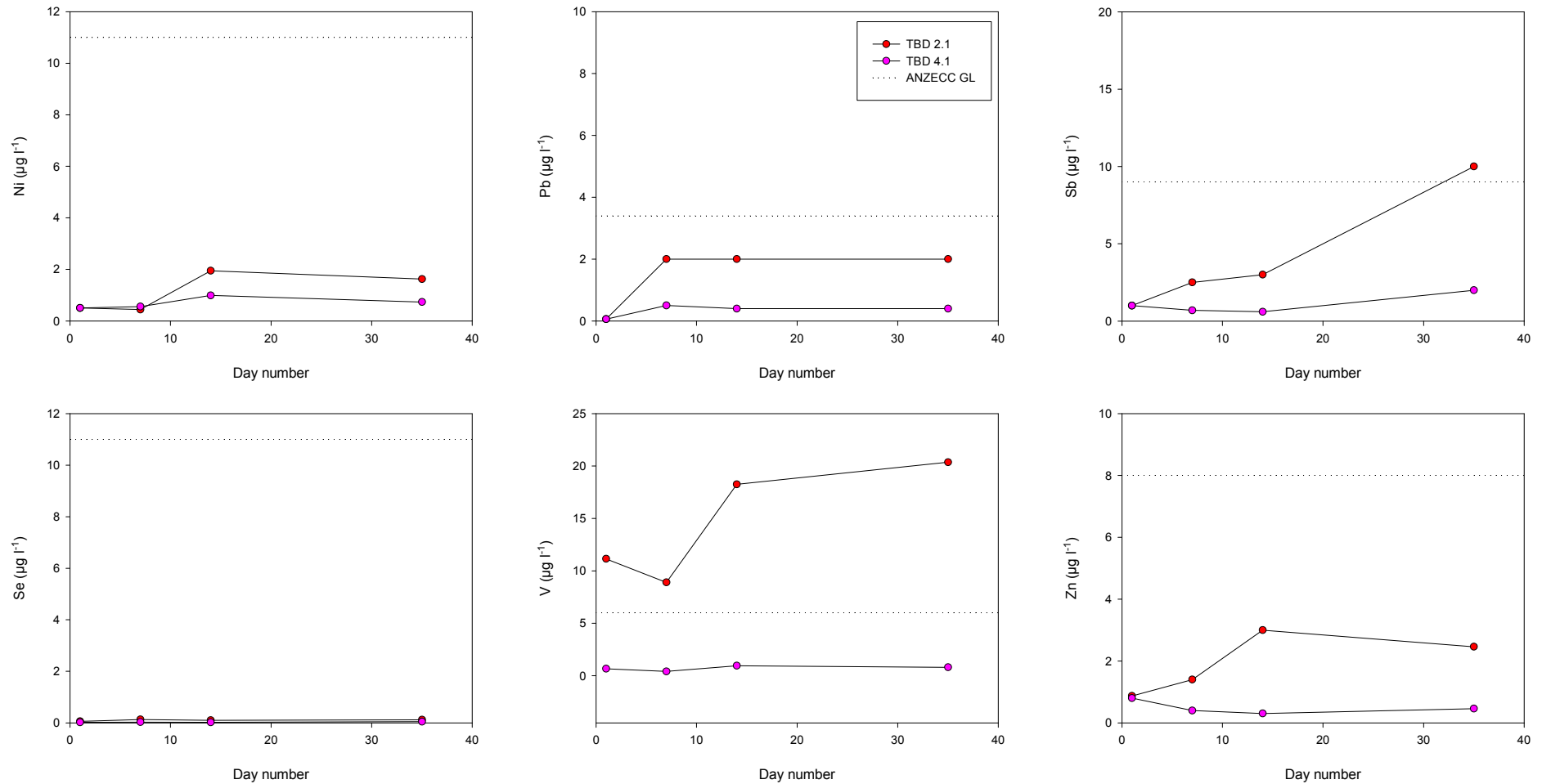


Figure 3-3 Contaminant and metalloid dynamics results for Taillem Bend wetland soil materials for nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), vanadium (V) and zinc (Zn).

