



# Assessment of Acid Sulfate Soil Materials (Phase 2) Jury Swamp, South Australia

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Report to the Murray-Darling Basin Authority

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## **EXECUTIVE SUMMARY**

An initial Phase 1 acid sulfate soil investigation of Jury Swamp in November 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 Jury Swamp 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 reactive metals results showed that concentrations were below sediment quality guidelines (SQG) and soil ecological investigation levels. Although concentrations of other elements did not breach sediment quality guidelines or soil ecological investigation level trigger values, the concentrations of many elements were high enough that they may impact water quality if mobilised, particularly for aluminium (Al) and iron (Fe).

The **contaminant and metalloid dynamics** tests were undertaken to assess the release of metals during a water extraction, and to assess dynamics in response to saturation over time by incubating soil materials for periods of 1, 7, 14 and 35 days. The degree to which metal and metalloid concentrations exceed guideline values (ANZECC/ARMCANZ 2000) was used to characterise the degree of hazard. For Jury Swamp, aluminium (Al), cobalt (Co) and iron (Fe) were assigned a high hazard with concentrations exceeding ANZECC/ARMCANZ environmental protection guidelines by more than 100 times, and cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), vanadium (V) and zinc (Zn) 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 sediments at the time of the extractions. The soils displayed little trend in pH throughout the tests, with most remaining very acidic. The presence of iron hydroxysulfates in the soils is considered to be important in buffering the pH to low values as well as releasing metals and metalloids into solution during wetting of the soils. Over the duration of the analysis, there was a slight decrease in Eh, which is thought to be partly responsible for increasing iron (Fe) solubility over time.

Jury Swamp has been classified as low conservation status by the SA Murray-Darling Basin Natural Resources Management Board (Miles *et al.* 2010). However, recent data shows the wetland is one of the last remaining strongholds for the endangered Purple-spotted Gudgeon. 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 **very high** risk rating due to **acidification** and **contaminant mobilisation** of **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 **high** (minor consequence) to **very high** (major consequence) risk rating due to both **acidification** and **contaminant mobilisation**. The risk associated with *deoxygenation* from monosulfides is considered to be **medium to high** as monosulfides were found in the wetland during initial field surveys and the textures of dried soil were previously interpreted as being monosulfidic black ooze.

In designing a management strategy for dealing with acid sulfate soils in Jury Swamp, 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 high to very high risks to the wetland values associated with acidification and metal mobilisation in Jury Swamp, a monitoring program is strongly recommended.

## **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).

This report outlines the results of Phase 2 activities on selected surface soil samples from Jury Swamp.

Jury Swamp was selected for Phase 2 detailed assessment following analysis of results from the Phase 1 detailed assessment (Fitzpatrick *et al*. 2010) and the priority ranking criteria adopted by the Scientific Reference Panel of the MDB ASSRAP (see Table 1-1). Sampling sites from Phase 1 are shown on Figure 1-1 and Figure 1-2. The Phase 1 assessment identified 3 high priority sites based on the presence of sulfuric materials, all of which also contained sulfidic materials with up to 0.19 %  $S_{CR}$ . Phase 2 investigations were carried out on selected surface soil samples from high priority sites identified in the Phase 1 assessment (Fitzpatrick *et al*. 2010).

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



**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).** 

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





## **Table 1-3 Summary of Jury Swamp samples analysed for Phase 2 assessment.**



**Figure 1-1 Jury Swamp aerial photograph with Phase 1 sampling sites identified.** 



**Figure 1-2 Acid sulfate soil map of Jury Swamp showing distribution of the different types of acid sulfate soils (e.g. sulfuric cracking clays, sulfuric organic clays to hypersulfidic subaqueous clays), features (salt efflorescences and dried and wet monosulfidic materials) and sampling sites (from Fitzpatrick** *et al***. 2010).** 

## **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).** 

<b>Parameter</b>	<b>Objective</b>	
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<sup>2+</sup>) and total iron (Fe<sup>2+</sup> + Fe<sup>3+</sup>) fractions were immediately fixed following extraction. The ferrous iron trap was made up from a phenanthroline solution with an ammonium acetate buffer (APHA 2005), and the total iron trap also included a hydroxylamine solution (APHA 2005). The iron species were quantified colorimetrically using a Hach DR 2800 spectrophotometer.

