



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

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Report to the Murray-Darling Basin Authority

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Taworri wetland
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EXECUTIVE SUMMARY

An initial Phase 1 acid sulfate soil investigation of the Taworri wetland during February 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 Taworri 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 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), iron (Fe) and manganese (Mn).

The **contaminant and metalloid dynamics** tests were undertaken to assess the release of metals during a water extraction, and to assess dynamics in response to saturation over time by incubating soil materials for periods of 1, 7, 14 and 35 days. The degree to which metal and metalloid concentrations exceed ANZECC/ARMCANZ environmental protection guideline values was used to characterise the degree of hazard. For Taworri wetland, iron (Fe) was assigned a high hazard with concentrations exceeding ANZECC/ARMCANZ environmental protection guidelines by more than 100 times. Aluminium (Al) and cobalt (Co) were assigned a moderate hazard with concentrations exceeding ANZECC/ARMCANZ environmental protection guidelines by more than 10 times. The dominant control on metal solubility is the pH of the extractions. Three of the four soils analysed showed an increase in pH which limits the solubility of many metals. Only one sampled showed little change in pH, remaining acidic over the 35 day duration of the tests. High aluminium (Al) was found in the acidic layer, and also in one sample with circumneutral pH, significantly above equilibrium concentrations. It is concluded that much of this aluminium (Al) exists as colloidal particles, thus less toxic than Al^{3+} the dominant form at lower pH. All samples showed a decrease in Eh, but the extent of decrease was different in the two profiles studied, with one decreasing to very low values. Iron (Fe) increased with time, the dominant control being the decrease in Eh. The concentrations of a number of metals were higher than ANZECC/ARMCANZ environmental protection guidelines, but iron (Fe) and cobalt (Co) were the elements of most concern. The metalloid arsenic (As) increased in concentration in 3 of the 4 samples studied, probably released from iron (Fe) oxides, but appeared to stabilise by day 35 in all but the most acidic sample. Vanadium (V) increased in all samples over time.

The Taworri 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 **medium** risk rating for **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 a **low** risk rating for **acidification** and **low to medium** risk rating for **contaminant mobilisation** respectively. 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 Taworri 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 soil acidification and contaminant mobilisation in Taworri wetland, a monitoring program is strongly recommended during any disturbance to the soils.

1. INTRODUCTION

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

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

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

Following the Taworri 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), Taworri wetland was selected for Phase 2 detailed assessment.

The Phase 1 assessment sampled 3 sites in Taworri wetland (Figure 1-1). The Phase 1 assessment identified one high priority site based on the presence of sulfuric materials, no high priority sites based on the presence of hypersulfidic materials, 1 high priority site based on hyposulfidic materials with $S_{CR} \geq 0.10\%$ and 1 moderate priority site based on the presence of hyposulfidic materials with $S_{CR} < 0.10\%$. Phase 2 investigations were carried out on selected surface soil 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>

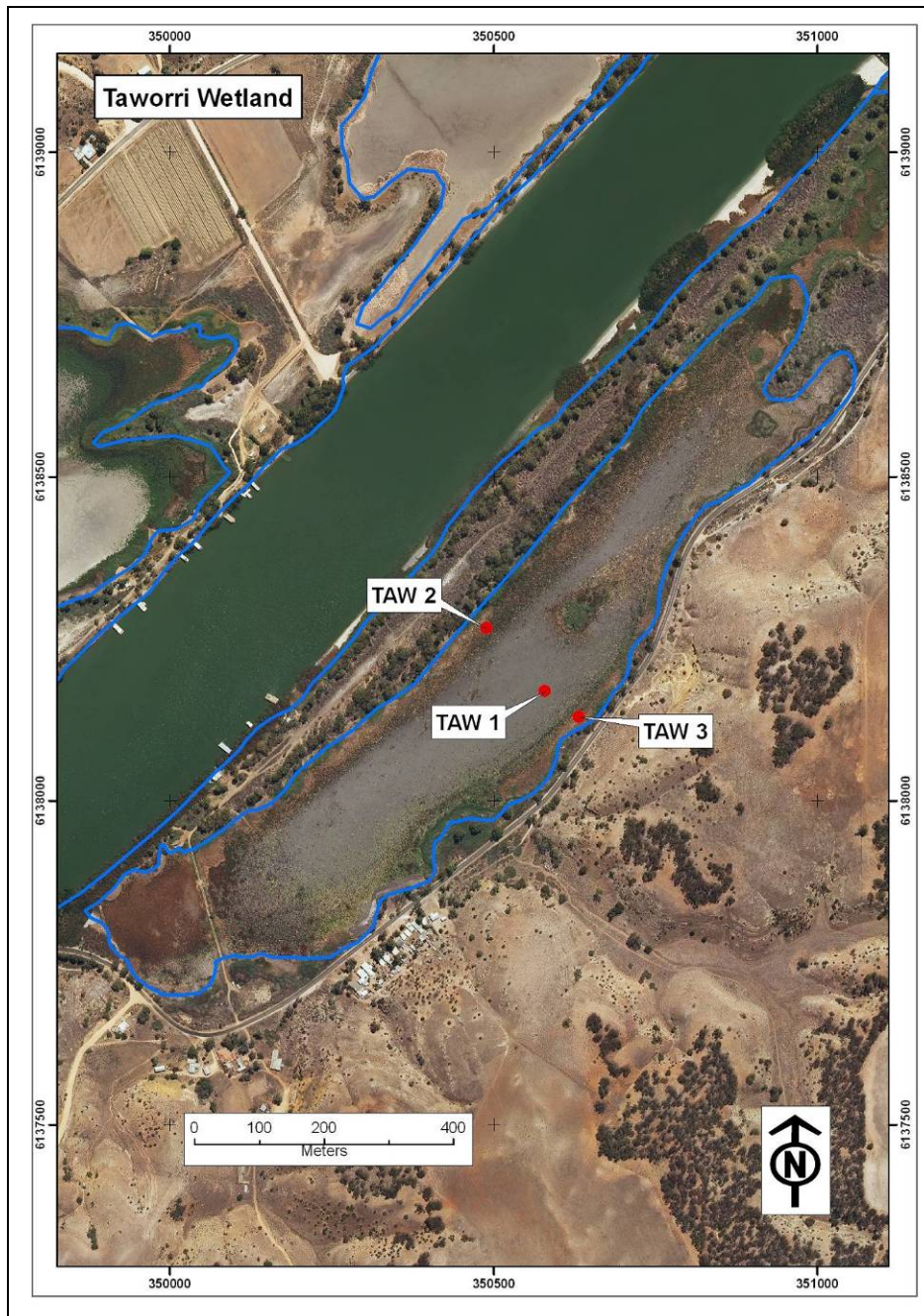


Figure 1-1 Taworri wetland aerial photograph with Phase 1 sampling sites identified.