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

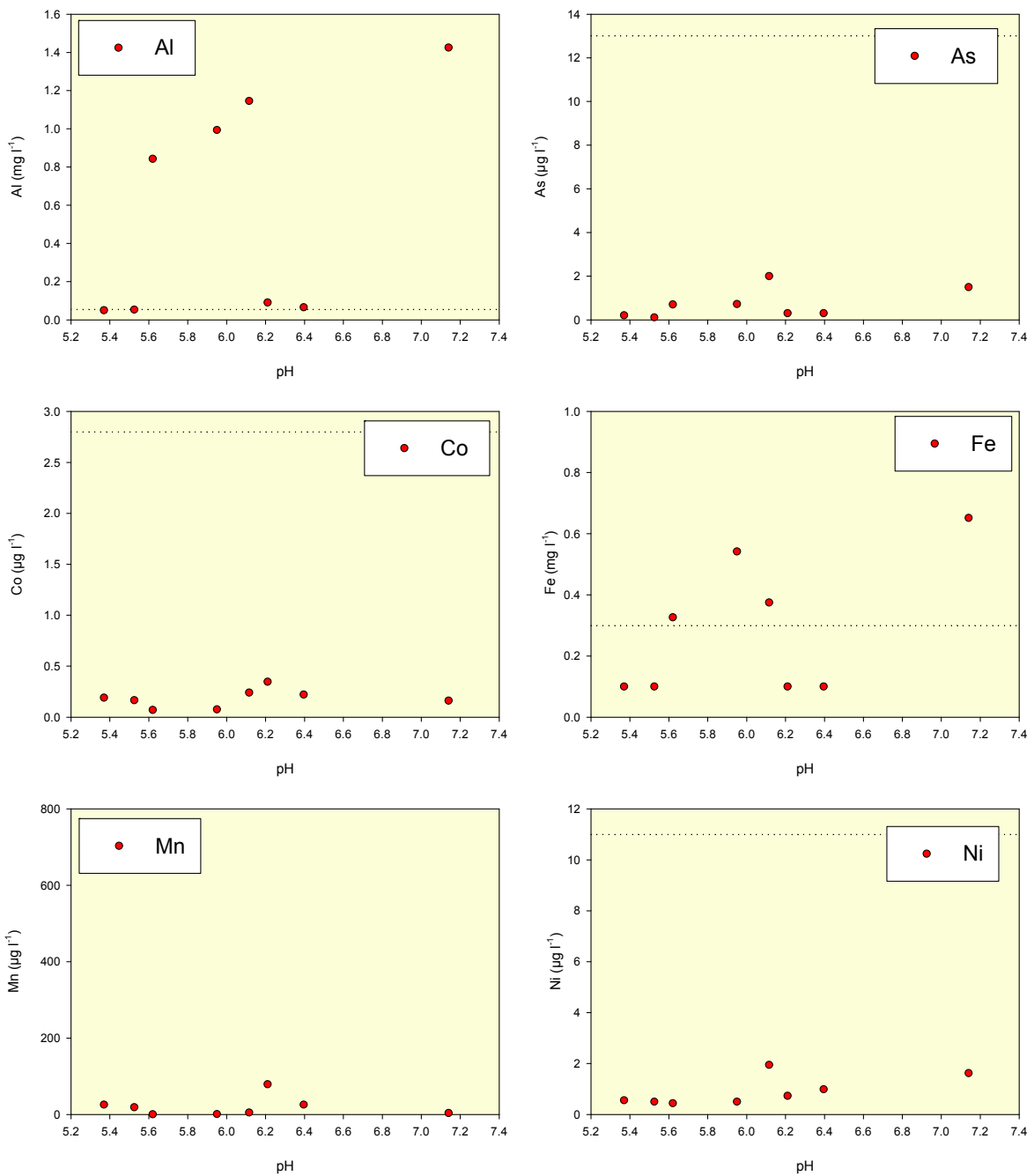


Figure 3-4 Selected trace elements plotted against pH.