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

### **2.1.5. Mineral identification by x-ray diffraction**

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

## **2.2. Quality assurance and quality control**

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

Reagent blanks and method blanks were prepared and analysed for each method. All blanks examined here were either at, or very close to, the limits of detection. On average, the frequencies of quality control samples processed were: 10% blanks, 10% laboratory duplicates, and 10% laboratory controls. The analytical precision was ±10% for all analyses. In addition, for all samples, reactive metals and contaminant and metalloid dynamics tests were duplicated. For the reactive metals, two International Standards (Reference Stream Sediment STSD-2 and STSD-3 Canadian Certified Reference Materials) were processed in an identical manner to the samples. Precision was excellent with the coefficient of variation (standard deviation/mean\*100) typically being in the range < 1 to 2 %.

## **3. RESULTS AND DISCUSSION**

## **3.1. Summary of soil laboratory results**

## **3.1.1. Reactive metals data**

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

The concentrations of metals and metalloids were below sediment quality guideline values and soil ecological investigation levels for all elements for which a guideline exists (Table 3-1). The concentrations for most reactive metals and metalloids are relatively low, but relatively high for aluminium (Al), iron (Fe) and for some samples, chromium (Cr), nickel (Ni) and vanadium (V).



### **Table 3-1 Jury Swamp reactive metals data.**

Concentrations in mg kg<sup>-1</sup> and  $\mu$ g kg<sup>-1</sup> as indicated.

\* Units are in µg kg-1

< value is below detection limit

<sup>1</sup>SQG: Sediment Quality Guideline Value (Australian and New Zealand Guidelines for Fresh and Marine Water Quality 2000)<br><sup>2</sup>Seil Ell : Seil - Ecclesiael Investigation Lavel (NEDC 1900)  $2$ Soil EIL: Soil – Ecological Investigation Level (NEPC 1999)

## **3.1.2. Contaminant and metalloid dynamics data**

The contaminant and metalloid dynamics data for the seven Jury Swamp 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).

<b>Parameter</b>	units	<b>ANZECC</b> <b>Guidelines</b>	<b>Jury Swamp</b>		
			Min.	<b>Median</b>	Max.
pH		$6.5 - 8.0$	2.6	3.6	5.9
EC*	$\mu$ S cm <sup>-1</sup>	2200	470	1220	6715
Eh	mV		92	553	774
Ag	$\mu$ g l $^{-1}$	0.05	< 0.01	< 0.05	< 0.4
$AI^A$	$mgI^{-1}$	0.055	< 0.05	2.5	29
$\mathsf{As}^{\mathsf{B}}$	$\mu g \Gamma^1$	13	< 0.5	5.5	<b>104</b>
Cd	$\mu$ g l <sup>-1</sup>	0.2	< 0.01	0.44	3.1
Co	$\mu$ g l <sup>-1</sup>	2.8	0.77	52	290
$Cr^C$	$\mu$ g l <sup>-1</sup>	$\mathbf{1}$	< 0.2	3.6	40
Cu <sup>H</sup>	$\mu$ g l <sup>-1</sup>	1.4	< 0.4	5.2	104
Fe <sup>1</sup>	mg $\Gamma^1$	0.3	< 0.1	18	331
Mn	$\mu$ g l' <sup>1</sup>	1700	74	1184	7741
Ni <sup>H</sup>	$\mu$ g l <sup>-1</sup>	11	$<$ 1	71	363
$Pb^{H}$	$\mu$ g l' <sup>1</sup>	3.4	< 0.4	$2$	$20$
Sb	$\mu g \Gamma^1$	9	$-0.6$	100	100
Se	$\mu$ g l <sup>-1</sup>	11	< 0.03	0.43	$2$
V	$\mu g \Gamma^1$	6	$-0.6$	9.0	191
$Zn^{H}$	$\mu g \Gamma^1$	8	1.3	79	647

**Table 3-2 Summary of contaminant and metalloid dynamics data** 



#### *Notes.*

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

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

*A Guideline is for Aluminium in freshwater where pH > 6.5.* 

*B Guideline assumes As in solution as Arsenic (AsV).* 

*C Guideline for Chromium is applicable to Chromium (CrVI) only.* 

*H Hardness affected (refer to Guidelines).* 

*I Fe Guideline for recreational purposes.* 

The pH of the soil materials were, with the exception of one sample (JUR 7.4), very acidic, with most soil samples being sulfuric. All soil samples remained below the ANZECC/ARMCANZ environmental protection guideline value of pH 6.5. However, some samples displayed a slight increase over time (Figure 3-1).