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 Taworri 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 Taworri wetland samples analysed for Phase 2 assessment.

Soil Laboratory Test	Taworri wetland samples	Sample depth (cm)	Number of samples analysed
Reactive metals	TAW1.1	0-2	4
	TAW1.2	2-15	
	TAW3.1	0-5	
	TAW3.2	5-40	
Contaminant and metalloid dynamics	TAW1.1	0-2	4
	TAW1.2	2-15	
	TAW3.1	0-5	
	TAW3.2	5-40	
Monosulfide formation potential	TAW1.1	0-2	1
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 0.1M 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 ($\text{Fe}^{2+} + \text{Fe}^{3+}$) 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 test 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 for which guidelines are available. The concentrations for most reactive metals and metalloids are relatively low, but relatively high for aluminium (Al), iron (Fe) and manganese (Mn).

Table 3-1 Taworri 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
TAW 1.1	3.8	427	1.1	85	3.7	119	3.5	532	198	6.6	2.4	< 1.6	31	11	8.8
TAW 1.2	5.3	534	1.6	92	4.2	136	5.1	1301	180	7.5	3.7	< 1.7	61	16	8.9
TAW 3.1	5.3	465	0.79	57	2.7	82	3.7	888	58	6.5	2.5	< 2.4	30	9.9	3.7
TAW 3.2	4.0	872	1.0	47	1.1	106	2.6	621	24	4.5	1.7	< 2.5	31	11	5.1
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 four Taworri 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	Taworri		
			Min.	Median	Max.
pH		6.5-8.0	3.9	5.4	6.9
EC*	µS cm ⁻¹	2200	152	311	876
Eh	mV	-	-19	358	522
Ag	µg l ⁻¹	0.05	<0.01	<0.01	<0.1
Al ^A	mg l ⁻¹	0.055	<0.05	<0.05	0.62
As ^B	µg l ⁻¹	13	<0.2	2.8	37
Cd	µg l ⁻¹	0.2	<0.01	<0.06	0.30
Co	µg l ⁻¹	2.8	0.07	12	33
Cr ^C	µg l ⁻¹	1	<0.3	0.60	3.0
Cu ^H	µg l ⁻¹	1.4	<0.8	1.3	<10
Fe ^I	mg l ⁻¹	0.3	<0.1	0.39	33
Mn	µg l ⁻¹	1700	3.2	673	3255
Ni ^H	µg l ⁻¹	11	<0.4	18	30
Pb ^H	µg l ⁻¹	3.4	<0.2	<0.8	6.0
Sb	µg l ⁻¹	9	<0.6	<5	<10
Se	µg l ⁻¹	11	<0.08	0.31	1.3
V	µg l ⁻¹	6	<0.2	5.7	38
Zn ^H	µg l ⁻¹	8	<1	7.1	30

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 for 3 of the 4 soil materials studied increased over the 35 day period (Figure 3-1), with the samples initially being slightly acidic to acidic. However, the sample TAW 3.1 had a lower pH throughout, and decreased over the 35 day period remaining well below ANZECC/ARMCANZ environmental protection guideline values. The SEC was variable, either showing little change, or an increase followed by a decrease (TAW 1.2).

The Eh showed a significant and consistent decrease over the day 35 period for all samples, however, the decrease was much greater for samples from profile TAW 1 than TAW 3, reaching very reducing conditions by day 35 (Figure 3-1).

Iron (Fe) increased to values much higher than ANZECC/ARMCANZ environmental protection guideline values in 3 of the 4 samples. Manganese (Mn) changed in a similar manner, but only breached the ANZECC/ARMCANZ environmental protection guideline value in one sample (TAW 3.2). These increases are consistent with the change from oxidising to moderately reducing conditions, where manganese (Mn) and then iron (Fe) become soluble.

Aluminium (Al) concentrations were relatively high in some samples, but the highest increase was in sample TAW 3.2, which had a relatively high pH. At the pH observed it is likely that this represents colloidal aluminium (Al) for TAW 3.2. The moderately high aluminium (Al) in TAW 3.1 is probably a function of its low pH and probably represents dissolved Al^{3+} . Arsenic concentrations increased in all samples. In the high pH samples the trend was for increasing arsenic with time, which appeared to reach a maximum by day 14 (Figure 3-1). For the acidic soil sample, arsenic started to increase dramatically by day 35. Cadmium (Cd) and chromium (Cr) were high in some samples initially, but decreased with time. Cobalt (Co) showed little systematic change, remaining high in 3 of the 4 samples, whilst nickel (Ni) increased in 3 of the 4 samples, reaching a plateau after 14 days (Figure 3-3). Both breached ANZECC/ARMCANZ environmental protection guidelines

Vanadium (V), which forms an oxyanion similar to arsenic, showed a continuous increase with time in most samples, showing different behaviour to arsenic. Zinc (Zn) showed little change, except in the most acidic sample (TAW 3.1), where it initially increased, followed by a decrease.

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).

Most elements display little clear trend with pH (Figure 3-4), but are partly controlled by the Eh of the soil solutions. Iron and manganese (Mn) are both controlled more by Eh (see Appendix 2). There is thus a complex interplay between pH, Eh and metal availability in the samples. The pH-Eh values for TAW 3.2 show that this sample plots in the $Fe(OH)_3$ (solid phase) stability field on a pH-Eh diagram, explaining the low iron (Fe), manganese (Mn) and other trace elements, whilst the pH-Eh for the other samples sit in the stability field for dissolved iron (Fe^{2+}).