3.1.3. Monosulfide formation potential data

The monosulfide formation potential data for sample analysed for Taillem Bend wetland (TBD 4.1) are shown in Table 3-3. The pH of the soil water changed from 5.13 to 4.39 over the seven week incubation period (Table 3-3). The decrease in pH is different from the contaminant and metalloid dynamics tests, where pH increased to pH 6.21 (Figure 3-1). This discrepancy may be due to fermentation of organic substrate added (sucrose) which caused acidification of the pore waters.

The Eh decreased from 463 to 334 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 467 to 294 mV (Figure 3-1).

Table 3-3 Summary of monosulfide formation potential data for the Taillem Bend wetland surface soil material TBD 4.1 after 7 weeks (3.6 g/L sucrose).

Inundation Time	Parameter	Units	Tailem Bend (TBD 4.1)
Day 0	Total Fe	mg/kg	10894
	Fe(II) ⁻	mg/kg	826
	Sulfate*	mg/kg	207
	pH		5.13
	Eh	mV	463
Week 7	pH		4.39
	Eh	mV	334
	S _{AV}	Wt. %S	<0.01
	S ⁰	Wt. %S	<0.01
	Pyrite-S	Wt. %S	0.01
	Dissolved S ²⁻	µg/L	1313

* completed during Phase 1

After 7 weeks, acid volatile sulfide (S_{AV}) and elemental sulfur (S⁰) were both <0.01% (Table 3-3). It appears, therefore, that monosulfide formation has not occurred in this sample during the tests. The sample originally contained <0.01% S_{CR} (S_{AV} + pyrite-S) (Grealish *et al.* 2010) and it, therefore, appears that pyrite has also not formed in the sample during the experiment. Dissolved sulfide was however, present (Table 3-3), suggesting that the sample has the potential to form sulfides, however the Eh appears inconsistent with the data.

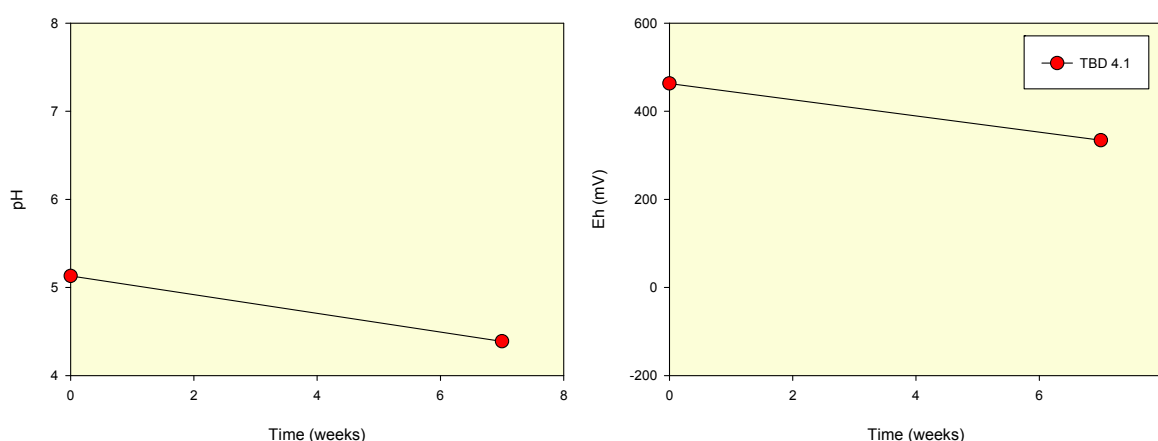


Figure 3-5 pH and Eh dynamics during monosulfide formation potential tests in surface soil sample TBD 4.1 from Taillem Bend wetland.

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 (Goody *et al.* 1995). Although guideline values exist for soils and sediments (ANZECC/ARMCANZ 2000), these are generally for total soil concentrations, and therefore, are not directly appropriate for the data from metal mobilisation studies. Nevertheless, they provide a basis for comparison; and concentrations close to or above guideline values indicate an elevated hazard.

The reactive metal and metalloid concentrations were all below sediment quality guidelines and soil ecological investigation level values (Table 3-1). Concentrations of aluminium (Al) and iron (Fe) are considered high for this partial extraction, consistent with the relatively low initial pH. The low concentrations of other metals and metalloids in these peaty and clay soils suggests a lack of metal availability in these soil surface layers.