The Eh was initially high to very high in all samples, reflecting the strongly oxidised nature of these wetland soils. All samples showed a decrease in Eh over the 35 day tests, but the extent of decrease varied. The organic-rich soils (JUR 6.4 and 6.5; Figure 1-2) and the

deepest clay soil (JUR 7.4), showed the smallest decrease, possibly related to the lower pH in these samples which may slow down reduction processes (Figure 3-1). The SEC showed little variation with time. Most samples were relatively saline (up to ca. 2000  $\mu$ S cm<sup>-1</sup>), but one surface sample (JUR 7.3) had much higher SEC (Figure 3-1). This sample formed a fluffy brown fine-grained material, possibly the weathering product of monosulfidic black ooze.

Manganese concentrations varied significantly, with three samples having concentrations higher than the ANZECC/ARMCANZ environmental protection guideline value. The concentrations of manganese showed little change with time (Figure 3-2). Iron was also very variable, but with most samples showing an increase in concentration with time (Figure 3-2). The lowest iron concentration was generally in the organic-rich soils.

There was a large range in the concentrations of most metal and metalloid concentrations in the samples (Figure 3-1 to Figure 3-3). Aluminium was particularly high in the clay soils (JUR 7), with concentrations up to 29 mg  $I^1$ . The lowest concentrations were present in the highest pH sample, consistent with solubility controls where aluminium (Al) concentrations increase with decreasing pH. Arsenic (As) increased in most samples reaching 104  $\mu$ g l<sup>-1</sup>. The trends varied, with some showing a continuous increase, whilst others showed a peak at 14 days, subsequently decreasing by day 35 (Figure 3-1).

The large variations noted for the abovementioned elements were also apparent in the other metals. Samples from profile JUR 7 were very high for a number of metals and metalloids, particularly aluminium (Al), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni) and zinc (Zn), and maximum concentrations were much higher than the ANZECC/ARMCANZ environmental protection guidelines (Table 3-2).

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) SEC; 8) clay content; 9) microbial activity; 10) temperature; and 11) porosity (MDBA 2010). Overall, the samples displayed a good trend with pH (Figure 3-4), with the highest concentrations of most metals and metalloids being present in the lowest pH waters (Figure 3-4). The correlation of iron (Fe) and manganese (Mn) with these metals suggests a control by dissolution of iron and manganese oxyhydroxides and mobilisation of the sorbed metals and metalloids.

The dissolution of iron-minerals by reductive dissolution is also likely to have played a major role in controlling the solubility of both metals and metalloids. The release of iron (Fe) and manganese (Mn) by dissolution of hydroxysulfate minerals is thought to be responsible for the initial rapid release of iron (Fe), manganese (Mn) and other metals and metalloids.



**Figure 3-1 Contaminant and metalloid dynamics results for Jury Swamp 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 Jury Swamp soil materials for cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe) and manganese (Mn).** 



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

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



**Figure 3-4 Selected trace elements plotted against pH.** 

### **3.1.3. Monosulfide formation potential data**

No samples were selected from this wetland for monosulfide formation potential studies as monosulfides were found to be present during initial field surveys (see figure 1-2; Fitzpatrick *et al*. 2008).

## **3.1.4. Mineral identification by x-ray diffraction**

Eight surface mineral efflorescences were sampled from the profiles in Jury Swamp: JURB2.1, 2.2, JURA6.1-6.4, JURB7.1 and 7.2 corresponding to the profiles studied for reactive metals and contaminant and metalloid dynamics. The mineralogy is shown on Table 3-3, and photographs and X-ray diffraction patterns provided in Appendix 3. A range of salts, mineral efflorescences and precipitates were found including jarosite  $(KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>),$ natrojarosite (NaFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>), gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O), halite (NaCl), hexahydrite  $(MgSO_4.6H_2O)$ , epsomite  $(MgSO_4.7H_2O)$ , tamarugite  $(NaAl(SO_4)_2.6H_2O)$ , and possibly sideronatrite (Na<sub>2</sub>Fe<sup>3+</sup>(SO<sub>4</sub>)<sub>2</sub>OH.3H<sub>2</sub>O). The salts gypsum, hexahydrite, epsomite and halite may have an impact on salinity in surface waters, but do not generate acidity upon dissolution. The iron and aluminium hydroxysulfate minerals, however, act as stores of acidity and may generate acidity during dissolution. The rare minerals sideronatrite and tamarugite are stable at very low pH forming where evaporation during drying led to extremely low pH.