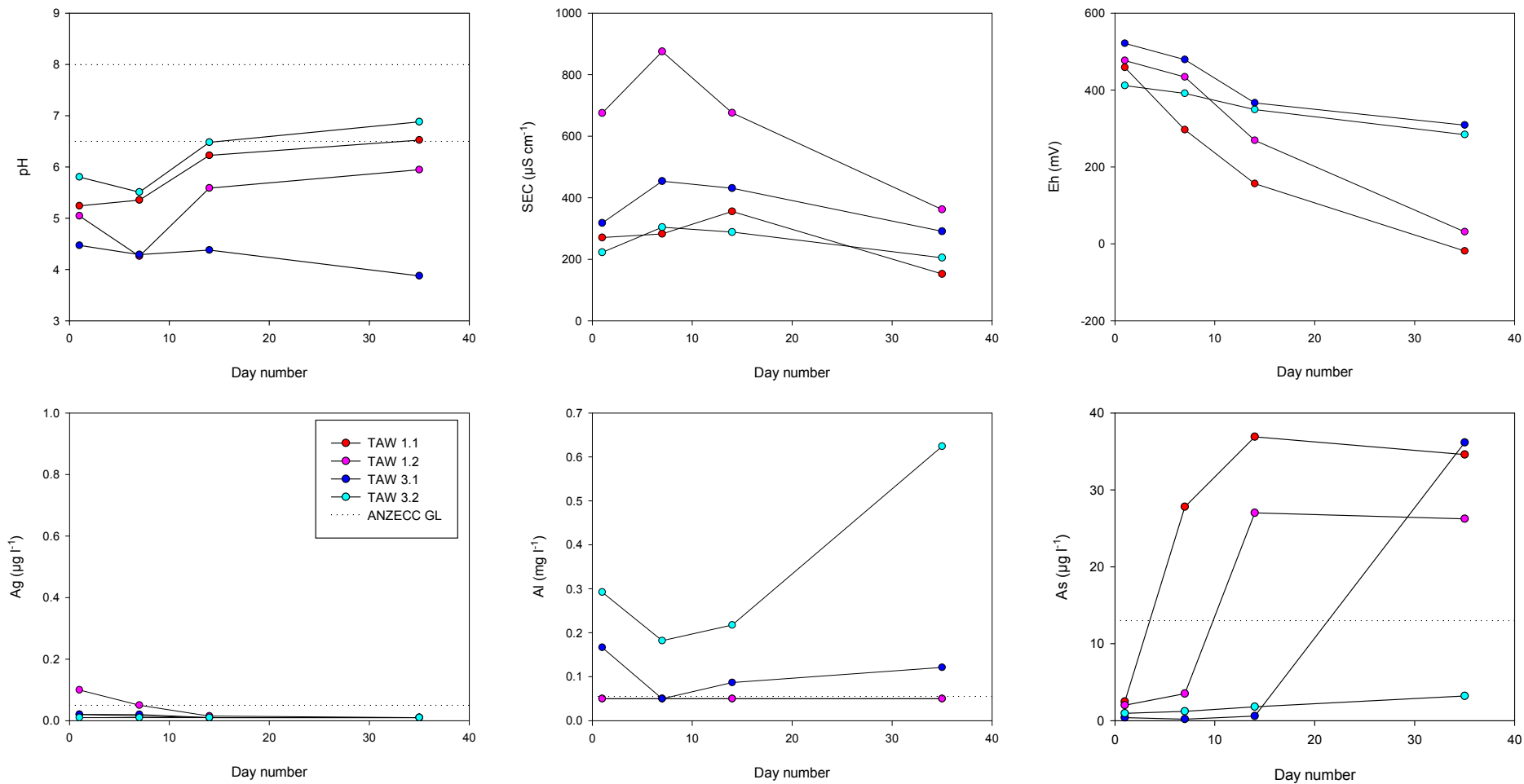


Figure 3-1 Contaminant and metalloid dynamics results for Taworri wetland soil materials for pH, SEC, Eh, silver (Ag), aluminium (Al) and arsenic (As).
 Note: silver (Ag) was all < detection limit, data represent detection limits which vary according to required dilutions.