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

Although there was a slight decrease in Eh, it appears that reductive processes have been rather limited. The surface soils were moist at the time of sampling and contained abundant organic matter, hence it is surprising that Eh has remained relatively high.

The degree to which samples analysed 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 10 $\mu\text{g l}^{-1}$). It is therefore not possible to group

antimony (Sb) in Table 3-4, although it can be concluded that they either sit in the No hazard or Low Hazard grouping. The data are shown in Appendix 1 which displays the detection limits for individual analyses.

Apart from high aluminium (Al) in one of the samples, a shallow peaty soil, over the duration of the contaminant and metalloid dynamics work, it does not appear that acidification and metal mobilisation pose high hazards at this site. The data are consistent with the low net acidities noted by Grealish *et al.* (2011) which suggest that these shallow soils may take little time to recover in terms of acidity and metal mobility. The high aluminium (Al) in the shallowest sample was maintained in the contaminant and metalloid dynamics extractions even at circumneutral pH where aluminium (Al) solubility should be very low. It is likely that the aluminium (Al) exists as colloidal material and hence may pose less of a risk than truly dissolved aluminium (Al³⁺).

Table 3-4 Summary of the degree of hazard associated with the measured contaminant and metalloid concentrations in the Taillem Bend wetland.

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

Note: Sb is below detection limits due to dilutions, but is likely to be in the low or no hazard classification.

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 (S⁰). The lack of acid volatile sulfide (S_{AV}) ranks the monosulfide formation potential hazard as 'No hazard' (Table 3-5).

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

Degree of Hazard	Guideline Threshold
No Hazard	< 0.01 % S _{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.

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 soils, the acid generating potential and the buffering capacity of the 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, soil type, hydraulic conductivity and degree and depth of soil cracking.

The Taillem Bend wetland has been classified as low conservation status by the SA Murray-Darling Basin Natural Resources Management Board (Miles *et al.* 2010).

4.2.1. Risks associated with acidification

The low net acidities in shallow samples from Taillem Bend suggest that the acidification hazard is low. Net acidities were highest in the hypersulfidic soils at depth at the site (Grealish *et al.* 2011), but at depths which are unlikely to pose a risk unless sub-surface water levels decrease significantly (to below 60-80 cm depth). The risks are therefore assigned based on the shallow soils as used in this study.

It would appear unlikely that soil acidification would pose a serious problem as suggested by the measured pH and increase in pH 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. The consequences are likely to be insignificant for soil ecology, and the timescale for soil recovery from acidification probably rapid. An **insignificant** 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 **low** (Table 4-4). A rating for surface water acidification will depend on surface and sub-surface hydrology. The highest risk is likely to be during low flows where the soil to water ratio is high: acidity will be most concentrated. The 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 consequence rating is therefore considered as insignificant. The *risk to surface water acidification* is therefore likely to be **low** (Table 4-4).

4.2.2. Risks associated with contaminant mobilisation

The risks of metal and metalloid mobilisation are controlled primarily by metal abundance and availability, geochemical controls on speciation and transport mechanisms. The master variables pH and Eh exert a direct major influence on the solubility of individual metals and metalloids and minerals such as iron (Fe) and manganese (Mn) oxides and hydroxides which are important sorbents of metal and metalloids species. The 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 and contaminant and metalloid dynamics results attest to the limited availability and mobility of a number of metals (e.g. in sample TBD 2.1 where iron (Fe) was high and aluminium (Al) which was present at concentrations more than 10 x the ANZECC/ARMCANZ environmental protection guideline value). However, it was suggested above that the aluminium (Al) may be in colloidal form, hence less toxic than Al³⁺ which is the dominant form at low pH. In addition, aluminium (Al) is likely to precipitate rapidly as pH increases and unlikely to be impacted by a return to reducing conditions since it is not redox-sensitive.

Although the timescales cannot be assessed with existing information, the data suggest that metal availability is not particularly high. However, comparisons with other studies (e.g. Nelwart Lagoon; Shand *et al.* 2010), suggest that at these pH levels, reductive processes may occur rapidly once initiated, and soil recovery may be rapid. Since pH remained relatively high for wetland soils, a **minor** rating is applied for consequence as problems are likely to be localised and relatively short term. This provides a risk rating for contaminant mobilisation in soils of **medium** (Table 4-4).