It is likely that the acid-generating iron-hydroxysulfate salts also store metals and metalloids which may be released during dissolution of these minerals following rewetting.

### **3.2. Interpretation and discussion of results**

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

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

provide a basis for comparison; and concentrations close to or above guideline values indicate an elevated hazard.

All metal and metalloid concentrations in the acid extracts were below the sediment quality guidelines and the soil ecological investigation level values (Table 3-1). Although the concentrations were less than guideline values, the concentrations of some metals were moderately high for this partial extraction technique, particularly for aluminium (Al) and iron (Fe). Nevertheless, the concentrations of many metals are sufficiently high (mg kg<sup>-1</sup>) compared to water quality guidelines (generally µg kg<sup>-1</sup>) that significant release could pose a hazard to soil and surface water quality.

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 which 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.

It is evident that reductive processes have begun in the samples analysed with a decrease in Eh for the soil samples by day 35. The largest decreases in Eh were typically in the surface samples, probably due to elevated organic matter typical of shallow soils in wetlands. However, the organic-rich soils retained relatively high Eh, possibly because these remained relatively acidic, hence reducing the kinetics of reduction. Nevertheless, the pH in most soils remained acidic, with pH varying from pH 2.65 to 5.89 on day 35 of the contaminant and metalloid dynamics work.

The low pH and high availability of many metals has led to very high concentrations of metals and metalloids in the soil pore-waters during the contaminant and metalloid dynamics experiments. It is likely that many were incorporated into the hydroxysulfate minerals identified by X-ray diffraction. Dissolution of these minerals would help buffer the pH to low values, as well as release metals and metalloids to solution. It is likely that these species would remain in solution until pH increases by further reduction reactions. The data suggest that a change to reducing conditions may take some time.

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 for some samples. Antimony (Sb) was below detection limit for all samples (detection limits varying between 1 and 100  $\mu$ g l<sup>-1</sup>). It is therefore not possible to determine hazard classifications for antimony (Sb), as well as silver (Ag) and lead (Pb) in Table 3-4, although it can be concluded that these generally either sit in the no to moderate hazard grouping.

Of particular significance for Jury Swamp are the high and moderate hazard rankings for a number of elements (Table 3-4). The data are consistent with the generally high net acidities noted by Fitzpatrick et al. (2008), which varied from -40 up to 22,400 mol H<sup>+</sup>/tonne, which means that the soils are likely to take little time to recover from drying and any associated local acidification.

#### **Table 3-4 Summary of the degree of hazard associated with the measured contaminant and metalloid concentrations in Jury Swamp.**



Note: Ag, Pb and Sb were below detection limits due to dilutions, and therefore are likely to be classified as no to moderate hazard (see Appendix 2 for data).

The monosulfide formation potential test assists in determining the propensity for monosulfides to form during future inundation. Monosulfidic black ooze was identified during earlier field investigations (Fitzpatrick *et al*. 2010)

## 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 4-2 determines the likelihood (i.e. probability) of disturbance for each hazard, ranging from rare to almost certain. This requires an understanding of the nature and severity of the materials (including the extent of acid sulfate soil materials, the acid generating potential and the buffering capacity of wetland soil materials) as well as contributing factors influencing the risk (MDBA 2011). Examples of disturbance include: (i) rewetting of acid sulfate soil materials after oxidation, (ii) acid sulfate soil materials that are currently inundated and may be oxidised, or (iii) acid sulfate soil materials that are currently inundated and may be dispersed by flushing (e.g. scouring flows) (MDBA 2011). As mentioned previously, the consequence of a hazard occurring and the likelihood rating for the disturbance scenario for each hazard are then ranked using a standardised risk assessment matrix (Table 4-3).



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

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



It is suggested that:

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

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

## **4.2. Assessment of risks**

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

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

Jury Swamp 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 high to very high net acidities in samples from Jury Swamp indicate that the acidification hazard is high. Net acidities were very high in most samples and any acid neutralising capacity (ANC) is confined to the deeper soil layers. The dominant components of the net acidity are retained acidity and titratable actual acidity, although stored acidity from chromium-reducible sulfur is also significant.