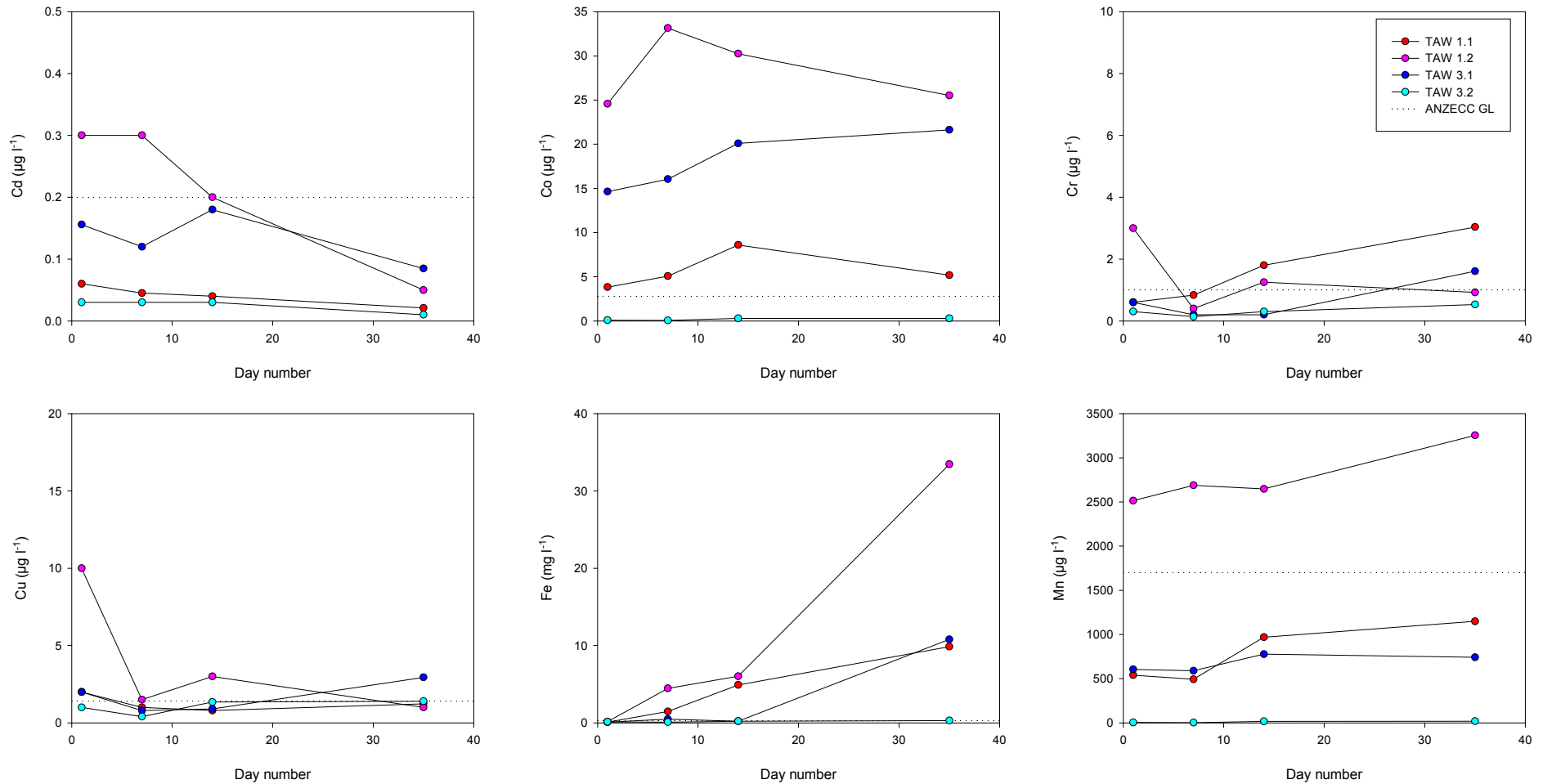


Figure 3-2 Contaminant and metalloid dynamics results for Taworri wetland soil materials for cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe) and manganese (Mn).

Note: copper (Cu) was < detection limit in some samples, data represent detection limits which vary according to required dilutions.

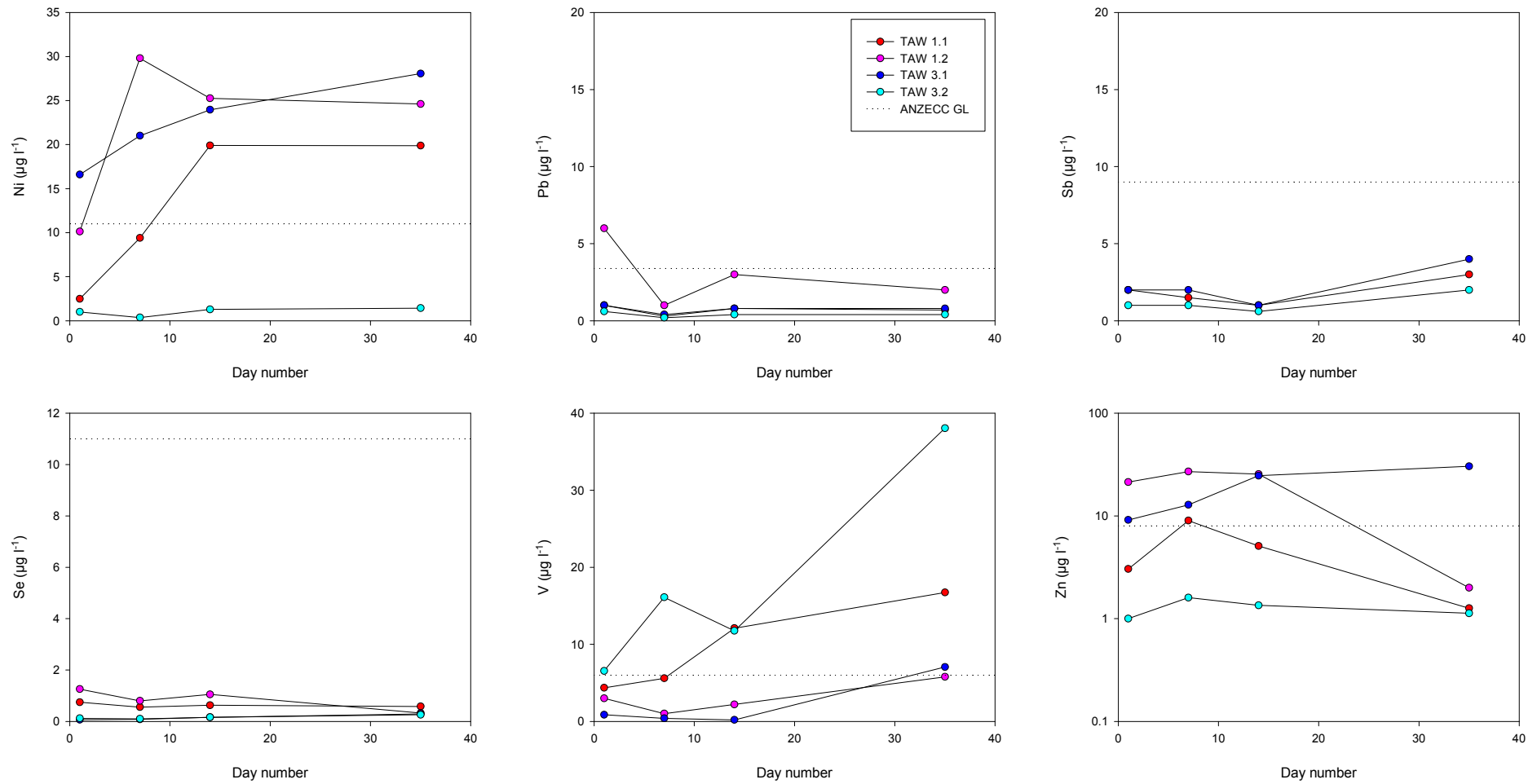


Figure 3-3 Contaminant and metalloid dynamics results for Taworri wetland soil materials for nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), vanadium (V) and zinc (Zn).