A rating for surface water impacts from metals and metalloids will depend on surface and sub-surface hydrology. The slightly acidic to circumneutral pH values in this study, however, means that longer term impacts are unlikely. Chemical reactions with soils and interactions at the soil/water interface are likely to diminish any minor hazards from metal flux. The highest risk is likely to be during low flows where the soil to water ratio is high: metals will be most concentrated. The minimum risk to surface metal and metalloid flux is considered lowest where high flows are available to both dilute metal and metalloid concentrations and transport these downwards in the soil profile. Due to enhanced mobility of metalloids at higher pH, the hazard cannot be assumed to be insignificant with the limited time series data available in this study, hence a **minor** consequence is applied. The risk to surface waters from metal mobilisation is therefore considered to be **medium** (Table 4-4).

4.2.3. Risks associated with de-oxygenation

Monosulfidic materials are considered the main cause of deoxygenation risk in acid sulfate soils. Monosulfidic black ooze was not identified in the wetland during the Phase 1 survey (Grealish *et al.* 2011). The water soluble sulfate concentrations were, however, high and above the trigger value for monosulfidic black ooze formation (MDBA 2010). One surface sample (TBD 4.1) with a water soluble sulfate concentration of 207 mg kg⁻¹ was selected for monosulfide formation potential.

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. The consequence of deoxygenation is considered to be **insignificant** due to the lack of an identified hazard. As such, the risk associated with deoxygenation was determined to be **low** as there was no identified hazard associated with monosulfide formation and no evidence of monosulfides either in the wetland at the time of the Phase 1 field survey or forming during laboratory experiments.

Table 4-4 Summary of risks associated with acid sulfate soil materials in the Taillem Bend wetland.

Acidification Risk		Contaminant mobilisation		Deoxygenation
<i>Soil</i>	<i>Water</i>	<i>Soil</i>	<i>Water</i>	
Low	Low	Medium	Medium	Low

5. BROAD ACID SULFATE SOIL MANAGEMENT OPTIONS

The options available for rehabilitation of inland waterways containing acid sulfate soils has recently been reviewed (Baldwin & Fraser 2009) and incorporated into the *National guidance on managing acid sulfate soils in inland aquatic ecosystems* (EPHC & NRMCC 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 conservation status for this wetland is low and thus the management responses need to take this into account when aligning with the options suggested following the risk assessment ratings (Table 4-3).

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

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

The medium risks identified in this study are due to soil and water 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, at the pH's observed, the increase in pH over the 35 day period and limited contaminant mobilisation imply that any risks are likely to be localised in nature. The highest risks are likely to be associated with deeper drying and cracking as sulfide minerals are present at depth at very high concentrations (Grealish *et al.* 2011).

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 recommended that surface water monitoring be undertaken at this wetland. Based on the data from this study and elsewhere (Shand *et al.* 2010), it is likely that soil recovery will be relatively rapid as pH is relatively high and increased in experiments in this study over time.

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
<p>1. Minimising the formation of acid sulfate soils in inland aquatic ecosystems</p>	<p>Reduce secondary salinisation through:</p> <ul style="list-style-type: none"> • 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.
<p>2. Preventing oxidation of acid sulfate soils or controlled oxidation to remove acid sulfate soils</p>	<p>Preventing oxidation:</p> <ul style="list-style-type: none"> • Keep the sediments covered by water • Avoid flow regimes that could re-suspend sediments. <p>Controlled oxidation:</p> <ul style="list-style-type: none"> • 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.
<p>3. Controlling or treating acidification</p>	<ul style="list-style-type: none"> • 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.
<p>4. Protecting adjacent or downstream environments if treatment of the affected aquatic ecosystem is not feasible</p>	<ul style="list-style-type: none"> • Isolate the site • Neutralise and dilute surface water • Treat discharge waters by neutralisation or biological treatment.
<p>5. Limited further intervention</p>	<ul style="list-style-type: none"> • 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