The probability of soil acidification is very high as evidenced by the generally high positive net acidities in most samples studied in the wetland and the abundance of sulfuric materials. Due to the wetlands location adjacent to the river and connectivity, the likelihood of disturbance is considered **almost certain** as flows return to normal in the future. Due to the low hydraulic conductivities in the clays and organic-rich clays in this wetland, it is unlikely that soil acidification will be mediated by high flows. The consequences are likely to be significant for soil ecology, but the timescale for soil recovery from acidification cannot be assessed with existing information. Studies in other wetlands e.g. Nelwart Lagoon (Shand *et al*. 2010) indicate that in areas with strongly acidic soils, the timescale is likely to be months to years). A **major** rating is therefore applied for consequence as long-term damage to soil water chemistry is considered likely. This provides a *risk rating for soil acidification* of **very high**. A rating for surface water acidification will depend on surface and sub-surface hydrology. The highest risk is likely to be during low flows where the soil to water ratio is high: acidity will be most concentrated. The risk to surface water acidification is considered lowest where high flows are available to both dilute acidity and transport acidity downwards in the soil profile. The consequence rating is considered to be minor to major. The *risk rating for surface water acidification* is therefore likely to vary from **medium** to **very high** depending on future scenarios.

### **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 high acidification hazard due to the oxidation of sulfide minerals means that if metals and metalloids have been released they are likely to be mobile. Although reduction processes may lead to reincorporation of metals and metalloids into sulfide minerals (following sulfate reduction), at intermediate redox potentials mobility may be high where iron (Fe) and manganese (Mn) are soluble. The reactive metals and contaminant metalloid dynamics results attest to the availability and mobility of a number of metals, particularly aluminium (Al), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), vanadium (V) and zinc (Zn). At the concentrations measured (>10-100 x ANZECC/ARMCANZ environmental protection guidelines), the consequences are likely to be significant for soil pore-waters and soil/sediment ecology. As in assessing the acidification risk, the timescales cannot be assessed with existing information. However, comparisons with other studies (e.g. Nelwart Lagoon, Shand *et al.* 2010), soil recovery in such acidic systems is likely to mean that at least short term impacts are likely. Since pH remained low in soil samples from the middle of the wetland, a **major** rating is applied for consequence as short-term damage to soil ecology is considered likely. This provides a risk rating for contaminant mobilisation in soils of **very high**.

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

### **4.2.3. Risks associated with deoxygenation**

Monosulfidic materials are considered the main cause of deoxygenation risk in acid sulfate soils. Monosulfidic black ooze was identified in the wetland during earlier surveys (Fitzpatrick *et al.* 2010; see figure 1-2), in the north-western corner where irrigation return water was pumped to the wetland, and also in the channel connecting the wetland to the river. Although the wetland was dry at the time of sampling, the textures of the top soil layer were interpreted as being dried MBO (Fitzpatrick *et al*. 2010). Water soluble sulfate concentrations were not measured but likely to be high, as sulfate soils were abundant on the soil surface The consequences for deoxygenation are considered to be minor to moderate, and therefore the risk rating is medium to high.





## **5. BROAD ACID SULFATE SOIL MANAGEMENT OPTIONS**

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

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

In designing a management strategy for dealing with acid sulfate soils in affected inland wetlands, other values and uses of a wetland need to be taken into account to ensure that any intervention is compatible with other management plans and objectives for the wetland. Jury Swamp has been classified as low conservation status by the SA Murray-Darling Basin Natural Resources Management Board (Miles *et al*. 2010). However, recent data shows the wetland is one of the last remaining strongholds for the endangered Purple-spotted Gudgeon (SA MDB NRM Board pers. comm.). Therefore, it is suggested that the management responses required should align with those suggested following the risk assessment ratings (Table 4-3).

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

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

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

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

The impacts on surface and sub-surface ecosystems are not well understood and are worthy of further work, particularly long term impacts on ecosystem functionality and diversity.





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# **APPENDICES**

## **APPENDIX 1 REACTIVE METALS DATA**

Jury Swamp



Units are mg kg<sup>-1</sup> unless indicated otherwise as below

\* Units are in  $\mu$ g kg<sup>-1</sup>

< value is below detection limit\*

## **APPENDIX 2 CONTAMINANT AND METALLOID DYNAMICS DATA**

Jury Swamp





< value is below detection limit

# **APPENDIX 3 X-RAY DIFFRACTION DATA**

Sample ID: JURb 2.1





Sample ID: JURb 2.2





















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Sample ID: JURb 7.1





Sample ID: JURb 7.2





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