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

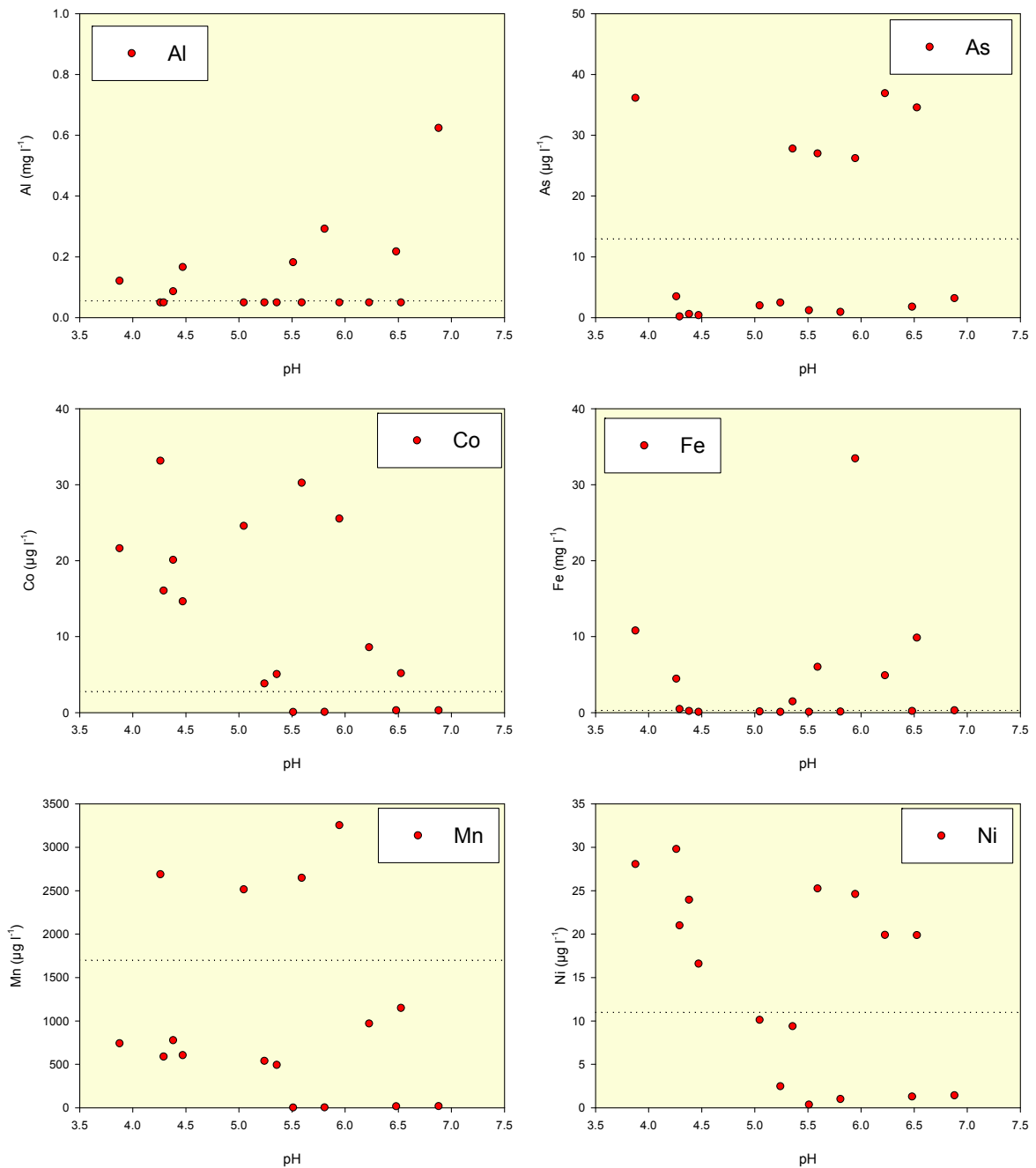


Figure 3-4 Selected trace elements plotted against pH.

3.1.3. Monosulfide formation potential data

The monosulfide formation potential data for sample TAW 1.1 are shown in Table 3-3. The pH of the soil water changed from 7.05 to 4.59 over the seven week incubation period (Figure 3-5). The decrease in pH is different from the contaminant and metalloids dynamics tests, where pH changed from pH 5.24 to pH 6.53 (Figure 3-1). This may be due to fermentation of organic substrate added (sucrose) which caused acidification of the pore-waters.

The Eh decreased significantly from 386 to 239 mV (Table 3-3) indicating a change to slightly more reducing conditions. The Eh data are also not consistent with the contaminant and metalloid dynamics experiments where Eh decreased from 459 to -19 mV i.e. becoming much more reducing.

Table 3-3 Summary of monosulfide formation potential data for the Taworri wetland surface soil material TAW 1.1 after 7 weeks (3.6 g/L sucrose).

Inundation Time	Parameter	Units	Taworri (TAW 1.1)
Day 0	Total Fe	mg/kg	5165
	Fe(II) ⁻	mg/kg	1390
	Sulfate*	mg/kg	1642
	pH		7.05
	Eh	mV	386
Week 7	pH		4.59
	Eh	mV	239
	S _{AV}	Wt. %S	<0.01
	S ⁰	Wt. %S	<0.01
	Pyrite-S	Wt. %S	0.12
	Dissolved S ²⁻	µg/L	45

* 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 0.08 % S_{CR} (pyrite-S + S_{AV}) and it, therefore, appears that significant concentrations of pyrite have not formed in the sample during the experiment. Dissolved sulfide was present at low concentrations (Table 3-3), suggesting that conditions may be approaching those for sulfides to form, but have not reached sufficiently low Eh for the precipitation of monosulfides or pyrite to occur.

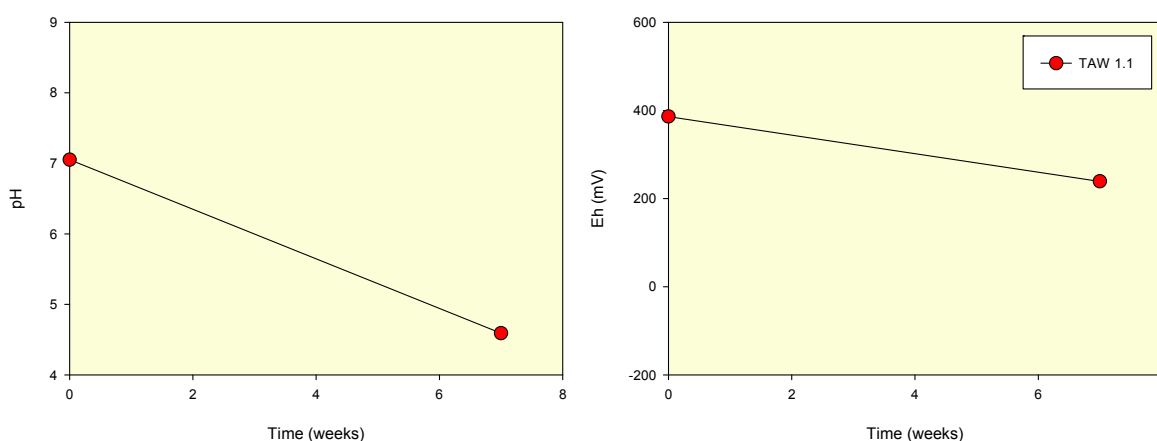


Figure 3-5 pH and Eh dynamics during monosulfide formation potential tests in surface soil sample TAW 1.1 from Taworri wetland.

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, these are generally for total soil concentrations, and therefore, are not directly appropriate for the data from metal mobilisation studies. Nevertheless, they provide a basis for comparison; and concentrations close to or above guideline values indicate an elevated hazard.

The metal and metalloid concentrations were all below sediment quality guidelines (SQG) and soil ecological investigation level values (Table 3-1). Concentrations of iron (Fe) and manganese (Mn) (and to a lesser degree aluminium) 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 under the ambient conditions during sampling.