Tailem Bend wetland

Sample	Depth	Analysis	Ag*	Al	As	Cd*	Co	Cr*	Cu	Fe	Mn	Ni	Pb	Sb*	Se*	V	Zn
TBD 2.1	0-15	a	5.5	1017	0.57	18	0.38	97	2.1	455	15	2.5	1.5	< 22	39	9.2	2.5
		b	6.1	1001	0.59	21	0.49	97	2.6	610	21	3.4	1.7	< 22	42	13	2.7
TDB 4.1	0-10	a	5.5	774	1.2	261	0.75	137	3.1	1338	34	4.6	3.2	< 37	41	11	2.2
		b	4.6	1388	1.5	70	1.1	137	4.2	2447	40	8.7	2.2	< 37	64	18	3.2

Units are in 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

Taillem Bend wetland

Sample	Day	Depth cm	Analysis	Eh mV	EC μ S/cm	pH	Ag μ g/L	Al mg/L	As μ g/L	Cd μ g/L	Co μ g/L	Cr μ g/L	Cu μ g/L	Fe mg/L	Mn μ g/L	Ni μ g/L	Pb μ g/L	Sb μ g/L	Se μ g/L	V μ g/L	Zn μ g/L
TBD 2.1	1	0-15	a	399	117	6.15	<0.01	0.66	0.80	<0.04	0.08	<0.2	<1	0.30	1.1	<0.5	<0.06	<1	0.05	10	0.88
			b	399	102	5.75	<0.01	1.3	0.64	<0.04	0.07	0.22	<1	0.78	1.0	<0.5	<0.06	<1	0.06	12	0.86
	7		a	374	83	5.08	<0.04	1.0	<1	<0.3	0.08	<0.5	<1	0.39	<1	0.40	<3	<4	<0.2	8.0	<2
			b	364	74	6.16	<0.02	0.65	<0.4	<0.1	0.06	<0.2	0.40	0.26	0.40	0.48	<1	<1	<0.06	9.8	<0.8
	14		a	364	89	6.03	<0.01	1.1	<2	<0.2	0.20	<0.5	<2	0.43	5.6	1.2	<2	<3	<0.1	13	2.0
			b	354	94	6.20	<0.01	1.2	<2	<0.2	0.28	<0.5	<2	0.32	4.8	2.7	<2	<3	<0.1	24	4.0
	35		a	274	68	7.62	<0.002	1.1	<1.5	<0.002	0.16	<0.45	2.2	0.58	4.5	1.4	<2	<10	0.16	18	2.2
			b	269	56	6.66	<0.002	1.7	<1.5	<0.002	0.17	<0.45	2.5	0.72	3.6	1.9	<2	<10	0.08	23	2.8
TDB 4.1	1	0-10	a	464	306	5.39	<0.01	0.05	<0.1	<0.04	0.19	<0.2	<1	<0.1	22	<0.5	<0.06	<1	0.03	0.66	<0.8
			b	469	296	5.66	<0.01	0.05	0.12	<0.04	0.14	<0.2	<1	<0.1	16	<0.5	<0.06	<1	<0.02	0.66	<0.8
	7		a	384	289	4.50	<0.01	<0.05	<0.2	<0.05	0.20	<0.1	<0.2	<0.1	23	0.60	<0.5	<0.7	<0.03	0.40	<0.4
			b	389	286	6.24	<0.01	<0.05	<0.2	<0.05	0.18	<0.1	<0.2	<0.1	29	0.52	<0.5	<0.7	<0.03	0.40	<0.4
	14		a	409	198	5.59	<0.01	0.05	<0.3	<0.03	0.23	<0.1	<0.3	<0.1	25	0.90	<0.4	<0.6	0.02	0.90	0.30
			b	409	202	7.20	<0.01	0.08	<0.3	<0.03	0.21	<0.1	<0.3	<0.1	27	1.1	<0.4	<0.6	<0.02	1.0	0.30
	35		a	294	152	5.51	<0.001	0.10	<0.3	0.00	0.27	<0.09	<0.2	<0.1	72	0.70	<0.4	<2	0.04	0.97	0.62
			b	294	156	6.91	<0.001	0.08	<0.3	0.00	0.43	0.09	0.25	<0.1	86	0.77	<0.4	<2	0.04	0.61	<0.3

< value is below detection limit



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