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

Most of the soils increased in pH, the exception being TAW 3.1 which decreased from pH 4.37 to 3.88, the latter having the highest net acidity of 120 mol H⁺/tonne. All samples showed a significant decrease in Eh (Figure 3-1) with samples from profile TAW 1 showing the largest decrease from moderately oxidising to reducing. Increases in iron (Fe) and manganese (Mn) were associated with decrease in Eh in most samples, suggesting that

reductive processes are responsible. The increase in a number of metals and metalloids is likely to be related to the reductive dissolution of iron (Fe) and manganese (Mn) minerals, but for most metals solubility will be limited as the pH increases and/or precipitation of sulfides occurs. Many elements showed a maximum increase over the duration of the experiments, in some cases a decrease was noted by day 35 of the contaminant and metalloid dynamics experiments. Vanadium (V) was an exception, which showed continued increase.

The degree to which samples exceed guideline concentrations has been used to assign a degree of hazard (Table 3-4). For some samples which required dilution, the detection limits were slightly above ANZECC/ARMCANZ environmental protection guideline values due to required dilution. Antimony (Sb), for example, was below detection limits for all samples (detection limit varying between 1 and 10 µg l⁻¹) as was silver (Ag), while copper (Cu) was below detection limits for some samples. It is therefore not possible to group these in Table 3-4, although it can be concluded that they either sit in the 'No hazard' or 'Low Hazard' grouping (10 of the 12 samples had concentrations <5 µg l⁻¹). The data are shown in Appendix 1 which displays the detection limits for individual analyses.

The data are consistent with the moderately high net acidities noted by Grealish *et al.* (2010). Nevertheless, the contaminant and metalloid dynamics data suggest that most soils may take little time to recover in terms of acidity. Higher pH will limit the solubilities of most trace metals, although the concentrations in this study suggest that mobilisation will occur but be limited and of short duration. It is likely that the aluminium (Al) exists as colloidal material in some samples and hence may pose less of a risk than truly dissolved Al³⁺. The metalloid elements arsenic (As) and vanadium (V), which form oxyanions, are likely to be controlled by the reductive dissolution of iron (Fe) and manganese (Mn) oxides and may remain at relatively high concentrations over longer timescales, at least until further reduction into the field of iron sulfide stability, in which case they may be scavenged by precipitating iron (Fe) sulfides.

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

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

Note: Ag, Cu and Sb are below detection limits in some samples due to dilutions, and therefore are likely to have a 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 the 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 contaminant mobilisation impacts on benthic organisms. Nevertheless, the following sections detail the hazards and likelihood of a number of scenarios and discuss consequences based on limited previous work (e.g. McCarthy *et al.* 2006; Shand *et al.* 2010). The risks to soil water quality and surface water quality are necessarily different. The risks to soil water quality in terms of acidification and contaminant release are easier to assess from the tests carried out in this study than the risks posed to surface water quality. The impacts on surface water quality will be largely controlled by upward flux of acidity and metals from the soils and sediments into the water column. This will be controlled by *inter alia* surface water volume and groundwater connectivity, soil type, hydraulic conductivity, degree and depth of soil cracking.

The Taworri 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 relatively high net acidities in shallow samples from Taworri wetland suggest that the acidification hazard is high. However, the increases in pH over the 35 days of contaminant and metalloid dynamics (CMD) experiments in 3 of the 4 soils indicates significant pH buffering in the soils. The exception, TAW 3.1, indicate that some surface soils may take longer to recover and this will depend largely on hydrological conditions e.g. high flows will provide some buffering and allow the acidity flux to move downwards in the soil profile. The acidification hazard is therefore considered to be moderate and probably localised in the wetland.

It would appear unlikely that soil acidification would pose a serious problem as suggested by the measured pH and increase to circumneutral values in 3 of the 4 samples over the 35 days of the contaminant and metalloid dynamics incubations. Due to the wetland being dry and its location adjacent to the river and connectivity, the likelihood of disturbance is considered **almost certain** as flows return to normal in the future. The consequences for soil ecology are likely to be short term and localised in nature and the timescale for soil recovery from acidification will probably be rapid if there is sufficient flows, as indicated in the contaminant and metalloid dynamics experiments. A **minor** rating is therefore applied for consequence as short-term damage to soil water chemistry is considered likely. This provides a *risk rating for soil acidification* of **medium**. 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. Surface water acidification is likely to be lower than soil acidification, due to limited transport and buffering reactions at the soil/water interface, therefore an **insignificant** categorisation is given for consequence. 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 metalloid species. The medium to high acidification hazard due to the oxidation of sulfide minerals means that metals and metalloids are likely to be present at moderately high concentrations, depending on availability. The data suggest that aluminium (Al), cobalt (Co) and iron (Fe) are the elements with the highest hazard. 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 main exceptions being iron (Fe) and manganese (Mn), and locally aluminium (Al). The release of iron (Fe) and manganese (Mn) during a return to reducing conditions in the dried soils suggests that these metals as well as arsenic (As) and vanadium (V) pose a hazard to soil and surface waters. These metalloids are mobile at high pH and their increase over the 35 day period suggests that these pose a significant hazard. Although aluminium (Al) was also high it is suggested that the aluminium (Al) may be in colloidal form, hence less toxic than Al^{3+} 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 significant for some metals. Comparisons with other studies (e.g. Nelwart Lagoon, Shand *et al.* 2010), suggest that at the pH levels noted in the contaminant and metalloid dynamics experiments for most samples, reductive processes may occur rapidly once initiated, and soil recovery may be rapid. A **minor** rating is applied for consequence due to the presence of a number of metals and metalloids. This provides a risk rating for contaminant mobilisation in soils of **medium**.

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 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** consequence is applied. The risk to surface waters from metal mobilisation is therefore considered to be **low to 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. 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 therefore considered to be **insignificant** and as such the risk associated with deoxygenation is **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).

Table 4-4 Summary of risks associated with acid sulfate soil materials in Taworri wetland.

Acidification Risk		Contaminant mobilisation		Deoxygenation
<i>Soil</i>	<i>Water</i>	<i>Soil</i>	<i>Water</i>	
Medium	Low	Medium	Low-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 management responses required should take into account the low conservation status for this wetland when considering the options 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 acidification and contaminant mobilisation. The likelihood of water refilling the wetland is high as flows return to normal levels. The limited number of case studies on refilling wetlands makes prediction of risk difficult in terms of determining whether reversible or irreversible damage is likely to occur. However, at the pH's observed, the increase in pH over the 35 day period and limited metal 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 where sulfide minerals may be present at higher concentrations.

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.

REFERENCES

- ANZECC/ARMCANZ 2000 *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*, Australian and New Zealand Environment and Conservation Council and agriculture and Resource Management Council of Australia and New Zealand, Canberra.
- APHA 2005 Standard methods for the examination of water and wastewater (21st Ed.). (American Public Health Association - American Water Works Association: Baltimore, USA).
- Baldwin D & Fraser M 2009 Rehabilitation options for inland waterways impacted by sulfidic sediments. *Journal of Environmental Management* 91:311–319.
- Claff SR, Sullivan LA, Burton ED & Bush RT 2010 A sequential extraction procedure for acid sulfate soils: Partitioning of iron. *Geoderma* **155**, 224-230.
- Cline ID 1969 Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnology and Oceanography* **14**, 454-458.
- EPHC & NRMCC (Environment Protection and Heritage Council and Natural Resource Management Ministerial Council) 2011 National Guidance for the management of acid sulfate soils in inland aquatic ecosystems, Canberra, ACT.
- Fitzpatrick RW, Shand P, Thomas M, Grealish G, McClure S, Merry RH & Baker A 2010 Acid Sulfate Soil investigations of vertical and lateral changes with time in five managed wetlands between Lock 1 and Wellington. CSIRO Land and Water Science Report 03/10.
- Fitzpatrick RW, Shand P, Thomas M, Merry RH, Raven MD & Simpson S 2008 Acid sulfate soils in subaqueous, waterlogged and drained soil environments of nine wetlands below Blanchetown (Lock 1), South Australia: properties, genesis, risks and management. CSIRO Land and Water Science Report 42/08.
- Goody DC, Shand P, Kinniburgh DG & Van Riemsdijk WH 1995 Field-based partition coefficients for trace elements in soil solutions. *Journal of Soil Science*, 46, 265-285.
- Grealish G, Fitzpatrick RW & Shand P 2011 Assessment of Acid Sulfate Soil Materials in the Lock 1 to Wellington Region of the Murray-Darling Basin. CSIRO: Water for a Healthy Country National Research Flagship.
- Grealish G, Shand P, Grocke S, Baker A, Fitzpatrick R & Hicks W 2010 Assessment of Acid Sulfate Soil Materials in Lock 1 to Lock 5 Region of the Murray-Darling Basin. CSIRO: Water for a Healthy Country National Research Flagship. 769 pp.
- McCarthy B, Conalin A, D'Santos P & Baldwin DS 2006 Acidification, salinisation and fish kills at an inland wetland in south-eastern Australia following partial drying. *Ecological Management and Restoration*, vol. 7, pp. 218–23.
- McGuire MM & Hamers RJ 2000 Extraction and quantitative analysis of elemental sulfur from sulfide mineral surfaces by high-performance liquid chromatography. *Environmental Science & Technology* **34**, 4651-4655.
- MDBA 2010 Detailed Assessment of Acid Sulfate Soils in the Murray–Darling Basin: Protocols for sampling, field characterisation, laboratory analysis and data presentation. MDBA Publication No. 57/10, 58 pp.

MDBA 2011 Acid sulfate soils in the Murray–Darling Basin, Murray–Darling Basin Authority, Canberra. MDBA Publication No. 147/11.

Miles M, Wainwright P, Gonzalez D, Turner R, Frankiewicz D & Jones L 2010 Application of the South Australian River Murray wetland prioritisation methodology, Department for Environment and Heritage, Adelaide.

NEPC 1999 National environment protection (assessment of site contamination) measure 1999. National Environment Protection Council.

Shand P, Merry R, Grocke S, Thomas M, Fitzpatrick RW, Thomas B, Baker A & Creeper N 2010 Water and soil quality impacts during reflooding of Nelwart Lagoon, South Australia. CSIRO: Water for a Healthy Country National Research Flagship. 158 pp.

Standards Australia & Standards New Zealand 2004, HB 436: 2004, Risk Management, Sydney, NSW.

APPENDICES

APPENDIX 1 REACTIVE METALS DATA

Taworri wetland

Sample	Depth	Analysis	Ag*	Al	As	Cd*	Co	Cr*	Cu	Fe	Mn	Ni	Pb	Sb*	Se*	V	Zn
TAW 1.1	0-2	a	3.6	427	1.2	85	3.8	119	3.5	511	198	6.6	2.4	< 1.6	33	11	8.9
		b	4.0	427	0.98	85	3.6	119	3.5	554	198	6.6	2.3	< 1.6	29	11	8.7
TAW 1.2	2-15	a	5.1	529	1.6	93	4.1	133	5.1	1269	180	7.5	3.6	< 1.7	60	16	8.7
		b	5.6	540	1.7	92	4.2	140	5.1	1334	180	7.5	3.7	< 1.7	63	16	9.1
TAW 3.1	0-5	a	5.6	396	0.70	49	2.4	77	3.6	882	54	5.6	2.5	< 2.4	29	9.8	3.3
		b	5.1	534	0.89	66	3.0	87	3.8	894	61	7.4	2.6	< 2.4	31	10	4.0
TAW 3.2	5-40	a	3.8	949	0.96	54	1.0	101	2.4	525	23	4.7	1.5	< 2.5	32	12	5.4
		b	4.3	795	1.1	41	1.1	111	2.8	717	26	4.4	1.8	< 2.5	30	11	4.8

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

Taworri 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
TAW 1.1	1	0-2	a	265	295	4.67	<0.02	<0.05	2.4	<0.06	4.4	<0.6	<2	<0.1	633	2.9	<1	<2	0.90	3.9	4.1
			b	255	246	5.81	<0.02	<0.05	2.5	<0.06	3.3	<0.6	<2	<0.1	446	2.1	<1	<2	0.60	4.8	2.0
	7		a	90	303	5.65	<0.02	<0.05	28	<0.06	5.6	0.90	1.2	1.6	540	11	<0.4	<2	0.56	6.4	15
			b	105	262	5.06	<0.01	<0.05	27	<0.03	4.6	0.77	0.80	1.3	447	8.0	<0.2	<1	0.56	4.8	2.8
	14		a	-20	361	6.25	<0.01	<0.05	37	<0.04	8.9	2.0	0.80	5.3	983	20	<0.8	<1	0.72	12	5.4
			b	-65	350	6.20	<0.01	<0.05	37	<0.04	8.3	1.6	0.80	4.6	955	20	<0.8	<1	0.54	12	4.8
35	a	-235	167	6.69	<0.01	<0.05	35	<0.02	4.9	3.1	0.82	9.7	1146	20	<0.8	<4	0.58	16	1.5		
	b	-200	137	6.36	<0.01	<0.05	34	0.02	5.5	3.0	1.6	10.0	1151	20	0.59	<2	0.59	17	1.0		
TAW 1.2	1	2-15	a	285	618	4.98	<0.1	<0.05	<2	<0.3	24	<3	<10	0.14	2423	<10	<6	<10	1.4	<3	18
			b	270	732	5.11	<0.1	<0.05	<2	<0.3	25	<3	<10	0.17	2605	10	<6	<10	1.1	<3	24
	7		a	225	957	4.08	<0.05	<0.05	4.5	0.40	40	<0.4	2.0	5.6	3089	36	<1	<5	0.80	<1	30
			b	245	794	4.44	<0.05	<0.05	2.5	<0.2	27	<0.4	<1	3.3	2287	23	<1	<5	0.80	<1	24
	14		a	80	737	5.08	<0.02	<0.05	26	<0.2	44	<2	<4	8.2	3520	36	<4	<6	0.90	0.90	39
			b	60	614	6.10	<0.01	<0.05	28	<0.2	16	<0.5	<2	3.9	1774	14	<2	<3	1.2	3.5	12
35	a	-160	358	5.95	<0.01	<0.05	28	<0.05	22	0.99	<1	31	3297	23	<2	<10	0.37	6.1	<2		
	b	-175	366	5.94	<0.01	<0.05	25	<0.05	29	0.85	<1	36	3212	26	<2	<10	0.28	5.4	<2		
TAW 3.1	1	0-5	a	320	353	4.40	<0.02	0.20	<0.4	0.12	17	<0.6	<2	<0.1	679	19	<1	<2	0.08	1.1	11
			b	325	283	4.54	<0.02	0.13	<0.4	0.19	13	<0.6	<2	<0.1	531	14	<1	<2	0.04	<0.6	7.6
	7		a	275	452	4.27	<0.02	<0.05	<0.2	0.12	16	0.20	0.40	0.35	575	20	<0.4	<2	<0.08	<0.4	12
			b	285	456	4.31	<0.02	<0.05	<0.2	0.12	17	0.20	1.2	0.63	602	22	<0.4	<2	<0.08	<0.4	14
	14		a	135	375	4.34	<0.01	0.09	<0.6	0.18	21	0.20	0.60	0.14	787	25	<0.8	<1	0.16	<0.2	23
			b	200	487	4.42	<0.01	0.08	<0.6	0.18	19	0.20	1.2	0.29	769	23	<0.8	<1	0.16	<0.2	26
35	a	60	307	3.69	<0.01	0.19	63	0.10	23	2.6	4.4	17	825	31	<0.8	<4	0.47	14	29		
	b	160	275	4.06	<0.01	<0.05	9.3	0.07	20	0.61	1.5	4.6	658	25	<0.8	<4	0.12	0.25	32		
TAW 3.2	1	5-40	a	210	204	6.22	<0.01	0.29	0.72	<0.03	0.09	<0.3	<1	0.15	5.8	<1	<0.6	<1	0.10	4.8	<1
			b	215	240	5.39	<0.01	0.30	1.2	<0.03	0.07	<0.3	<1	0.13	3.7	<1	<0.6	<1	0.13	8.3	<1
	7		a	195	308	5.34	<0.01	0.16	1.1	<0.03	0.07	0.14	0.40	<0.1	3.2	0.32	<0.2	<1	0.08	13	2.8
			b	190	300	5.68	<0.01	0.21	1.3	<0.03	0.07	0.14	0.40	<0.1	3.1	0.40	<0.2	<1	0.12	19	0.40
	14		a	155	292	7.01	<0.01	0.24	2.1	<0.03	0.33	0.40	1.5	0.22	18	1.5	<0.4	<0.6	0.16	13	1.5
			b	145	285	5.95	<0.01	0.19	1.5	<0.03	0.24	0.20	1.2	0.20	16	1.1	<0.4	<0.6	0.16	11	1.2
	35		a	90	204	7.46	<0.01	0.60	3.4	<0.01	0.30	0.54	1.4	0.29	19	1.5	<0.4	<2	0.29	43	1.1
			b	80	206	6.30	<0.01	0.64	3.0	<0.01	0.29	0.52	1.4	0.31	19	1.4	<0.4	<2	0.24	33	1.1

< value is below detection limit

APPENDIX 3 MONOSULFIDE FORMATION POTENTIAL DATA

Taworri wetland

MBO Formation Potential (MBO FP) - DAY 0

IRON DATA

DAY 0

Sample No.	org	Site Name	Site ID	Total Reactive Fe (mg/kg)				Fe(II) (mg/kg)				Eh (mV)				pH			
				Replicate 1	Replicate 2	Mean	+/-	Replicate 1	Replicate 2	Mean	+/-	Replicate 1	Replicate 2	Mean	+/-	Replicate 1	Replicate 2	Mean	+/-
19	csiro	Taworri	TAW1.1	5748	4582	5165	583	1581	1198	1390	191	374	399	386	12	7.07	7.03	7.05	0.02
32	-	Blank	-	0.3	0.1	0.2	0.1	<0.1	<0.1	<0.1	<0.1	183	186	185	2	6.17	6.10	6.14	0.04

MBO Formation Potential (MBO FP) - Week 7

Sample No.	org	Site Name	Site ID	AVS (%S)				Pyrite (%S)				ES (%S)				pH				Eh (mV)				Aqueous Sulfide (µg/L)			
				Replicate 1	Replicate 2	Mean	+/-	Replicate 1	Replicate 2	Mean	+/-	Replicate 1	Replicate 2	Mean	+/-	Replicate 1	Replicate 2	Mean	+/-	Replicate 1	Replicate 2	Mean	+/-	Replicate 1	Replicate 2	Mean	+/-
19	csiro	Taworri	TAW1.1	0.00	0.00	<0.01	<0.01	0.12	0.13	0.12	<0.01	0.00	0.00	<0.01	<0.01	4.62	4.55	4.59	0.04	253	225	239	14	43.0	46.6	44.8	1.8
32	csiro	Blank	-												5.45	5.42	5.44	0.02	325	338	331	6	<0.1	<0.1	<0.1	<0.1	



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